ELUCIDATION OF PHOTOINDUCED ENERGY AND ELECTRON TRANSFER MECHANISMS IN
MULTIMODULAR ARTIFICIAL PHOTOSYNTHETIC SYSTEMS

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Dissertation Prepared for the Degree of

DOCTOR OF PHILOSOPHY

UNIVERSITY OF NORTH TEXAS

May 2017

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Multimodular designs of electron donor-acceptor systems are the ultimate strategy in fabricating antenna-reaction center mimics for artificial photosynthetic applications. The studied photosystems clearly demonstrated efficient energy transfer from the antenna system to the primary electron donor, and charge stabilization of the radical ion pair achieved with the utilization of secondary electron donors that permits either electron migration or hole transfer. Moreover, the molecular arrangement of the photoactive components also influences the route of energy and electron transfer as observed from the aluminum(III) porphyrin-based photosystems. Furthermore, modulation of the photophysical and electronic properties of these photoactive units were illustrated from the thio-aryl substitution of subphthalocyanines yielding red-shifted Q bands of the said chromophore; hence, regulating the rate of charge separation and recombination in the subphthalocyanine-fullerene conjugates.

These multicomponent photosystems has the potential to absorb the entire UV-visible-NIR spectrum of the light energy allowing maximum light-harvesting capability. Furthermore, it permits charge stabilization of the radical ion pair enabling the utilization of the transferred electron/s to be used by water oxidizing and proton reducing catalysts in full-scale artificial photosynthetic apparatuses.
ACKNOWLEDGEMENTS

I would like to express my deepest and sincerest gratitude to my research advisor Dr. Francis D’Souza for without him all of these wouldn’t have been possible. I thank him for his constant guidance and for motivating me to do the best I can in everything I do. I would also like to thank Dr. William Acree, Jr., Dr. Paul Marshall, Dr. Arup Neogi, and Dr. Paul Pantano for agreeing to be part of my research committee for my Ph.D. dissertation. Your comments and critiques are greatly appreciated for it will certainly aid my professional growth.

My genuine appreciation to our collaborators Dr. Prashanth Poddutoori, Dr. Art van der Est, Dr. Paul Karr, Dr. Melvin Zandler, and the rest of our collaborators that have immensely helped me in the research projects that we have worked together. A heartfelt gratitude to the entire faculty and staff of the Chemistry Department at the University of North Texas for providing me the opportunity to obtain the highest academic degree possible. I would like to thank my colleagues in Dr. D’Souza’s lab, both former and current, who are always there for support and intellectual discussions, and for making graduate school a little less stressful.

I am forever grateful to my family and friends for their constant encouragement and support especially at times when the challenges in life seemed to be overwhelming. Thank you for believing in me even when there are times that I doubt myself. Thank you very much for I could’ve never done it without you.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>viii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF SCHEMES</td>
<td>xxxii</td>
</tr>
</tbody>
</table>

## CHAPTER 1. INTRODUCTION

1.1 Introduction                                                        | 1    |
1.2 Non-renewable and Renewable Sources of Energy                      | 2    |
1.3 Solar Energy: Clean Power for the Future                           | 3    |
1.4 Photosynthesis                                                     | 5    |
1.4.1 Natural Photosynthesis                                           | 5    |
1.4.2 Artificial Photosynthesis                                        | 8    |
1.5 Principles of Steady-State Absorption, Fluorescence and Phosphorescence Emissions | 11   |
1.6 Fluorescence Quenching                                             | 13   |
1.6.1 Collisional Quenching                                           | 14   |
1.6.2 Static Quenching                                                | 15   |
1.6.3 Photoinduced Energy Transfer                                     | 17   |
1.6.3.1 Föster Resonance Energy Transfer                              | 19   |
1.6.3.2 Dexter Energy Transfer                                         | 23   |
1.7 Photoinduced Electron Transfer                                     | 25   |
1.7.1 Marcus Theory                                                    | 26   |
1.7.2 Application of Marcus Theory to Electron Transfer                | 27   |
1.7.3 Single and Multistep Electron Transfer Processes                 | 30   |
1.8 Analytical Methods for the Characterization of Artificial Photosynthetic Systems | 34   |
1.8.1 Steady-State Absorption, Fluorescence Emission, and Phosphorescence Emission Spectroscopy | 35   |
1.8.2 Time-Resolved Fluorescence Emission Measurements                | 36   |
1.8.3 Electrochemical Studies                                          | 38   |
1.8.4 Spectroelectrochemical Technique                                 | 39   |
1.8.5 Transient Absorption Spectroscopy                                | 40   |
1.9 Current Antenna-Reaction Center Mimics for Artificial Photosynthesis | 44   |
1.9.1 Common Chromophores used in Supramolecular Photosystems          | 45   |
1.9.2 Rehm-Weller Approach for Free Energy Calculations                | 48   |
1.9.3 Porphyrin-Based Light-Harvesting Systems                         | 50   |
1.9.3.1 Zinc Porphyrin-Based Antenna-Reaction Center Mimics            | 51   |
1.9.3.2 Aluminum(III) Porphyrin-Based Antenna-Reaction Center Mimics   | 69   |
1.9.4 Subphthalocyanine-Based Light-Harvesting Systems                 | 84   |
1.10 Scope of Present Work                                             | 95   |

## CHAPTER 2. MATERIALS AND PHYSICAL METHODS

2.1 Materials                                                          | 99   |
2.2 Physical Methods
  2.2.1 Physical Methods 99
  2.2.2 Electrochemical Studies 100
  2.2.3 Time-Resolved Fluorescence Emission Spectroscopy 100
  2.2.4 Transient Absorption Measurements 100
    2.2.4.1 Femtosecond Transient Absorption Spectroscopy 100
    2.2.4.2 Nanosecond Laser Flash Photolysis 101
    2.2.4.3 Transient Electroparamagnetic Resonance Spectroscopy 101

2.3 Computational Studies 102

CHAPTER 3. ZINC PORPHYRIN-BASED SELF-ASSEMBLED MULTIMODULAR ANTENNA-
REACTION CENTER MIMICS
3.1 A Supramolecular Tetrad Featuring Covalently Linked Ferrocene-Zinc Porphyrin-
BODIPY Coordinated to Fullerene: A Charge Stabilizing, Photosynthetic Antenna-
Reaction Center Mimic 103
  3.1.1 Introduction 103
  3.1.2 Results and Discussion 106
    3.1.2.1 Synthesis of Fc-ZnP-BODIPY triad 106
    3.1.2.2 Optical Absorption and Fluorescence Studies 107
    3.1.2.3 Computational and Electrochemical Studies 110
    3.1.2.4 Energy Level Diagram depicting Excited State Events 114
    3.1.2.5 Femtosecond and Nanosecond Transient Absorption Studies 116
  3.1.3 Summary 121
  3.1.4 Supporting Information 122

3.2 Charge Separation in Supramolecular Ferrocene(s)-Zinc Porphyrin-Fullerene
Triads: A Femtosecond Transient Absorption Study 127
  3.2.1 Introduction 127
  3.2.2 Results and Discussion 130
    3.2.2.1 Femtosecond Transient Absorption Studies 137
  3.2.3 Summary 144

CHAPTER 4. ALUMINUM(III) PORPHYRIN-BASED AXIALLY SELF-ASSEMBLED
MULTIMODULAR ANTENNA-REACTION CENTER MIMICS
4.1 Axially Assembled Photosynthetic Reaction Center Mimics Composed of
Tetrathiafulvalene, Aluminum(III) Porphyrin and Fullerene Entities 146
  4.1.1 Introduction 146
  4.1.2 Results and Discussion 150
    4.1.2.1 Synthesis 150
    4.1.2.2 Characterization by UV-Visible Spectroscopy 151
    4.1.2.3 DFT Calculations 154
    4.1.2.4 Energy Level Diagram 155
    4.1.2.5 Fluorescence Spectroscopy 157
    4.1.2.6 Femtosecond Transient Absorption Studies (fs-TA) 159
4.1.2.7 Nanosecond Transient Absorption Studies (ns-TA) 164
4.1.2.8 Time-Resolved EPR Spectroscopy (TREPR) 166
4.1.3 Conclusions 171
4.1.4 Supporting Information 172

4.2 Modulation of Energy Transfer into Sequential Electron Transfer upon Axial Coordination of Tetrathiafulvalene in Aluminum(III) Porphyrin-Free Base Porphyrin Dyad 196
4.2.1 Introduction 196
4.2.2 Results and Discussion 199
  4.2.2.1 Synthesis 199
  4.2.2.2 Structural Characterization 200
  4.2.2.3 UV-Visible Absorption Spectroscopy 201
  4.2.2.4 Cyclic Voltammetry 204
  4.2.2.5 Fluorescence Spectroscopy 207
  4.2.2.6 Femtosecond Transient Absorption Spectroscopy 212
4.2.3 Conclusions 222
4.2.4 Supporting Information 223

4.3 Ultrafast Charge Separation and Charge Stabilization in Axially Linked ‘Tetrathiafulvalene-Aluminum(III) Porphyrin-Gold(III) Porphyrin’ Reaction Center Mimics 240
4.3.1 Introduction 240
4.3.2 Results and Discussion 244
  4.3.2.1 Synthesis 244
  4.3.2.2 Structural Characterization 244
  4.3.2.3 UV-Visible Absorption Spectroscopy 247
  4.3.2.4 Cyclic Voltammetry and Energetics 250
  4.3.2.5 Fluorescence Spectroscopy 253
  4.3.2.6 Femtosecond Absorption Spectroscopy 256
  4.3.2.7 Role of Axial Porphyrin (H$_2$Por vs AuPor$^+$) in dyads and triads 262
4.3.3 Conclusions 263
4.3.4 Experimental Section 264
  4.3.4.1 Synthesis 264
  4.3.4.2 Preparation of AlPor-Ph-AuPor•PF$_6$ 265
4.3.5 Supporting Information 266

CHAPTER 5. SUBPHTHALOCYANINE-BASED MULTIMODULAR DONOR-ACCEPTOR CONJUGATES
5.1 Effect of Spacer Connecting the Secondary Electron Donor Phenothiazine in Subphthalocyanine- Fullerene Conjugates in Promoting Electron Transfer Followed by Hole Shift Process 276
5.1.1 Introduction 276
5.1.2 Results and Discussion 279
  5.1.2.1 Synthesis 279
  5.1.2.2 Absorption, Fluorescence and Computational Studies 280
  5.1.2.3 Electrochemical Studies and Energy Level Diagram 285
  5.1.2.4 Pump-probe Transient Spectral Studies 289
5.1.3 Conclusions 296
5.1.4 Supporting Information 296

5.2 Tuning Optical and Electron Donor Properties by Peripheral Thio-Aryl Substitution of Subphthalocyanine: A New Series of Donor-Acceptor Hybrids for Photoinduced Charge Separation 303
  5.2.1 Introduction 303
  5.2.2 Results and Discussion 306
    5.2.2.1 Synthesis 306
    5.2.2.2 Optical Absorption and Emission Studies 309
    5.2.2.3 Electrochemical Studies and Energy Level Diagram 311
    5.2.2.4 Transient Absorption Studies 316
  5.2.3 Conclusions 321
  5.2.4 Supporting Information 322

CHAPTER 6. SUMMARY 330

APPENDIX LIST OF PUBLICATIONS 334

LIST OF REFERENCES 339
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Photophysical and electrochemical properties of the common chromophores used in antenna-reaction center systems.</td>
<td>47</td>
</tr>
<tr>
<td>1.2</td>
<td>Functionalized zinc porphyrin units for the self-assembled supramolecular constructs for artificial photosynthesis.</td>
<td>53</td>
</tr>
<tr>
<td>1.3</td>
<td>Reduction potential of the BQ electron acceptors and the second-order rate constants, $k_{ET}$, for the electron transfer from 19 to BQ.</td>
<td>71</td>
</tr>
<tr>
<td>1.4</td>
<td>Fluorescence emission bands ($\lambda_F$), lifetimes ($\tau_f$), and quenching rate constants ($k_q$).</td>
<td>77</td>
</tr>
<tr>
<td>1.5</td>
<td>Fluorescence lifetimes ($\tau_f$) and quenching rate constants ($k_q$) of 26, 27, and its control compound in dichloromethane and benzonitrile.</td>
<td>81</td>
</tr>
<tr>
<td>1.6</td>
<td>Modified subphthalocyanine-based antenna-reaction centers photosystems.</td>
<td>85</td>
</tr>
<tr>
<td>1.7</td>
<td>UV-visible spectra of the modified subphthalocyanines.</td>
<td>90</td>
</tr>
<tr>
<td>1.8</td>
<td>Optical studies of 39a-42a in toluene.</td>
<td>91</td>
</tr>
<tr>
<td>1.9</td>
<td>Transient absorption studies of 39a-42a and one-electron oxidized SubPc in toluene.</td>
<td>92</td>
</tr>
<tr>
<td>1.10</td>
<td>Photophysical parameters (steady-state and transient) of SubPc-C$_{60}$ dyads 39-42 in toluene.</td>
<td>98</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Binding constants for axial coordination of fullerene ligands to ferrocene-zinc porphyrin dyads in DCB at 298 K.</td>
<td>132</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Electrochemical half-wave potentials (vs. Fc/Fc$^+$) of the Fc-ZnP:C$_{60}$ triads in o-dichlorobenzene, 0.1 M (TBA)ClO$_4$, geometric parameters from B3LYP/3-21G(*) calculations, and free-energy change associated for different radical ion-pairs formation from the initial singlet excited zinc porphyrin.</td>
<td>133</td>
</tr>
<tr>
<td>4.1.1</td>
<td>B3LYP/6-311G(d, p) (for H, N, C and O) and 6-311G(df) (Al and S) optimized edge-to-edge and center-to-center distances for the investigated series of dyads and triads.</td>
<td>154</td>
</tr>
<tr>
<td>4.1.2</td>
<td>Charge separation and recombination lifetimes from fs- and ns-transient absorption and TREPR data. Parameters used to simulate the TREPR data.</td>
<td>164</td>
</tr>
</tbody>
</table>
Table 4.1.1  Optical and electrochemistry data of investigated triads, dyads and their reference compounds.  182
Table 4.2.1  UV-visible absorption and steady-state fluorescence data of investigated compounds.  203
Table 4.2.2  Redox Potential Data of Investigated Compounds in Dichloromethane with 0.1 M TBAClO₄ as a Supporting Electrolyte.  205
Table 4.2.51  UV-visible absorption titration data and binding constants in dichloromethane.  230
Table 4.3.1  UV-visible absorption, fluorescence and redox potential data of investigated compounds in dichloromethane.  249
Table 4.3.2  Transient data of investigated compounds in o-DCB.  262
Table 5.1.1  Redox potentials in benzonitrile containing 0.1 M (tBu₄N)ClO₄ (V vs Ag/Ag⁺), HOMO and LUMO energies, and free-energy change associated with electron transfer of the studied dyads.  284
Table 5.2.1  Spectral (absorption and fluorescence), electrochemical redox potentials, and free-energy change associated with electron transfer data of the investigated compounds in o-DCB.  312
Table 5.2.2  Kinetics of charge separation, \( k_{CS} \) and charge recombination, \( k_{CR} \) of the investigated \( \alpha- \) and \( \beta- \) thio aryl substituted SubPc covalently linked to C₆₀.  320
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.1</td>
<td>World energy consumption by energy source, 1990-2040 (quadrillion British thermal units, Btu).</td>
<td>2</td>
</tr>
<tr>
<td>Figure 1.2</td>
<td>Renewable and non-renewable sources of energy.</td>
<td>3</td>
</tr>
<tr>
<td>Figure 1.3</td>
<td>Detailed description of the light energy conversion processes in oxygenic photosynthetic membrane.</td>
<td>6</td>
</tr>
<tr>
<td>Figure 1.4</td>
<td>Structure of the oxygen-evolving catalyst (OEC), Mn₄CaO₅ cluster. Shown are the distances (in Å) between the metal atoms and the oxo-bridges, and water molecules.</td>
<td>7</td>
</tr>
<tr>
<td>Figure 1.5</td>
<td>Simplified scheme of an artificial photosynthetic system. WOC = water oxidizing catalyst, PRC = proton reducing catalyst.</td>
<td>10</td>
</tr>
<tr>
<td>Figure 1.6</td>
<td>Jablonski Diagram illustrating the transitions between electronic states. The wave lines indicate non-radiative transitions.</td>
<td>11</td>
</tr>
<tr>
<td>Figure 1.7</td>
<td>Stern-Volmer plot of $F_d/F$ vs $[Q]$. The red line shows the slope at room temperature while the blue (collisional quenching) and green (static quenching) broken lines are the slopes at higher temperatures.</td>
<td>16</td>
</tr>
<tr>
<td>Figure 1.8</td>
<td>Proposed schemes for energy transfer pathways in antenna-reaction center photosystems: (a) a linear arrangement, (b) a two-dimensional planar distribution, and (c) depicts the antenna system as an energy funnel to the reaction center.</td>
<td>18</td>
</tr>
<tr>
<td>Figure 1.9</td>
<td>Demonstration of the FRET process with (a) showing the non-radiative energy transfer from the excited donor chromophore ($D^*$) to the acceptor chromophore ($A$), and (b) the spectral overlap, $J(\lambda)$, between the donor emission spectrum and acceptor absorption spectrum.</td>
<td>20</td>
</tr>
<tr>
<td>Figure 1.10</td>
<td>Illustration of the (a) relevant vectors and angles to the orientation factor $\kappa^2$ calculation and (b) the resulting $\kappa^2$ values with the different orientation of the transition dipoles of the donor and acceptor.</td>
<td>21</td>
</tr>
<tr>
<td>Figure 1.11</td>
<td>A Jablonski diagram depicting Dexter energy transfer.</td>
<td>23</td>
</tr>
<tr>
<td>Figure 1.12</td>
<td>Reaction coordinate diagrams at varying reactant (blue) and product (red) reaction free energies ($\Delta G^0$) depicted as Morse potentials.</td>
<td>27</td>
</tr>
<tr>
<td>Figure 1.13</td>
<td>Marcus plot of the intramolecular electron transfer from biphenyl anions to different electron acceptors.</td>
<td>30</td>
</tr>
</tbody>
</table>
Figure 1.14  Schematic illustration of photophysical processes in chromophores.

Figure 1.15  Schematic illustration of a) simple, b) multimodular, and c) antenna-donor-acceptor reaction centers.

Figure 1.16  Modified Jablonski diagram depicting the mechanism of transient absorption spectroscopy.

Figure 1.17  Schematic diagram of ultrafast transient absorption spectroscopy.

Figure 1.18  Difference absorption spectrum illustrating the different contributing transient events.

Figure 1.19  Structures of common chromophores used for artificial photosynthetic systems. BODIPY = boron dipyrromethene, azaBODIPY = azadipyrromethene, M = 2 or 3 H's, transition metals (i.e., Mg, Mn, Cu, Zn, Al, Au, etc.), X = F, Cl, Br.

Figure 1.20  Donor-acceptor systems for artificial photosynthesis illustrating the different modes of interaction in supramolecular assemblies.

Figure 1.21  Structures of the photosensitizer units of the zinc porphyrin-based antenna-reaction center mimics.

Figure 1.22  Transient absorption spectra of 8:17 obtained using 530 nm laser excitation in Ar-saturated (a) benzonitrile and (b) o-dichlorobenzene. Inset: time profiles at a) 700 and 1000 nm, and b) 850 and 1000 nm bands.

Figure 1.23  Energy level diagrams of ZnTPP:Ca6Im (8:17) donor-acceptor dyad in a) o-dichlorobenzene and b) benzonitrile.

Figure 1.24  Steady-state a) absorption spectra of (i) ZnP, (ii) 9, and (iii) BODIPY; b) fluorescence spectra of (i) BODIPY, (ii) equimolar amounts of ZnP and BODIPY, (iii) 9, and (iv) ZnP excited at 502 nm; c) fluorescence spectra (i) ZnP and (ii) 9 excited at 550 nm in o-dichlorobenzene.

Figure 1.25  Nanosecond transient absorption spectra of a) dyad 9 and b) 9:17 after 550 and 500 nm laser irradiation, respectively, in Ar-saturated o-dichlorobenzene. Inset: time profiles at a) 625, and b) 1020 nm bands.

Figure 1.26  Energy level diagram depicting the different photophysical and photochemical processes occurring in the self-assembled 9:17 antenna-reaction center mimic after BODIPY photoexcitation. Solid, and thin and broken arrows indicate the major and minor events occurring,
respectively.

Figure 1.27 Steady-state a) absorption, b) fluorescence emission (\(\lambda_{\text{exc}} = 505\) nm), and c) excitation spectra (held at 662 nm emission monochromator) of (i) 10, (ii) 11, (iii) 12, and (iv) BODIPY in o-dichlorobenzene.

Figure 1.28 Steady-state a) absorption and b) fluorescence (\(\lambda_{\text{exc}} = 495\) nm) spectra of (i) 13, (ii) 18, (iii) BODIPY, and (iv) ZnP-crown ether control compounds in benzonitrile excited; c) absorption and d) fluorescence (\(\lambda_{\text{exc}} = 510\) nm) spectra if (i) 14, (ii) ZnP, and (iii) BODIPY-crown ether in benzonitrile.

Figure 1.29 Femtosecond transient absorption spectra of 14 excited at a) 430 nm and b) 510 nm in benzonitrile (inset: time profiles at a) 460 and b) 630 nm bands); c) femtosecond and d) nanosecond transient absorption spectra of 14:18 in benzonitrile excited at 430 nm (inset: time profiles at c) 460 and 700 nm, and d) 1000 nm bands).

Figure 1.30 Energy level diagrams illustrating the photophysical and photochemical events occurring in self-assembled a) 13:18 and b) 14:18 antenna-reaction center mimics. Solid, and thin and broken arrows indicate the major and minor events occurring, respectively. Adapted from references 88a and b, respectively.

Figure 1.31 Steady-state a) absorption and b) fluorescence (\(\lambda_{\text{exc}} = 555\) nm) spectra of (i) 15, (ii) 16, and (iii) Fc-(TPA)\(_2\)ZnP; c) fluorescence spectra of (i) 15, (ii) (TPA)\(_2\)ZnP, (iii) (TPA)\(_3\)H\(_2\)P-C\(_{60}\), and (iv) (TPA)\(_3\)H\(_2\)P excited at 307 nm. All solutions were in o-dichlorobenzene.

Figure 1.32 a) Femtosecond and b) nanosecond transient absorption spectra of 15 in Ar-saturated benzonitrile laser irradiated at 430 and 532 nm, respectively. Inset: time profiles at a) 1000 and b) 1300 nm.

Figure 1.33 a) Femtosecond and b) nanosecond transient absorption spectra of 16 in Ar-saturated benzonitrile laser irradiated at 430 nm. Time profiles at a) 640 and 1000 nm, and b) 1000 nm (inset).

Figure 1.34 Energy level diagrams depicting the different photophysical and photochemical events occurring in the antenna-reaction center mimics of pentads a) 15 and b) 16. Solid, and thin and broken arrows indicate the major and minor events occurring, respectively.

Figure 1.35 Structures of the aluminum(III) porphyrin-based antenna-reaction center mimics.
Figure 1.36  a) Transient absorption spectra of \textbf{19:20g} in deaerated benzonitrile at 298 K irradiated at 599 nm; b) time profiles at 410 (dotted line) and 490 nm (solid line); c) Decay time profiles at 500 nm of \textbf{19:20a} in deaerated benzonitrile; and d) plot of the pseudo-first order rate constant ($k_{obs}$) vs molar concentration of \textbf{20a}.

Figure 1.37  Energy level diagram of the donor-acceptor photosystem \textbf{21}.

Figure 1.38  Steady-state a) absorption and b) fluorescence ($\lambda_{exc} = 550$ nm) spectra of Fc (wine-red), C$_{60}$COOMe (black), \textbf{19} (red), \textbf{22b} (blue), \textbf{22a} (green), and \textbf{22} (magenta) in dichloromethane and o-dichlorobenzene, respectively. Inset: 600-750 nm region illustrating C$_{60}$ absorption.

Figure 1.39  Nanosecond transient absorption spectra of a) \textbf{22b} and b) \textbf{22} in Ar-saturatured o-dichlorobenzene laser irradiated at 532 nm. Inset: time profiles at 1020 nm.

Figure 1.40  Energy level diagram of \textbf{22}.

Figure 1.41  Absorption spectra of PTZpy (red), TPTZpy (green), C$_{60}$COOMe (blue), \textbf{19} (magenta), and \textbf{22b} (wine) in dichloromethane. Inset: 600-750 nm region illustrating C$_{60}$ absorption.

Figure 1.42  Nanosecond transient absorption spectra of a) \textbf{23}, b) \textbf{24}, c) py:22b, and d) 22b in Ar-saturatured o-dichlorobenzene laser irradiated at 532 nm. Inset: time profiles at 1020 nm.

Figure 1.43  Energy level diagram of \textbf{23} and \textbf{24} depicting the photophysical and photochemical events occurring in the self-assembled multimodular donor-acceptor system.

Figure 1.44  Absorption spectra of \textbf{19} (dashed line), NDI-Ph (dotted line), and \textbf{25} (solid line) in dichloromethane. Inset: absorption spectra of TTF-py and TTF-Ph-py.

Figure 1.45  Signal decay and qualitative model of charge recombination in \textbf{27}.

Figure 1.46  Energy level diagram for the self-assembled multimodular donor-acceptor systems \textbf{26} and \textbf{27}.

Figure 1.47  Structures and acronyms for the types of substituted subphthalocyanines: D (dodecasubstituted), U (unsymmetrically trisubstituted), H$_{\alpha}$ (hexasubstituted at the $\alpha$ positions), H$_{\beta}$ (hexasubstituted at the $\beta$ positions), and N (subnaphthalocyanine).
Figure 1.48 a) Absorption and b) fluorescence spectra ($\lambda_{\text{exc}} = 525$ nm) of dyads 30, 31, and its control compounds in benzonitrile.

Figure 1.49 Differential transient absorption spetra of a) 29, b) 30, and c) 31 obtained upon femtosecond flash photolysis ($\lambda_{\text{exc}} = 440$ nm) in benzonitrile; d) nanosecond transient absorption spectra of 30 in benzonitrile ($\lambda_{\text{exc}} = 570$ nm). Inset: time profiles at 600 (a, b, and c) and 450 nm (d).

Figure 1.50 Energy level diagram for dyads 30 and 31 illustrating the electron transfer events.

Figure 1.51 Differential absorption spectra obtained upon femtosecond flash photolysis ($\lambda_{\text{exc}} = 550$ nm) of a) 32 and b) 33 in THF.

Figure 1.52 Differential absorption spectra obtained upon a) picosecond and b) nanosecond flash photolysis ($\lambda_{\text{exc}} = 532$ nm) of 40a in nitrogen saturated toluene at time delay 25 ps and 50 ns, respectively.

Figure 1.53 Differential absorption spectra obtained upon picosecond flash photolysis ($\lambda_{\text{exc}} = 532$ nm) of 40 in nitrogen saturated toluene at time delay a) 50 and b) 2500 ps, respectively.

Figure 1.54 Differential absorption spectra obtained upon nanosecond flash photolysis ($\lambda_{\text{exc}} = 532$ nm) of 42 in nitrogen saturated benzonitrile at 50 ns time delay.

Figure 3.1.1 Proposed photochemical events in the supramolecular Fc-(ZnP:ImC60)-BODIPY tetrad featuring a zinc porphyrin (ZnP) as primary electron donor, BODIPY as energy transferring antenna, ferrocene (Fc) as charge stabilizing hole-shift agent, and fullerene (C60Im) as terminal electron acceptor. Abbreviations: EnT – excited energy transfer, ET = excited electron transfer, HS = hole shift and CR = charge recombination. The photochemical events are shown as 1, 2, according to their appearance upon selective excitation of the BODIPY entity of the supramolecular assembly.

Figure 3.1.2 (a) Absorption and (b) emission spectrum ($\lambda_{\text{exc}} = 500$ nm) of Fc-ZnP-BODIPY, ZnP-BODIPY, BODIPY, Fc-ZnP and ZnP (8 \(\mu\)M each) in N2 saturated o-DCB.

Figure 3.1.3 (a) Absorbance and (b) fluorescence spectrum ($\lambda_{\text{exc}} = 500$ nm) of Fc-ZnP-BODIPY triad (8 \(\mu\)M) with increasing addition of C60Im (0.2 eq.
each) in o-DCB.

Figure 3.1.4 B3LYP/6-31G* optimized structures of supramolecular tetrad (Fc-(ZnP:ImC60)-BODIPY) assembled by coordinating C60Im to Fc-ZnP-BODIPY triad. Two structures, one in which the C60 is close to ferrocene and another in which the C60 is close BODIPY are shown.

Figure 3.1.5 Cyclic voltammograms of Fc-ZnP-BODIPY triad (dashed) and Fc-(ZnP:ImC60)-BODIPY tetrad (solid line) in o-DCB containing 0.1 M (TBA)ClO4. Scan rate = 100 mV/s.

Figure 3.1.6 Energy level diagram showing the different photochemical events of the supramolecular Fc-(ZnP:ImC60)-BODIPY tetrad after excitation of either the BODIPY ($\lambda_{exc} = 505$ nm) or ZnP ($\lambda_{exc} = $ Soret or visible band) entities in o-DCB. Abbreviations: $k$ stands for different kinetic processes. EnT = excited energy transfer, ET = excited electron transfer, HS – hole shift, EM = electron migration, CS = charge separation, ISC = intersystem crossing, and CR = charge recombination. Thick arrow – most probable process, and thin and dotted arrow – less likely process. Fc-(ZnP:1ImC60*)-BODIPY is abbreviated as 1ImC60* for simplicity.

Figure 3.1.7 Femtosecond transient absorption spectra of Fc-ZnP-BODIPY triad ($\lambda_{exc} = 400$ nm of 100 fs pulse width) at the indicated time intervals in N2 purged (a) o-DCB and (b) toluene solutions.

Figure 3.1.8 Femtosecond transient absorption spectra of the Fc-(ZnP:ImC60)-BODIPY tetrad ($\lambda_{exc} = 400$ nm of 100 fs pulse width) at the indicated time intervals in N2 purged (a) o-DCB and (b) toluene. Figure c and d show the time profile of the 1000 nm band in o-DCB and toluene, respectively.

Figure 3.1.9 Nanosecond transient absorption spectra of the Fc-(ZnP:ImC60)-BODIPY tetrad ($\lambda_{exc} = 430$ nm of 7 ns pulse width) at the indicated time intervals in Ar purged (a) o-DCB and (b) toluene. Figures c and d show the time profile of the 1040 nm band in o-DCB and toluene, respectively.

Figure 3.1.S1 Excitation spectrum of the Fc-ZnP-BODIPY triad in DCB. The spectrum was recorded by holding the emission monochromator to 650 nm corresponding to ZnP emission and scanning the excitation monochromator wavelength.

Figure 3.1.S2 Femtosecond transient spectra of ZnTTP in (a) o-DCB and (b) toluene upon excitation using 400 nm laser.
Figure 3.1.S3 Fluorescence spectrum of ZnP (black line), ZnP-BODIPY (green line), Fc-ZnP-BODIPY (red line) in (a) o-DCB and (b) toluene. The samples were excited at their respective Soret band wavelength position.

Figure 3.1.S4 Femtosecond transient absorption spectra of the ZnP:ImC_{60} dyad (λ_{exc} = 400 nm of 100 fs pulse width) at the indicated time intervals in N_{2} purged (a) o-DCB and (b) toluene. Figure c and d show the time profile of the 1000 nm band in o-DCB and toluene, respectively.

Figure 3.1.S5 Femtosecond transient spectra of fullerene, C_{60} upon excitation using 400 nm laser in toluene.

Figure 3.1.S6 MALDI-mass spectrum of Fc-H_{2}P-BODIPY triad.

Figure 3.1.S7 MALDI-mass spectrum of Fc-ZnP-BODIPY triad.

Figure 3.1.S8 1H-NMR spectrum of (a) Fc-H_{2}P-BODIPY and (b) Fc-ZnP-BODIPY in CDCl_{3}.

Figure 3.1.S9 13C-NMR spectrum of Fc-ZnP-BODIPY in CDCl_{3}.

Figure 3.2.1 Structure of the donors (1 to 4) and acceptors (5 and 6) utilized to form supramolecular dyads (1:5 or 1:6) and triads (binding of 2, 3, or 4 to 5 or 6) via metal-ligand axial coordination of zinc porphyrin. The symbol ‘:’ refers to metal-ligand axial coordination bond.

Figure 3.2.2 Normalized absorption and fluorescence spectrum (λ_{exc} = 550 nm) of zinc porphyrin, 1 and ferrocene-zinc porphyrin derivatives (2-4) and phenylimidazole functionalized fullerene, 6 in N_{2} saturated toluene.

Figure 3.2.3 Energy level diagram showing the different photochemical events of the supramolecular triad composed of ferrocene, zinc porphyrin and fullerene entities (λ_{exc} = 400 nm) in DCB. Abbreviations: k stands for different kinetic processes. HS = hole shift, CS = charge separation, ISC = intersystem crossing, and CR = charge recombination. Thick and solid arrows – most probable process, and dashed arrow – less likely process.

Figure 3.2.4 Spectral changes observed for compound 2 during (a) second oxidation corresponding to the formation of Fc^{+}-ZnP^{++} and (b) first reduction corresponding to the formation of Fc-ZnP^{+} species in DCB containing 0.2 M (TBA)ClO_{4}. Please note that first oxidation corresponding to the formation of Fc^{+}-ZnP revealed no significant spectral changes in the monitored spectral window. Figure inset are spectra in the visible region enlarged vertically by a factor of 10.

Figure 3.2.5 Femtosecond transient absorption spectra of (a) 1, (b) 2, (c) 3 and (d) 4.
in toluene at the excitation wavelength of 400 nm. Figure inset in b and d shows time profile of the 680 nm peak corresponding to ZnP•.

Figure 3.2.6 Time profile of the 460 nm peak representing decay of zinc porphyrin singlet excited state in pristine zinc porphyrin and ferrocene-zinc porphyrin dyads in toluene.

Figure 3.2.7 Femtosecond transient absorption spectra of (a) 2:5 (0.05 mM each) and (b) 2:6 (0.05 mM each) in toluene at the excitation wavelength of 400 nm. Figures b, c and d show the time profile of the 680, 726 and 1020 nm bands of 2:5. Figures f, g and h show the time profile of the 680, 722 and 1020 nm bands of 2:6.

Figure 3.2.8 Femtosecond transient absorption spectra of (a) 3:5, and (b) 3:6 in toluene at the excitation wavelength of 400 nm. Figures b and c show the time profile of the 710 and 1020 nm bands of 3:5. Figures e and f show the time profile of the 723 and 1020 nm bands of 3:6.

Figure 3.2.9 Femtosecond transient absorption spectra of (a) 4:5, and (b) 4:6 in toluene at the excitation wavelength of 400 nm. Figures b, c and d show the time profile of the 680, 710 and 1020 nm bands of 4:5. Figures f, g and h show the time profile of the 685, 710 and 1020 nm bands of 4:6.

Figure 4.1.1 Structures of the axial supramolecular triads investigated in this study.

Figure 4.1.2 (a) UV-visible absorption spectra in dichloromethane. AlPor-Ph-C60 (purple), AlPor-Ph2-C60 (maroon), AlPor-Ph3-C60 (green), AlPor-Ph (red) and C60-Ph-COOMe (blue); inset: TTF-py (orange) and TTF-Ph-py (cyan). The porphyrin Q bands and TTF bands were multiplied by factor of 10. (b) Absorption titrations of AlPor-Ph2-C60 with TTF-py in α-DCB. The inset shows the Benesi-Hildebrand plot of the absorbance change at 604 nm. Calculated binding constant \(K = 1.2 \times 10^3\ \text{M}^{-1}\). (c) Fluorescence spectra of AlPor-Ph (red), AlPor-Ph-C60 (purple), AlPor-Ph2-C60 (maroon) and AlPor-Ph3-C60 (green) in α-DCB. Excitation light wavelength 550 nm. (d) Fluorescence titrations of AlPor-Ph2-C60 with TTF-py in α-DCB. The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations. In titrations TTF-py was added up to 1.9 \times 10^{-3} \text{M} in 10 \mu l (1.12 \times 10^{-4} \text{M}) increments to a 1 ml (6 \times 10^{-5} \text{M}) solution of AlPor-Ph2-C60.

Figure 4.1.3 (a-f) Optimized structures of TTF-Ph\_n-py→AlPor-Ph\_m-C60 (n = 0, 1 and m = 1, 2, 3). (g - k) Show the molecular electrostatic potential map (MEP), LUMO+3, HOMO-1, HOMO and LUMO of TTF-Ph-py→AlPor-Ph-C60.
Figure 4.1.4 Energy level diagram illustrating the major photophysical processes in newly constructed dyads and triads in o-DCB.

Figure 4.1.5 Femtosecond transient absorption spectra of (a) AlPor-Ph-C₆₀ and (b) AlPor-Ph₂-C₆₀ in toluene at the indicated time intervals. (c) The time profile of the 1000 nm radical peak of C₆₀ for (i) AlPor-Ph-C₆₀, and (ii) AlPor-Ph₂-C₆₀. (d) Normalized to the peak maxima decay of the 1240 nm peak of (i) AlPor-Ph, (ii) AlPor-Ph₃-C₆₀, (iii) AlPor-Ph₂-C₆₀, and (iv) AlPor-Ph-C₆₀.

Figure 4.1.6 Femtosecond transient absorption spectra of (a) TTF-py→AlPor-Ph₂-C₆₀ and (b) TTF-Ph-py→AlPor-Ph₂-C₆₀ in toluene. The normalized to the peak maxima time profiles of the 1240 nm peak of ¹¹AlPor⁺ for the investigated AlPor-Ph-C₆₀, AlPor-Ph₂-C₆₀, and AlPor-Ph₃-C₆₀ dyads (black) in the presence of TTF-py (red) and TTF-Ph-py (blue) to form triads are shown in Figures c, d, and e, respectively. Note that the 1240 nm peak is too noisy due to rapid decay, for that reason only decay fit curves are shown.

Figure 4.1.7 (a) Nanosecond transient absorption spectra of 0.1 mM TTF-py→AlPor-Ph-C₆₀ observed by 532 nm (ca. 3 mJ/pulse) laser irradiation in o-DCB. Inset: Absorption time profile at 1020 nm. (b) Absorption time profile at 470 nm.

Figure 4.1.8 Room temperature spin-polarized transient EPR spectra of the TTF-Phₙ-py→AlPor-Phₘ-C₆₀ triads. The spectra on the right and left have been extracted from the time/field data sets in time windows centered at 75 and 550 ns, respectively. The black traces are experimental spectra, and the red traces are simulations. The details of the simulations are given in the text.

Figure 4.1.9 Time evolution of the population distribution of the radical pair spin states and the spin-polarized transient EPR signals. Top: qualitative diagram showing the time evolution of the population distribution of the spin states of the weakly coupled radical pair TTF⁺C₆₀⁻⁻. Bottom: time traces of the spin-polarized EPR signal at the maximum of the absorptive signal near 347.4 mT. The black traces are the experimental data. The red traces are fits. The lifetime of the initial decay is indicated next to each trace.

Figure 4.1.10 Distance dependence of the exchange coupling and back reaction rate. (a) exchange coupling from the simulations of the TREPR spectra. (b) back reaction rate from nanosecond transient absorbance and singlet recombination rate from TREPR data.
Figure 4.1.S1  
$^1$H (top) and $^1$H-$^1$H COSY (bottom) NMR spectra (300 MHz) of AlPor-Ph$_2$-C$_{60}$ in CDCl$_3$.  

Figure 4.1.S2  
$^1$H (top) and $^1$H-$^1$H COSY (bottom) NMR spectra (300 MHz) of AlPor-Ph$_3$-C$_{60}$ in CDCl$_3$.  

Figure 4.1.S3  
UV-visible absorption spectra of 0.1 mM solutions of AlPor-Ph-C$_{60}$ (purple), AlPor-Ph$_2$-C$_{60}$ (maroon), AlPor-Ph$_3$-C$_{60}$ (green), AlPor-Ph (red), C$_{60}$COOMe (blue) and 1:1 mixture (magenta) of AlPor-Ph and C$_{60}$COOMe in dichloromethane. Inset: Magnified spectra between 650-850 nm.  

Figure 4.1.S4  
Structural information of investigated reference compound (AlPor-Ph), dyads and pyridine appended TTF derivatives (TTF-py and TTF-Ph-py).  

Figure 4.1.S5  
$^1$H NMR (300 MHz) spectra of 2.3 mM solutions of TTF-Ph-py (bottom), AlPor-Ph-C$_{60}$ (middle) and TTF-Ph-py→AlPor-Ph-C$_{60}$ (top) in CDCl$_3$.  

Figure 4.1.S6  
$^1$H NMR spectrum (300 MHz) of 2.9 mM TTF-py→AlPor-Ph-C$_{60}$ in CDCl$_3$.  

Figure 4.1.S7  
Spectral titrations of AlPor-Ph-C$_{60}$ with TTF-py in o-DCB. TTF-py was added up to $1.9 \times 10^{-3}$ M in $1.12 \times 10^{-4}$ M increments to a $6 \times 10^{-5}$ M solution of AlPor-Ph-C$_{60}$. Left: Absorption titrations, inset shows the Benesi-Hildebrand plot of the change of absorbance at 604 nm. Right: Fluorescence titrations, the excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.  

Figure 4.1.S8  
Spectral titration of AlPor-Ph-C$_{60}$ with TTF-Ph-py in o-DCB. TTF-Ph-py was added up to $1.9 \times 10^{-3}$ M in $1.12 \times 10^{-4}$ M increments to a $6 \times 10^{-5}$ M solution of AlPor-Ph-C$_{60}$. Left: Absorption titrations, inset shows the Benesi-Hildebrand plot of the change of absorbance at 604 nm. Right: Fluorescence titrations, the excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.  

Figure 4.1.S9  
Spectral titrations of AlPor-Ph$_2$-C$_{60}$ with TTF-Ph-py in o-DCB. Pyridine was added up to $4.51 \times 10^{-3}$ M in $3.48 \times 10^{-4}$ M increments to a $6 \times 10^{-5}$ M solution of AlPor-Ph$_2$-C$_{60}$. Left: Absorption titrations, inset shows the Benesi-Hildebrand plot of the change of absorbance at 604 nm. Right: Fluorescence titrations, the excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.  

Figure 4.1.S10  
Spectral titrations of AlPor-Ph$_2$-C$_{60}$ with TTF-Ph-py in o-DCB. TTF-Ph-py was added up to $1.9 \times 10^{-3}$ M in $1.12 \times 10^{-4}$ M increments to a $6 \times 10^{-5}$
M solution of AlPor-Ph2-C60. Left: Absorption titrations, inset shows the Benesi-Hildebrand plot of the change of absorbance at 604 nm. Right: Fluorescence titrations, the excitation wavelength was chosen at the isosbestic point, 554 nm, obtained from UV-visible titrations.

Figure 4.1.S11  Spectral titrations of AlPor-Ph2-C60 with py in o-DCB. Pyridine was added up to $1.9 \times 10^{-3}$ M in $1.12 \times 10^{-4}$ M increments to a $6 \times 10^{-5}$ M solution of AlPor-Ph2-C60. Left: Absorption titrations, inset shows the Benesi-Hildebrand plot of the change of absorbance at 604 nm. Right: Fluorescence titrations, the excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.

Figure 4.1.S12 Spectral titrations of AlPor-Ph3-C60 with TTF-py in o-DCB. TTF-py was added up to $1.9 \times 10^{-3}$ M in $1.12 \times 10^{-4}$ M increments to a $6 \times 10^{-5}$ M solution of AlPor-Ph3-C60. Left: Absorption titrations, inset shows the Benesi-Hildebrand plot of the change of absorbance at 604 nm. Right: Fluorescence titrations, the excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.

Figure 4.1.S13 Spectral titrations of AlPor-Ph3-C60 with TTF-Ph-py in o-DCB. TTF-Ph-py was added up to $1.9 \times 10^{-3}$ M in $1.12 \times 10^{-4}$ M increments to a $6 \times 10^{-5}$ M solution of AlPor-Ph3-C60. Left: Absorption titrations, inset shows the Benesi-Hildebrand plot of the change of absorbance at 605 nm. Right: Fluorescence titrations, the excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.

Figure 4.1.S14 Spectral titrations of AlPor-Ph with TTF-py in o-DCB. TTF-py was added up to $1.9 \times 10^{-3}$ M in $1.12 \times 10^{-4}$ M increments to a $6 \times 10^{-5}$ M solution of AlPor-Ph. Left: Absorption titrations, inset shows the Benesi-Hildebrand plot of the change of absorbance at 604 nm. Right: Fluorescence titrations, the excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.

Figure 4.1.S15 Spectral titrations of AlPor-Ph with TTF-Ph-py in o-DCB. TTF-Ph-py was added up to $1.9 \times 10^{-3}$ M in $1.12 \times 10^{-4}$ M increments to a $6 \times 10^{-5}$ M solution of AlPor-Ph. Left: Absorption titrations, inset shows the Benesi-Hildebrand plot of the change of absorbance at 604 nm. Right: Fluorescence titrations, the excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.
Hildebrand plot of the change of absorbance at 604 nm. Right: Fluorescence titrations, the excitation wavelength was chosen at the isosbestic point, 554 nm, obtained from UV-visible titrations.

Figure 4.1.S17 Spectral titrations of AlPor-Ph with py in o-DCB. Pyridine was added up to $4.5 \times 10^{-3}$ M in $2.23 \times 10^{-4}$ M increments to a $6 \times 10^{-3}$ M solution of AlPor-Ph. Left: Absorption titrations, inset shows the Benesi-Hildebrand plot of the change of absorbance at 604 nm. Right: Fluorescence titrations, the excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.

Figure 4.1.S18 Spectral titrations of AlPor-Ph with TTF in o-DCB. TTF was added up to $3.53 \times 10^{-3}$ M in $2.10 \times 10^{-4}$ M increments to solution of $6 \times 10^{-5}$ M solution of AlPor-Ph. Left: Absorption titrations. Right: Fluorescence titrations, the excitation wavelength was chosen to be 555 nm.

Figure 4.1.S19 Molecular electrostatic potential map (MEP), HOMO-1, HOMO and LUMO of TTF-Ph-py→AlPor-Ph-C60.

Figure 4.1.S20 Molecular electrostatic potential map (MEP), HOMO-1, HOMO and LUMO of TTF-py→AlPor-Ph2-C60 (top) and TTF-Ph-py→AlPor-Ph2-C60 (bottom).

Figure 4.1.S21 Molecular electrostatic potential map (MEP), HOMO-1, HOMO and LUMO of TTF-py→AlPor-Ph3-C60 (top) and TTF-Ph-py→AlPor-Ph3-C60 (bottom).

Figure 4.1.S22 Differential pulse voltammograms of (a) Ferrocene (magenta), TTF-py (maroon) and TTF-Ph-py (blue) (b) 0.52 mM solution of AlPor-Ph (red), TTF-py→AlPor-Ph (maroon) and TTF-Ph-py→AlPor-Ph (blue) (c) 0.43 mM solution of AlPor-Ph-C60 (red), TTF-py→AlPor-Ph-C60 (maroon) and TTF-Ph-py→AlPor-Ph-C60 (blue) in 0.1 M TBAP, o-DCB.

Figure 4.1.S23 Left: Absorption (black) and fluorescence (red) spectra of AlPor-Ph in o-DCB at room temperature. Right: Phosphorescence spectrum of AlPor-Ph in CH2Cl2:C2H5OH (= 1:1) at 77K.

Figure 4.1.S24 Diagram illustrating the energies of the possible charge separated states in newly constructed dyads and triads in toluene. Note that the reported energies of TTF**AlPor**, AlPor**C60** and TTF**C60** are average values of two dyads (TTF-Phn-py→AlPor-Ph, n = 0, 1), three dyads (AlPor-Phm-C60, m = 1-3) and six triads (TTF-Phn-py→AlPor-Phm-C60, n = 0, 1 and m = 1-3), respectively.
Figure 4.1.S25 Femtosecond transient spectra of AlPor-Ph in toluene at the indicated time intervals. The time profiles of (i) 487, (ii) 448, (iii) 1240 and (iv) 648 nm are shown.

Figure 4.1.S26 Fluorescence decay curve of AlPor-Ph in Ar-saturated toluene. Excitation and emission wavelengths were at 560 and 590 nm, respectively.

Figure 4.1.S27 Femtosecond transient absorption spectra of AlPor-Ph-C\textsubscript{60} and TTF-py→AlPor-Ph-C\textsubscript{60} in toluene at different time intervals.

Figure 4.1.S28 (a) Nanosecond transient absorption spectra of 0.1 mM TTF-py→AlPor-Ph-C\textsubscript{60} observed by 532 nm (ca. 3 mJ/pulse) laser irradiation in o-DCB. Inset: Absorption-time profile at 1020 nm. (b) Absorption time profile at 470 nm.

Figure 4.2.1 Formation of vertically arranged self-assembled supramolecular triads through Lewis acid-base interactions.

Figure 4.2.2 \textsuperscript{1}H NMR (300 MHz) spectra of TTF-py (top), AlPor-Ph-H\textsubscript{2}Por (middle) and TTF-py→AlPor-Ph-H\textsubscript{2}Por (bottom) in CDCl\textsubscript{3}.

Figure 4.2.3 UV-visible absorption spectra of dyad AlPor-Ph-H\textsubscript{2}Por (green) and reference compounds H\textsubscript{2}Por-Ph (blue) and AlPor-Ph (red) in dichloromethane.

Figure 4.2.4 (a) Absorption and (b) fluorescence titrations of AlPor-Ph-H\textsubscript{2}Por with TTF-py in dichloromethane. The inset shows the Benesi-Hildebrand plot of the change of absorbance at 603 nm. TTF-py was added up to $1.88 \times 10^{-3}$ M in 20 μL ($2.22 \times 10^{-4}$ M) increments to 1 mL ($6 \times 10^{-5}$ M) solution of AlPor-Ph-H\textsubscript{2}Por. The excitation wavelength was chosen at the isosbestic point, 555 nm, which was obtained from absorption titrations.

Figure 4.2.5 Energy level diagram for the dyad and its corresponding self-assembled triads in dichloromethane. Black solid and dashed lines represent energy transfer and electron transfer, respectively.

Figure 4.2.6 (a) Steady-state fluorescence spectra of AlPor-Ph-H\textsubscript{2}Por (green), AlPor-Ph (red) and H\textsubscript{2}Por-Ph (blue) with excitation at 550 nm in dichloromethane. (b) Absorption (solid) and corrected fluorescence excitation (dashed) spectra of dyad in dichloromethane and the spectra were normalized between 610-650 nm. The excitation spectrum was collected at 720 nm emission band.
Figure 4.2.7 (a) Steady-state fluorescence spectra of AlPor-Ph-H₂Por (green), AlPor-Ph (red) and H₂Por-Ph (blue) with excitation at 560 nm in acetonitrile. (b) Absorption (solid) and corrected fluorescence excitation (dashed) spectra of dyad in acetonitrile and the spectra were normalized between 610-650 nm. The excitation spectrum was collected at 720 nm corresponding to emission of H₂Por.

Figure 4.2.8 Absorption (solid) and corrected fluorescence excitation (dashed) spectra of triad TTF-py→AlPor-Ph-H₂Por in dichloromethane and the spectra were normalized between 610-650 nm. The excitation spectrum was collected at 720 nm corresponding to emission band of H₂Por. TTF-py and AlPor-Ph-H₂Por are present in $1.88 \times 10^{-3}$ M and $6 \times 10^{-5}$ M in solution, respectively.

Figure 4.2.9 (a) Femtosecond transient absorption spectra and (b) decay profile at 1240 nm of AlPor-Ph-H₂Por in o-DCB.

Figure 4.2.10 (a) Femtosecond transient absorption spectra, and (b) decay profile at 1240 nm of TTF-py→AlPor-Ph (1:3 ratio) in o-DCB.

Figure 4.2.11 Femtosecond transient absorption spectra of (a) AlPor-Ph-H₂Por (black), TTF-py→AlPor-Ph-H₂Por (red) and TTF-Ph-py→AlPor-Ph-H₂Por at a delay time of 500 ps, (b) decay profile at 1244 nm of TTF-py→AlPor-Ph-H₂Por and (c) decay profile at 1244 nm of TTF-Ph-py→AlPor-Ph-H₂Por in o-DCB.

Figure 4.2.12 (a) Femtosecond transient absorption spectra of AlPor-Ph (red), H₂Por-Ph (blue) and AlPor-Ph-H₂Por (green) at 200 ps, and (b) time profile at ~1205 nm of AlPor-Ph-H₂Por in acetonitrile.

Figure 4.2.13 Proposed modulation of photoinduced processes in dyad and its corresponding triads.

Figure 4.2.S1 $^1$H NMR (300 MHz) spectrum of H₂Por-Ph-COOCH₃ in CDCl₃.

Figure 4.2.S2 $^1$H NMR (300 MHz) spectrum of H₂Por-Ph-COOH in CDCl₃.

Figure 4.2.S3 $^1$H NMR (300 MHz) spectrum of AlPor-Ph-H₂Por in CDCl₃.

Figure 4.2.S4 $^1$H NMR (300 MHz) spectrum of H₂Por-Ph-COOH (top) and AlPor-Ph-H₂Por (bottom) in CDCl₃.

Figure 4.2.S5 $^1$H NMR (300 MHz) spectrum of TTF-Ph-py→AlPor-Ph-H₂Por in CDCl₃.
Figure 4.2.S6 UV-visible absorption spectra of dimer AlPor-Ph-H₂Por (green) and its reference compounds AlPor-Ph (red) and H₂Por-Ph (blue) in acetonitrile.

Figure 4.2.S7 UV-visible absorption spectra of TTF-py (orange) and TTF-Ph-py (maroon) in dichloromethane.

Figure 4.2.S8 (a) Absorption and (b) fluorescence titration of AlPor-Ph-H₂Por with TTF-Ph-py in dichloromethane. The insets show the Benesi-Hildebrand plot of the change of absorbance at 603 nm. TTF-Ph-py was added up to 1.88 x 10⁻³ M in 20 μL (2.22 x 10⁻⁴ M) increments to 1 mL (6 x 10⁻⁵ M) solution of dimer. The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.

Figure 4.2.S9 (a) Absorption (b) fluorescence titration of AlPor-Ph-H₂Por with TTF in dichloromethane. TTF was added up to 1.88 x 10⁻³ M in 20 μL (2.22 x 10⁻⁴ M) increments to 1 mL (6 x 10⁻⁵ M) solution of dimer. The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.

Figure 4.2.S10 (a) Absorption and (b) fluorescence titration of AlPor-Ph-H₂Por with py in dichloromethane. The insets shows the Benesi-Hildebrand plot of the change of absorbance at 603 nm. Py was added up to 1.88 x 10⁻³ M in 20 μL (2.22 x 10⁻⁴ M) increments to 1 mL (6 x 10⁻⁵ M) solution of dimer. The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.

Figure 4.2.S11 Cyclic voltammograms of AlPor-Ph (red), H₂Por-Ph (blue) and AlPor-Ph-H₂Por (green) in 0.1 M TBAP dichloromethane. Data were measured with ferrocene as an internal standard. Note that the oxidation at 0.48 V in all voltammograms is due to the ferrocene. Scan rate 25 mV/sec.

Figure 4.2.S12 Absorption (black) and fluorescence (red) spectra of (a) AlPor-Ph and (b) H₂Por-Ph at room temperature.

Figure 4.2.S13 Phosphorescence spectra of AlPor-Ph (red) and H₂Por-Ph (blue) in CH₂Cl₂:C₂H₅OH (1:1) at 77K.

Figure 4.2.S14 Energy level diagram for the dyad in acetonitrile. Black dashed lines represent electron transfer.

Figure 4.2.S15 (a) Spectral overlap between investigated porphyrin units: AlPor fluorescence spectrum (red) and H₂Por absorption spectrum (blue) in dichloromethane. (b) Steady-state fluorescence spectra of AlPor-Ph-
H_{2}Por (green), AlPor-Ph (red), H_{2}Por-Ph (blue) and the calculated spectrum of H_{2}Por-Ph+AlPor-Ph (orange) with excitation at 640 nm in dichloromethane.

Figure 4.2.S16 (a) Spectral overlap between investigated porphyrin units: AlPor fluorescence spectrum (red) and H_{2}Por absorption spectrum (blue) in acetonitrile. (b) Steady-state fluorescence spectra of AlPor-Ph-H_{2}Por (green), AlPor-Ph (red), H_{2}Por-Ph (blue) and the calculated spectrum of H_{2}Por-Ph+AlPor-Ph (orange) with excitation at 640 nm acetonitrile.

Figure 4.2.S17 Absorption (solid) and corrected fluorescence excitation (dashed) spectra of triad TTF-Ph-py→AlPor-Ph-H_{2}Por in dichloromethane and the spectra were normalized between 610-650 nm. TTF-Ph-py and AlPor-Ph-H_{2}Por are present in 1.88×10^{-3} M and 6×10^{-5} M in solution, respectively.

Figure 4.2.S18 (a) Femtosecond transient absorption spectra and (b) decay profile at 1247 nm of AlPor-Ph in o-DCB.

Figure 4.2.S19 (a) Femtosecond transient absorption spectra and (b) decay profile at 1061 nm of H_{2}Por-Ph in o-DCB.

Figure 4.2.S20 Fluorescence decay curve of (a) AlPor-Ph (collected at 608nm) and (b) H_{2}Por-Ph (collected at 708 nm) in dichloromethane. Excitation wavelength at 406 nm.

Figure 4.2.S21 Spectral changes during the reduction of H_{2}Por-Ph at -0.87V in o-DCB.

Figure 4.2.S22 Spectral changes during the oxidation (top) and reduction (bottom) of AlPor-Ph at 1.12V and -0.97V, respectively in o-DCB.

Figure 4.2.S23 Spectral changes during the oxidation of TTF-py at 0.69 V in o-DCB.

Figure 4.2.S24 Femtosecond transient absorption spectra of py→AlPor-Ph-H_{2}Por in o-DCB.

Figure 4.2.S25 (a) Femtosecond transient absorption spectra and (b) decay profile at 1257 nm of TTF-Ph-py→AlPor-Ph in o-DCB.

Figure 4.2.S26 Femtosecond transient absorption spectra of (a) TTF-py→AlPor-Ph-H_{2}Por, and (b) TTF-Ph-py→AlPor-Ph-H_{2}Por in o-DCB.

Figure 4.2.S27 Femtosecond transient absorption spectra of AlPor-Ph-H_{2}Por (black), TTF-py→AlPor-Ph-H_{2}Por (red) and TTF-Ph-py→AlPor-Ph-H_{2}Por (blue) in
o-DCB at different times after excitation.

Figure 4.2.S28 (a) Femtosecond transient absorption spectra of AlPor-Ph and (b) decay profile at 1213 nm in acetonitrile.

Figure 4.2.S29 Femtosecond transient absorption spectra of H2Por-Ph and (b) decay profile at 1020 nm in acetonitrile.

Figure 4.2.S30 Femtosecond transient absorption spectra of AlPor-Ph-H2Por in acetonitrile.

Figure 4.3.1 Formation of vertically arranged self-assembled supramolecular triads through Lewis acid-base interactions.

Figure 4.3.2 The proposed hexavalent complex between the PF6− ion and the Al center of AlPor in non-coordinating solvents.

Figure 4.3.3 UV-visible absorption spectra of (a) AlPor-Ph-AuPor+ (green), AuPor+-Ph (blue) and AlPor-Ph (red) in dichloromethane and (b) AlPor-Ph-AuPor.PF6 in dichloromethane at different concentrations.

Figure 4.3.4 Titrations of AlPor-Ph-AuPor+ with TTF-py in dichloromethane. TTF-py was added up to 1.88 × 10−3 M in 20 μL (2.22 × 10−4 M) increments to 1 mL (6 × 10−5 M) solution of AlPor-Ph-AuPor+. (a) Absorption titrations: Inset shows the Benesi-Hildebrand plot of the change of absorbance at 603 nm. (b) Fluorescence titrations: The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations. The inset shows Job’s plot where the total concentration of [AlPor-Ph-AuPor+]+[TTF-py] was maintained constant at 4.2 × 10−5 M.

Figure 4.3.5 Cyclic voltammograms of (a) AlPor-Ph, (b) AuPor+-Ph and (c) AlPor-Ph-AuPor+ with 0.1 M TBAClO4 in dichloromethane. Data were measured with ferrocene as an internal standard. Note that the oxidation at 0.48 V in all voltammograms is due to the internal standard ferrocene. Scan rate 25 mV/sec.

Figure 4.3.6 Energy level diagram of the dyad and its corresponding supramolecular self-assembled triads in dichloromethane. Black solid lines represent electron transfer or hole transfer processes.

Figure 4.3.7 Emission spectra of AlPor-Ph-AuPor+ (green), AlPor-Ph (red) and AuPor+-Ph (blue) in (a) dichloromethane at room temperature, excitation wavelength of 550 nm and (b) dichloromethane:ethanol ( = 1:1) at 77 K, excitation wavelength of 520 nm.
Figure 4.3.8  Spectral changes observed during the first reduction of AuPor*-Ph in o-DCB with 0.2 M TBAClO₄. 257

Figure 4.3.9  Femtosecond transient absorption spectra of AuPor*-Ph in o-DCB at the excitation wavelength of 400 nm. 258

Figure 4.3.10  Femtosecond transient absorption spectra of (a) AlPor-Ph-AuPor⁺, (b) TTF-py→AlPor-Ph-AuPor⁺ (3:1 ratio), and (c) TTF-Ph-py→AlPor-Ph-AuPor⁺ (3:1 ratio) in o-DCB at the excitation wavelength of 400 nm. Figures d, e and f show the time profile of transient peaks of AlPor-Ph-AuPor⁺, TTF-py→AlPor-Ph-AuPor⁺ and TTF-Ph-py→AlPor-Ph-AuPor⁺, respectively. 260

Figure 4.3.S1  ¹H NMR (300 MHz) spectrum of AuPor-Ph-COOH.PF₆ in CD₃CN. Note that the peaks at 5.45 and 3.81 ppm are due to solvent impurities. 267

Figure 4.3.S2  ³¹P NMR (121 MHz) spectrum of AuPor-Ph-COOH•PF₆ in CD₃CN. 267

Figure 4.3.S3  Figure 4.3.S3. ¹H NMR (300 MHz) spectrum of AuPor-Ph-COOH•PF₆ in CDCl₃. 268

Figure 4.3.S4  ¹H NMR (300 MHz) spectrum of AuPor-Ph-COOCH₃•PF₆ in CD₃CN. Note that the peaks at 5.45 and 3.81 ppm are due to solvent impurities. 269

Figure 4.3.S5  ¹H NMR (300 MHz) spectra of AlPor-Ph-AuPor•PF₆ at ~1 mM (top) and ~2mM (bottom) concentrations in CDCl₃. 270

Figure 4.3.S6  ¹H NMR (300 MHz) spectrum of AlPor-Ph-AuPor•PF₆ (~2 mM) in CD₃CN. 271

Figure 4.3.S7  ¹H NMR (300 MHz) spectrum of TTF-py→AlPor-Ph-AuPor⁺ in CDCl₃. 272

Figure 4.3.S8  ¹H NMR (400 MHz) spectrum of 0.6 mM TTF-Ph-py→AlPor-Ph-AuPor⁺ in CDCl₃. Note that peaks at 7.55, 7.26, 7.06 are to the solvent. 272

Figure 4.3.S9  UV-visible absorption spectra of TTF-py (orange) and TTF-Ph-py (maroon) in dichloromethane. 273

Figure 4.3.S10  (a) Absorption titrations and (b) fluorescence titration of AlPor-Ph-AuPor⁺ with TTF-Ph-py in dichloromethane. The inset shows the Benesi-Hildebrand plot of the change of absorbance at 603 nm. TTF-Ph-py was added up to 1.88 × 10⁻³ M in 20 μL (2.22 x 10⁻⁴ M) increments to 1 mL (6 × 10⁻⁵ M) solution of dyad. The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations. 273
Figure 4.3.S11  Spectral overlap between the AlPor emission (red) and AuPor\(^+\) absorption (orange) spectra in dichloromethane.

Figure 4.3.S12  (a) Absorption titrations and (b) fluorescence titration of AlPor-Ph-AuPor\(^+\) with TTF in dichloromethane. TTF was added up to \(1.88 \times 10^{-3}\) M in 20 µL \((2.22 \times 10^{-4}\) M) increments to 1 mL \((6 \times 10^{-5}\) M) solution of dyad. The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.

Figure 4.3.S13  (a) Absorption titrations and (b) fluorescence titration of AlPor-Ph-AuPor\(^+\) with py in dichloromethane. Pyridine was added up to \(3.80 \times 10^{-3}\) M to 1 mL \((2.4 \times 10^{-5}\) M) solution of dyad. The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.

Figure 4.3.S14  (a) Femtosecond transient absorption spectra and (b) decay profile at 1247 nm of AlPor-Ph in o-DCB.

Figure 5.1.1  (a) Absorption spectrum normalized to the intense visible band, and (b) fluorescence spectrum obtained upon excitation at the visible peak maxima of SubPc, 1 and 2 in benzonitrile.

Figure 5.1.2  B3LYP/3-21G(*) optimized structures of pentads 1 and 2 (a and b, respectively). The frontier HOMO and LUMO for each optimized structure is shown on the right.

Figure 5.1.3  Differential pulse voltammograms (DPVs) corresponding to both oxidation and reduction processes of 1 and 2 in benzonitrile containing 0.1 M \((t\text{-Bu}_4\text{N})\text{ClO}_4\). The DPV with an asterisk shows ferrocene oxidation (red curve) used as an internal standard. The vertical lines are drawn to compare the potentials of phenothiazine, and fulleropyrrolidine redox processes (see text for details). Scan rate = 5 mV/s, pulse width = 0.25 s, pulse height = 0.025 V. Potential vs. Ag/Ag\(^+\).

Figure 5.1.4  Energy level diagram showing the various photochemical events of pentads 1 and 2 in benzonitrile. The magenta lines correspond to the energy of radical ion pairs formed by 2. Abbreviations: CS = charge separation, CR = charge recombination, ISC = intersystem crossing, IC = internal conversion, T = triplet state emission.

Figure 5.1.5  Femtosecond transient absorption spectra of 1 in (a) benzonitrile and (b) toluene. The samples were excited with 400 nm femtosecond (pulse width = 100 fs) laser pulses. The corresponding decay time profile of the C\(_{60}\)\(^{**}\) monitored at 1000 nm is shown on the right.
Figure 5.1.6  Femtosecond transient difference absorption spectra of 2 in (a) benzonitrile and (b) toluene. The samples were excited with 400 nm femtosecond (pulse width = 100 fs) laser pulses. The decay time profile of the C$_{60}^+$ monitored at 1000 nm is shown on the right.

Figure 5.1.7  Nanosecond transient absorption spectra of 2 in (a) benzonitrile and (b) toluene. The samples were excited with 532 nm nanosecond (pulse width = 8 ns) laser pulses. Figure b and c show the time profile of 3SubPc$^*$ monitored at 475 nm in toluene and benzonitrile, respectively.

Figure 5.1.S1  Fluorescence emission spectrum of 2-phenyl fulleropyrrolidine (black), compound 1 (blue) and compound 2 (green) in benzonitrile at the excitation wavelength of 400 nm.

Figure 5.1.S2  B3LYP/3-21G(*) calculated (a) HOMO-2, (b) HOMO-1, (c) HOMO, (d) LUMO, (e) LUMO+1 and (f) LUMO+2 for the optimized structure of 2.

Figure 5.1.S3  Differential spectral changes observed during chemical oxidation using nitrosonium tetrafluoroborate of phenothiazine and 1 in benzonitrile.

Figure 5.1.S4  Differential absorption spectral changes observed during chemical oxidation of 2 in benzonitrile. Nitrosonium tetrafluoroborate was used as an oxidizing agent.

Figure 5.1.S5  Nanosecond transient absorption spectra of (a) 2-phenyl fulleropyrrolidine, (b) SubPc, and (c) (PTZ)$_3$SubPc (precursor compound of 1) in toluene at the indicated delay times. The samples were excited with 532 nm nanosecond (pulse width = 8 ns) laser pulses. The right hand panels show the time profile monitored at 700 nm, 455 nm and 456 nm of the corresponding transient absorption spectra shown in left.

Figure 5.1.S6  (a) Nanosecond transient absorption spectra of 1 in benzonitrile at the indicated delay times. The samples were excited with 532 nm nanosecond (pulse width = 8 ns) laser pulses. Figure b and c show the time profile of the C$_{60}^+$ monitored at 1000 nm in benzonitrile and toluene, respectively.

Figure 5.1.S7  $^1$H-NMR spectrum of 4-formylphenoxy[2,9,16-triiodo subphthalocyaninato] boron(III) in CDCl$_3$.

Figure 5.1.S8  $^1$H-NMR spectrum of 4-formylphenoxy[2,9,16-tri(10H-phenothiazine) subphthalocyaninato] boron(III) in CDCl$_3$.
Figure 5.1.S9  $^1$H-NMR spectrum of 2 in CDCl$_3$.

Figure 5.1.S10  MALDI-TOF-mass spectrum of 2.

Figure 5.2.1  Structures of newly synthesized SubPc-C$_{60}$ dyads with peripherally modified SubPc with thio-aryl entities. Structure of pristine SubPc used as control is also shown.

Figure 5.2.2  a) Absorption and b) emission spectra of compounds 1 and 3 along with control compounds 1c and 3c, and the reference compound, SubPc in DCB. The compounds were excited at the most intense visible band maxima of a given compound.

Figure 5.2.3  Differential pulse voltammograms of the indicated compounds (see Scheme 5.2.1 for structures) in o-DCB, 0.1 M (n-Bu$_4$N)ClO$_4$. Scan rate = 5 mV/s, pulse width = 0.25 s, pulse height = 0.025 V.

Figure 5.2.4  Energy level diagram showing different photochemical events occurring in the dyads, 1-5 in DCB. Solid line: major process, dashed line: minor process.

Figure 5.2.5  Femtosecond transient difference absorption spectra of compounds 1c-5c at the indicated delay times in Ar-saturated benzonitrile.

Figure 5.2.6  Femtosecond transient absorption difference spectra of compounds 1-5 at the indicated delay times in Ar-saturated benzonitrile.

Figure 5.2.7  Femtosecond transient difference absorption spectra of a) 1 (magenta) and 1c (wine) at a delay time of 100 ps, and b) 3 (magenta) and 3c (wine) at the delay time of 250 ps in Ar-saturated benzonitrile.

Figure 5.2.8  Nanosecond transient difference absorption spectra of dyads 1-5 at the indicated delay times in Ar-saturated benzonitrile.

Figure 5.2.S1  Absorption (a) and emission (b) spectrum of compounds 2, 4 and 5 along with control compounds 2c, 4c and 5c, and the reference compound, SubPc in DCB. The compounds were excited at the most intense visible band peak maxima of a given compound.

Figure 5.2.S2  Femtosecond transient difference absorption spectra of compounds 1c-5c at the indicated delay times in Ar-saturated o-DCB.

Figure 5.2.S3  Femtosecond transient absorption difference spectra of compounds 1-5 at the indicated delay times in Ar-saturated o-DCB.
Figure 5.2.S4  Spectral changes observed during first electrochemical oxidation of (a) 2c and (b) 4c in benzonitrile.  

Figure 5.2.S5  $^1$H-NMR spectrum of dyad 1 in CDCl$_3$.  

Figure 5.2.S6  $^{13}$C-NMR spectrum of dyad 1 in CDCl$_3$.  

Figure 5.2.S7  MALDI-mass spectrum of compound 1.  

Figure 5.2.S8  $^1$H-NMR spectrum of dyad 2 in CDCl$_3$.  

Figure 5.2.S9  $^{13}$C-NMR spectrum of dyad 2 in CDCl$_3$.  

Figure 5.2.S10  MALDI-mass spectrum of compound 2.  

Figure 5.2.S11  $^1$H-NMR spectrum of dyad 3 in CDCl$_3$.  

Figure 5.2.S12  $^{13}$C-NMR spectrum of dyad 3 in CDCl$_3$.  

Figure 5.2.S13  MALDI-mass spectrum of compound 3.  

Figure 5.2.S14  $^1$H-NMR spectrum of dyad 4 in CDCl$_3$.  

Figure 5.2.S15  $^{13}$C-NMR spectrum of dyad 4 in CDCl$_3$.  

Figure 5.2.S16  MALDI-mass spectrum of compound 4.  

Figure 5.2.S17  MALDI-mass spectra of compound 5.
LIST OF SCHEMES

Scheme 1.1 Self-assembled Supramolecular 8:17 Photosystem. 54
Scheme 1.2 Photophysical and Photochemical Events in Dyad 9. 57
Scheme 1.3 Photophysical and Photochemical Events in the Self-Assembled 13:18 Photosystem. 60
Scheme 1.4 Photophysical and Photochemical Events in the Self-Assembled 14:18 Photosystem. 60
Scheme 1.5 Photophysical and Photochemical Events in Photosystem 15. 65
Scheme 1.6 Photophysical and Photochemical Events in the Antenna-Reaction Center Photosystem 16. 65
Scheme 1.7 Structures of Triad 22 and its Control Compounds: 22a and 22b. 74
Scheme 1.8 Photophysical and Photochemical Events in the Self-Assembled Photosystem 23 and 24. 77
Scheme 1.9 Structure of Dyad 25, and the Photophysical and Photochemical Events in the Self-Assembled Photosystems 26 and 27. 80
Scheme 3.1.1 Structure of the newly synthesized Fc-ZnP-BODIPY and the control compounds, investigated in the present study. 104
Scheme 3.1.2 Synthetic methodology adopted for Fc-ZnP-BODIPY triad. 107
Scheme 3.2.1 Routes for formation of Fc^+:ZnP:C60^- charge separated state from Fc^-ZnP*:C60 in the investigated supramolecular triads. 129
Scheme 4.1.S1 Synthesis of C60-Ph2-COOH. Reaction conditions: (i) 2M Na2CO3, Pd(PPh3)4, DMF, stir at 110°C for 12 h under N2 (ii) 1M HCl and (iii) Toluene, reflux for 5 h under N2. 172
Scheme 4.1.S2 Synthesis of C60-Ph3-COOH. Reaction conditions: (i) 2M Na2CO3, Pd(PPh3)4, toluene/ethanol, reflux for 4 h under N2 (ii) KMnO4, aq. Na2CO3, acetone, reflux for 3 h, (iii) Con. HCl, (iv) 2M Na2CO3, Pd(PPh3)4, DMF, stir at 110°C for 5 h under N2 (v) 1M HCl and (vi) Toluene, reflux for 9 h under N2. 174
Scheme 4.1.S3 Synthesis of axial aluminum(III)porphyrin-fullerene dyads. Reaction conditions: (i) Toluene, stirring at 60-80°C for 12 h under nitrogen. 176
Scheme 4.1.S4  Self-assembly of supramolecular TTF-Phₙ-py→AlPor-Phₘ-C₆₀ triads.  180

Scheme 4.2.1  Structure of investigated compounds in this study  198

Scheme 4.2.S1  Synthesis of free-base porphyrin derivatives. Reaction conditions: (i) BF₃•(OEt)₂, dichloromethane, 3 h, room temperature, N₂ (ii) p-chloranil, 12 h (iii) TFA, HCl, reflux, 48 h.  223

Scheme 4.2.S2  Synthesis of investigated dimers AlPor-Ph-H₂Por. Reaction conditions: dichloromethane, 12 h, room temperature, N₂.  223

Scheme 4.3.1  Structural information of investigated compounds in this study.  243

Scheme 4.3.S1  Synthesis of gold(III) porphyrin derivatives. Reaction conditions: (i) BF₃•(OEt)₂, dichloromethane, 3 h, room temperature, N₂ (ii) p-chloranil, 12 h (iii) TFA, HCl, reflux, 48 h (iv) & (v) AuCl₃, AcOH, NaOAc, reflux, 16 h.  265

Scheme 4.3.S2  Synthesis of the investigated dyad AlPor-Ph-AuPor. Reaction conditions: dichloromethane, 12 h, room temperature, N₂.  266

Scheme 5.1.1  Structures of the tris(phenothiazine)-SubPc-C₆₀ conjugates developed to probe the role of spacer connecting the primary electron donor (SubPc) to the hole shift agent (PTZ).  278

Scheme 5.1.2  Synthetic methodology developed for 2.  280

Scheme 5.2.1  Synthetic scheme adopted for dyads 1 and 2.  307

Scheme 5.2.2  Synthetic scheme adopted for dyads 3 - 5.  308
CHAPTER 1
INTRODUCTION

1.1 Introduction

According to the International Energy Outlook 2016 (IEO2016) released by the U.S. Energy Information Administration, it is estimated that there will be a 48% increase in the world’s energy consumption from 2012 to 2040.\(^1\) The increase in energy demand is driven by the strong economic growth of developing countries. To accommodate the increasing global energy consumption, expansion in renewable energy sources and nuclear power has been considered and it is expected that there will be an average of 2.6% and 2.3% increase in production per year, respectively, through 2040. However, even with these projections, fossil fuel will still be the major source of energy and it is accounted for more than three-quarters of the world’s energy consumption as shown in Figure 1.1.

With the limited supply of fossil fuel (thus, called non-renewable energy) and its adverse effects to the earth’s condition (i.e., production of greenhouse gases which contributes to global warming and climate change)\(^2\), it is imperative that minimizing its consumption yet still delivering the global energy demand is necessary. This can be best achieved by increasing the production from renewable energy sources since its supply is abundant and unlimited, and is not detrimental to the environment, hence, called clean or green energy. Renewable energies include wind, geothermal, hydropower, solar energy, and biomass.\(^3\)

Among the renewable energies, the solar energy from the sun is the most accessible and abundant, covering the earth with approximately $1.2 \times 10^5$ terawatts (TW) of power in a year; an hour’s worth of this power would be more than enough to supply a year’s global energy
need. However, the biggest challenge for solar power production is the efficiency of its capture and conversion to electricity and fuel. Green plants, algae and cyanobacteria have found effective ways of converting solar energy to chemical energy in a process called photosynthesis. Thus, both extensive and intensive studies have been conducted to understand and elucidate these complex mechanisms in order to mimic and create a more efficient photoconversion method.

Figure 1.1. World energy consumption by energy source, 1990-2040 (quadrillion British thermal units, Btu). Adapted from reference 1.

1.2 Non-renewable and Renewable Sources of Energy

The energy production and consumption drives the global economy. From the simplest kitchen appliance to the most sophisticated computers, all these are being powered by electricity which comes from various energy sources. There are two classifications of energy source: non-renewable and renewable, see Figure 1.2. From the name itself, non-renewable energy comes from sources which cannot be replenished or if it does, will take millions of years to be restored once it’s been completely exhausted. These are fossil fuels which include coal,
oil, petroleum and natural gas, and nuclear power. Fossil fuel is widely used due to its very simple mode of energy conversion from chemical energy to heat from its combustion, then the heat produced is used to generate electricity. However, it poses a great threat to the environment due to its carbon emission which produces greenhouses gases that cause global warming and climate change.

Figure 1.2. Renewable and non-renewable sources of energy.

Renewable energy on the other hand comes from sources that are very much abundant and easily accessible. Such sources are wind, geothermal, hydropower, solar and biomass. Once renewable energy is consumed it can be easily regenerated and will be ready for use again. Furthermore, renewable energy has close to zero-carbon emission which makes it environmentally friendly.

1.3 Solar Energy: Clean Power for the Future

Fossil fuel is currently the energy source of choice stemming from its easy mode of energy conversion from its combustion and geopolitical issues. It is used to power vehicles and industrial machineries, and to supply electricity for our day-to-day activities. However,
consuming fossil fuel comes at a price. With its combustion comes carbon emission and as energy demand and its consumption increases, so is the increase in greenhouse gases emission which accelerates global warming and contributes to climate change. Furthermore, there is a limited supply of fossil fuel and once these deposits are consumed it will take millions of years for it to restore. Therefore, there is a need to find alternative sources that are abundant and renewable, and will provide a clean and environmentally friendly energy.

One of the alternative sources of energy is the sun which continuously delivers $10^5$ TW of power to earth annually which greatly exceeds the energy produced by any other sources, both renewable and non-renewable. The current global energy production and consumption is estimated to be 13 TW a year. An hour’s worth of the sun’s enormous power is enough to supply the annual global energy need.

Solar energy is a carbon-free energy which could greatly improve the earth’s present condition and with its abundance and availability, it is expected that the energy demand can be easily achieved. It is estimated that by 2050, at least 20 TW/year of carbon-free energy (either in the form of electricity, liquid and gaseous fuels) is needed in order to prevent any catastrophic drawback once we pulled out from fossil fuel dependence. However, harnessing the sun’s power is proven to be challenging since the current technology is not yet capable of capturing and converting solar energy to electricity and fuel at 100% efficiency. Furthermore, the current technology itself is not cost-effective allowing only a hand-full of people to use solar panels to harness solar energy. Therefore, a great deal of research is needed in order to find more effective methods in capturing and converting solar energy to electricity and fuel, and to create affordable technology that would be available to everyone.
1.4 Photosynthesis

Photosynthesis is the most vital process that secures the existence and sustainability of life on earth. Green plants, algae and cyanobacteria capture and absorb light energy through its green pigment, chlorophyll $a$. The absorbed light energy (photon) is funneled through a series of pigment-protein complex reaction centers while maintaining a near unity quantum efficiency. In the reaction center, sequence of energy and electron transfers take place which drives the conversion of carbon dioxide and water into chemical energy stored in the form of carbohydrates and release oxygen gas in the process. This is a very simple description of photosynthesis but a detailed picture is discussed in the subsequent section.

1.4.1 Natural Photosynthesis

Natural photosynthesis occurs in two conditions namely oxygenic and anoxygenic photosynthesis. Oxygenic photosynthesis involves the production of oxygen which occurs in green plants, algae and cyanobacteria. Photosynthesis that does not evolve oxygen on the other hand is called anoxygenic and takes place in purple bacteria.

The specific details and mechanisms of natural photosynthesis in green plants and algae are quite difficult to discern due to the complexity of its system. In contrast, cyanobacteria, being a simple life form, have a basic design and perform the same photosynthetic processes. Therefore, by understanding its functions we will be able to comprehend the intricate details of the photosynthetic system; and with the advancement of x-ray crystallography, crystal structures of the photosystems of *Synechococcus elongatus* and *Thermosynechococcus vulcanus* were obtained at a near-atomic and atomic resolution. Figure 1.3 shows the schematic illustration of the deduced photosystems in oxygenic photosynthetic membranes.
It was revealed that sunlight is captured by the light harvesting complex II (LHC II) composed of about 200 chlorophylls (Chls) and 50 carotenoids. The chlorophylls act as an antenna system absorbing photons which will then undergo a sequence of energy and electron transfer to photosystem II and I (PS II and PS I, respectively) with a remarkably high quantum efficiency. Meanwhile, the carotenoids upon excessive sun exposure protect the photosynthetic system from photodamage by dissipating the excess energy either to the surroundings or for other photochemical purposes.

As the series of energy and electron transfer takes place, a $P_{680}$-Chl dimer is oxidized rendering a highly oxidizing $P_{680}^{**}$ which drives the water-splitting reaction in the PS II reaction...
center with the aid of the oxygen-evolving catalyst (OEC). The OEC is a Mn₄CaO₅ cluster with five oxygen atoms serving as oxo-bridges that hold the five metal atoms together and four water molecules are bound to the Mn₄CaO₅ cluster. The water molecules are said to work as substrates for dioxygen formation, see Figure 1.4.⁵b-c The oxidized P₆₈₀⁺⁺⁺, having a +1.2 V oxidation potential vs NHE (normal hydrogen electrode), abstracts four electrons consecutively from the OEC, thus, two H₂O molecules are oxidized yielding one O₂ molecule and four protons (4 H⁺)¹⁶ as shown in Figure 1.3.

Figure 1.4. Structure of the oxygen-evolving catalyst (OEC), Mn₄CaO₅ cluster. Shown are the distances (in Å) between the metal atoms and the oxo-bridges, and water molecules. Adapted from reference 5b.

Bridging the electron and proton transfer between the PS II and PS I reaction centers is the cytochrome b₆f complex.⁵e The mediation is achieved by the oxidation of lipophilic plastoquinol then the reduction of plastocyanin or cytochrome c₆.⁵f The transported electron to PS I then generates a highly reducing potential (Eₘ~−1.3 eV) which is used to drive the production of biological hydrogen carriers, NADPH, while the proton promotes ATP synthesis. Both NADPH and ATP are essential for the conversion of CO₂ to sugars and lipids in plants.⁵d, ¹⁶b
Nature crafted a molecular nanomachine that has the ability to function at near 100% efficiency in harnessing the sun’s power and utilizing it in converting carbon dioxide and water to carbohydrates and oxygen gas that is vital in supporting life on earth. It is our task to pay a close attention to the details and be able to manufacture a synthetic nanomachine that will be able to function in the same manner as natural photosynthesis or even surpass its performance if possible.

1.4.2 Artificial Photosynthesis

Nature has given us a blueprint on how to use the sun’s energy for oxygen and fuel production from low energy, low molecular weight molecules: CO₂ and H₂O. However, direct replication of natural photosynthesis in a laboratory set-up is quite challenging since pigment-protein interfaces are very complex systems, and are unstable once extracted. Hence, different routes have been explored to mimic the natural photosynthetic processes.

Artificial photosynthesis is a fast growing research due to its appeal in generating a solar-driven carbon-free energy which will definitely help improve the current condition of the earth. Furthermore, the vast abundance of sunlight secures the certainty that its energy source will not run out. In order to mimic natural photosynthesis, the synthetic photosystem should be able to absorb sunlight, regulate and transfer the energy in a directional flow, prevent photodegradation, translate excited states to redox potentials, and for the redox potentials to promote proton motive force. Figure 1.5 shows a scheme of an artificial photosynthetic system. To achieve the requisites to mimic natural photosynthesis, the artificial molecular constructs should have:
(1) Light-harvesting antenna systems: The antenna system is an array of photoactive molecules called chromophores that has a strong and intense absorption band in the visible spectrum allowing it to capture and collect as much light energy as possible and funnel it to an energy trap. Since there’s no single chromophore that has the ability to absorb energy in the entire visible spectrum, a combination of chromophores with different photophysical properties is used. These chromophores must be stable in both their ground and excited states, and should also be easily tunable to provide ease with its synthesis. In addition, the molecular connectors linking the array of chromophores, and bridging the chromophores and the energy trap should warrant electronic coupling between the subunits to allow fast and efficient energy transfer though the coupling should not greatly perturb the photophysical characteristics of each subunit in order to maintain its individuality. In the antenna system, the collected light energy is funneled to an energy trap through a series of energy transfer, and is converted to electronic energy.

(2) Reaction center: The reaction center contains an electron donor-acceptor system that is coupled to the energy trap. The funneled photon from the trap is used to promote electron transfer in the donor-acceptor system producing a charge separated state: a positively charged donor and a negatively charged acceptor. The donor-acceptor system could either be assembled covalently or non-covalently (i.e., metal-ligand coordination). In the reaction center, the electronic energy is converted to redox energy.

(3) Multielectron transfer catalysts: Multielectron processes are required to perform a plausible conversion of low-energy content raw material (i.e., CO₂ and H₂O) to high-energy content species (i.e., H₂, reduced form of CO₂, etc.). A series of single electron transfer steps cannot be
used for the said conversion since the intermediate states will have a very high potential; consequently, the electrons need to be accumulated in charge pool devices for it to drive multielectron processes. Both water oxidation and proton reduction occurs in this site. The oxidation of water produces four electrons\textsuperscript{16a} while the reduction of protons requires two electrons. The multielectron catalysts use redox energy to produce chemical energy.\textsuperscript{18}

![Figure 1.5. Simplified scheme of an artificial photosynthetic system. WOC = water oxidizing catalyst, PRC = proton reducing catalyst. Adapted from reference 15.](image)

Design and construction of supramolecular assemblies for artificial photosynthetic systems is a taxing job but it offers great rewards once met. Artificial photosynthesis provides a very promising alternative source of energy that affords a clean (combustion of hydrogen fuel only generates water molecules) and renewable power. A great deal of research is still very much needed in order to create a molecular machine that will effectively utilize solar energy for the oxidation of water and production of hydrogen gas fuel.
1.5 Principles of Steady-State Absorption, Fluorescence and Phosphorescence Emissions

The antenna of both natural and artificial photosynthetic systems is composed of photoactive compounds called chromophores. Chromophores have distinct photophysical properties which allow them to absorb light energy or photon and be promoted to an excited state. Afterwards, the absorbed photon is emitted when the excited chromophore relaxes back to its ground state. The absorption and emission of photons in chromophores is best explained using the Jablonski diagram\textsuperscript{19} shown in Figure 1.6.

Figure 1.6. Jablonski Diagram illustrating the transitions between electronic states. The wave lines indicate non-radiative transitions.

The chromophore has different electronic states namely singlet ground, first, and second designated as $S_0$, $S_1$, and $S_2$, respectively. Moreover, each electronic state has different vibrational states labeled as 0, 1, 2, and etc. When a chromophore absorbs a photon that has sufficient energy, it is promoted from ground state to excited singlet state populating either the $S_1$ or $S_2$ electronic states. It also populates the higher vibrational states of either $S_1$ or $S_2$ excited...
states; though, these excited states will quickly undergo non-radiative relaxation to the lowest vibrational level of \( S_1 \). This typically occurs within \( 10^{-10} \) seconds or less and is called internal conversion. Since internal conversion is a non-radiative process, thus, the population of the lowest vibrational level of \( S_1 \) electronic state is a result from thermal equilibration. It is worth mentioning that light absorption occurs within \( 10^{-15} \) seconds; a time too fast to cause any significant nuclei displacement and is called the Franck-Condon principle.

After internal conversion, the excited chromophore could then decay back to the ground state emitting the photon in the process called fluorescence emission. Henceforth, light emitting chromophores are also called fluorophores due this specific photophysical property. Fluorescence emission takes place within \( 10^{-9}-10^{-6} \) seconds which indicates completion of internal conversion prior to emission (Kasha’s Rule).\(^{20}\) The relaxing chromophore could return to a higher vibrational level of the \( S_0 \) ground state which then quickly achieves thermal equilibrium within \( 10^{-12} \) seconds. As a result, fluorescence emission spectrum is mostly a mirror image of the absorption spectrum. Further, the relaxation or thermal equilibration of the excited chromophore to the lowest vibrational state of \( S_1 \) preceding emission is the reason why fluorescence emission is shifted to longer wavelengths (lower energies) and such shift is called the Stokes shift.

The excited chromophore at the \( S_1 \) singlet state could also undergo spin conversion. Thus, it transitions from \( S_1 \) excited singlet state to \( T_1 \) excited triplet state through a process called intersystem crossing. The emission resulting from \( T_1 \) excited triplet state is called phosphorescence and is shifted to even longer wavelengths relative to fluorescence emission. It is also a couple of magnitudes slower than fluorescence emission since conversion from \( T_1 \)
triplet state to $S_0$ ground state is forbidden. As a consequence, the time constants of phosphorescence emission are within several milliseconds. Phosphorescence can be favored in the presence of heavy atoms like iodine, palladium, platinum, and etc., subsequently enhancing its phosphorescence emission and quantum yield.\textsuperscript{19, 20}

The Jablonski diagram is a simple yet effective tool in understanding light absorption and emission phenomena in molecules. It is the backbone for the comprehension of energy transfer mechanisms in antenna systems for artificial photosynthesis which will be discussed in detail in the later section.

1.6 Fluorescence Quenching

When the intensity of the emitted photon of a fluorophore is reduced, it is said to have undergone fluorescence quenching. The quenching of the emitted light could be a result of:

1. Excited-state reaction: When two or more of the excited fluorophores react with each other and undergo photochemical reactions (i.e., polymerization).
2. Molecular rearrangement: The excitation energy of the molecule induces conformational changes (i.e., photoisomerization).
3. Collisional quenching: The excited fluorophore collides with an atom or molecule that facilitates a non-radiative relaxation to its ground state.
4. Ground-state complex formation: An excited fluorophore coordinates with another molecule which results to a photo-inactive complex, and it is also called static quenching.
5. Energy transfer: When the emitted photon of the excited fluorophore is transferred to another chromophore and as a consequence, the chromophore is excited while the fluorophore returns back to its ground state.
The chemical species that causes the decrease of the fluorescence emission intensity are called quenchers. These quenchers could either be atoms, molecules or ions that interact with the fluorophore which then induces photophysical and photochemical changes resulting in the reduction of the fluorophore’s emission intensity.\textsuperscript{19, 21} Collisional, and static quenching, and energy transfer will be discussed in the preceding subsections.

1.6.1 Collisional Quenching

Collisional quenching is when a quencher comes in contact with the fluorophore and then promotes a non-radiative decay of the fluorophore; thus, it is also called dynamic quenching.\textsuperscript{22} A common example of collisional quenching is the interaction of dissolved molecular oxygen with a fluorophore in a solution. When the fluorophore solution is irradiated with light, the fluorophore is promoted to its excited singlet state then later undergoes intersystem crossing. The excited triplet state fluorophore collides with excited triplet oxygen producing the reactive excited singlet oxygen.\textsuperscript{23} The fluorescence emission intensity of the fluorophore is subsequently decreased since intersystem crossing is favored.

Determination of collisional quenching can be assessed using the Stern-Volmer equation\textsuperscript{19} as shown below:

\[
\frac{F_0}{F} = 1 + k_q \tau_0 [Q] = 1 + K_D [Q]
\]  

(1.1)

where \(F_0\) and \(F\) are the fluorescence intensities in the absence and presence of the quencher, respectively; \(k_q\) is the bimolecular quenching constant; \(\tau_0\) is the lifetime of the fluorophore alone without any quencher; \([Q]\) is the molar concentration of the quencher; and \(K_D\) is the Stern-Volmer quenching constant for dynamic quenching; if it is otherwise, it is designated as \(K_{SV}\). The \(K_D\) value can be calculated by \(K_D = k_q \tau_0\).
A Stern-Volmer plot of $F_0/F$ vs $[Q]$ would result in a linear plot indicating a direct relationship between the $F_0/F$ and the quencher concentration, $[Q]$. The resulting slope will be the Stern-Volmer quenching constant, $K_D$. However, this does not guarantee a collision quenching mechanism because a linear Stern-Volmer plot is also obtained with static quenching which will be shown in the next subsection. Hence, additional experimentation is needed in order to distinguish collisional from static quenching.

1.6.2 Static Quenching

When a fluorophore coordinates to a quencher forming a photo-inactive complex in the ground state, the fluorescence emission intensity of the fluorophore decreases and such event is called static quenching. Some fluorescence emission will still be observed which is from the remaining uncoordinated fluorophore.

For static quenching, since a fluorophore-quencher complex is formed in the ground state, the association constant for the complex formation, $K_S$, is necessary and can be calculated from equation 1.2:

$$K_S = \frac{[F:Q]}{[F][Q]}$$  \hspace{1cm} (1.2)

where $[F:Q]$ is the concentration of the fluorophore-quencher complex; $[F]$ is the uncomplexed fluorophore concentration; and $[Q]$ is the concentration of the quencher. Since it is difficult to assess the fluorophore-quencher complex concentration, it is assumed that the complex is a fraction of the total fluorophore concentration: $[F]_0 = [F] + [F:Q]$. This can then be substituted to equation 1.2 which results to:

$$K_S = \frac{[F]_0-[F]}{[F][Q]} = \frac{[F]_0}{[F][Q]} - \frac{1}{[Q]}$$  \hspace{1cm} (1.3)
Further simplification of equation 1.3 by substituting the fluorophore concentrations with its fluorescence emission intensities and further rearrangement to set the emission intensities in one side of the equation will afford equation 1.4:

\[
\frac{F_0}{F} = 1 + K_S [Q] \tag{1.4}
\]

Equation 1.4 is similar to equation 1.1 which means that the degree of static quenching is also directly proportional to the quencher concentration. Therefore, when a Stern-Volmer plot of \( F_0/F \) vs \([Q]\) is constructed, it will also show a linear relationship between \( F_0/F \) and \([Q]\) which is the same with collisional quenching as shown in Figure 1.7.

![Figure 1.7. Stern-Volmer plot of \( F_0/F \) vs \([Q]\). The red line shows the slope at room temperature while the blue (collisional quenching) and green (static quenching) broken lines are the slopes at higher temperatures.](image)

In order to distinguish collisional quenching from static quenching, Stern-Volmer plot should be constructed at higher temperatures since both quenching are also temperature dependent. At higher temperatures, collisional quenching is preferred since the diffusion of the molecules increases resulting in higher chances of collision; while with static quenching, the weakly bound fluorophore-quencher complex could easily dissociate, thus, less quenching.\(^{26}\)
1.6.3 Photoinduced Energy Transfer

The capture and absorption of photons in both natural and artificial photosynthesis is the most crucial step in the photosynthetic process since the absorbed photons drive the entire photochemical reaction. Therefore, efficient energy transfer is necessary in order to obtain high quantum efficiency indicating very little energy loss which translates into high energy conversion. The flow of excitation energy from the chromophores to the reaction center is often called photoinduced energy transfer (PEnT).

The absorbed photons in the antenna system are funneled to an energy trap and the collected energy is then used to generate redox potentials through electron transfer in the donor-acceptor systems in the reaction center as discussed previously in section 1.4.2. Before we dwell further into the electron transfer process, let’s first focus our attention to the energy transfer routes in the antenna system.

The funneling of the photons to the energy trap is made possible through a sequence of energy transfers between the chromophores. The array of chromophores in the antenna system are linked together by molecular connectors that are highly π-conjugated which promotes electron coupling, thus, allowing a fast and efficient energy transfer. Figure 1.8 shows the proposed energy transfer models in antenna-reaction center photosystems.

The proposed linear arrangement of chromophores (Figure 1.8a) requires a large number of steps for the energy to be transferred to the reaction center as a consequence energy loss are most likely to happen. On the other hand, the two-dimensional planar model (Figure 1.8b) allows lesser number of steps, hence, minimizing energy loss compared to the previous model. Additionally, it permits the stream of energy from multiple chromophores to
the reaction center; nevertheless, energy loss can still ensue in the form of heat. The energy funnel model (Figure 1.8c) has the advantage over the other schemes because it allows a cascading energy transfer from the peripheral chromophores to the reaction center. The spatial and energetic overlap of the chromophores (which can be done through the modulation of the photophysical properties of the constituent pigments) ensures that energy is transferred unidirectionally towards the reaction center minimizing the loss of energy.\textsuperscript{12b, 27}

Figure 1.8. Proposed schemes for energy transfer pathways in antenna-reaction center photosystems: (a) a linear arrangement, (b) a two-dimensional planar distribution, and (c) depicts the antenna system as an energy funnel to the reaction center. Adapted from reference 27.

In order to have a better understanding of the energy transfer pathways in the antenna systems, we first need to establish the different energy transfer mechanisms which will be discussed in the next subsections.
1.6.3.1 Förster Resonance Energy Transfer

Förster resonance energy transfer (FRET) which is often called fluorescence resonance energy transfer is a non-radiative photon transfer from an excited chromophore (donor) to another chromophore (acceptor) which results in the excitation of the acceptor chromophore. Since it’s a non-radiative process the donor does not emit the photon and in a similar manner, the acceptor does not absorb the photon (see Figure 1.9a); thus, the term resonance energy is used because the transfer of energy is from the dipole-dipole interaction or coupling (Coulombic interaction) of the two chromophores and is most effective when the donor and acceptor chromophores are within 10 Å to 100 Å apart.\(^{28}\) One of the most important requirements in order for FRET to take place is the adequate spectral overlap of the fluorescence emission spectrum of the donor which is at shorter wavelengths with the absorption spectrum of the acceptor at longer wavelengths as shown in Figure 1.9b.\(^{29}\)

The rate of Förster dipole-dipole energy transfer \(k_T\) is given by the equation 1.5.\(^{28a}\)

\[
k_T = \left( \frac{1}{\tau_D} \right) \times \left( \frac{R_0}{R} \right)^6
\]

where \(\tau_D\) is the fluorescence lifetime of the donor in the absence of the acceptor; \(R\) is the distance between the donor and acceptor; and \(R_0\) is the Förster or critical transfer distance at which the energy transfer rate is equal to the decay rate, in other words, 50% of the energy has been transferred. There are instances where there’s only one single donor-acceptor configuration, then \(R=R_0\), thus, \(k_T = 1/\tau_D\).
Figure 1.9. Demonstration of the FRET process with (a) showing the non-radiative energy transfer from the excited donor chromophore (D*) to the acceptor chromophore (A), and (b) the spectral overlap, $J(\lambda)$, between the donor emission spectrum and acceptor absorption spectrum. Adapted from reference 29.

Furthermore, the critical transfer distance $R_0$ can be calculated from spectroscopic and mutual dipole orientational parameters of the donor and acceptor shown in equation 1.6:

$$R_0^6 = 8.785 \times 10^{-5} \frac{k^2 \Phi_D J}{n^4}$$

where $k^2$ is the orientation factor between the donor and acceptor and their spectroscopic properties; $\Phi_D$ is the quantum yield of the donor alone with no acceptor; $n$ is the refractive index of the solvent and is generally taken as 1.4 in aqueous solutions; and $J$ is the overlap integral between the donor and acceptor. The orientation factor $k^2$ describes the relative orientation of the transition dipoles of the donor and acceptor which takes into accounts the relative vectors and angles of their positions as shown in Figure 1.10a.
The dependence of the orientation factor $\kappa^2$ to the relevant vectors and angles of the donor and acceptor positions is given in equation 1.7:\textsuperscript{12b}

$$\kappa^2 = (\cos \theta_T - 3 \cos \theta_D \cos \theta_A)^2$$

$$\kappa^2 = (\sin \theta_D \sin \theta_A \cos \phi - 2 \cos \theta_D \cos \theta_A)^2$$

The value of the orientation factor $\kappa^2$ can range from 0 to 4 depending on the transition dipole orientations of the donor and acceptor as shown in Figure 1.10b. When the transition dipole of the donor and acceptor are perpendicular to each other, any energy transfer is prevented; thus, the $\kappa^2 = 0$. Meanwhile, when their transition dipoles are in a parallel position, $\kappa^2 = 1$ indicating some energy transfer. Finally, when their respective transition dipoles are aligned to each other, it provides a maximum energy transfer; hence, $\kappa^2 = 4$. However, when the orientation of the transition dipoles of the donor and acceptor are freely rotating and randomized, the geometric angles are averaged which results in $\kappa^2 = 2/3$. In macromolecular solutions (i.e., biological systems), $\kappa^2 = 2/3$ is oftentimes assumed since the macromolecule can adopt different conformations.\textsuperscript{31}
The overlap integral \( J(\lambda) \) indicates the degree of spectral overlap between the donor (emission) and acceptor (absorption), and can be calculated from equation 1.8:

\[
J(\lambda) = \int_{0}^{\infty} F_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda
\]  

(1.8)

where \( F_D \) is the peak-normalized fluorescence spectrum of the donor while \( \epsilon_A \) is the molar absorption coefficient of the acceptor.

Determination of the efficiency of energy transfer \( E \) is also of great importance since this will indicate if there is any energy loss in the FRET process and this can be obtained from either equation 1.9 or 1.10:

\[
E = 1 - \frac{F_{DA}}{F_D} = \frac{1}{1 + \left( \frac{R}{R_0} \right)^6}
\]

(1.9)

\[
E = 1 - \frac{\tau_{DA}}{\tau_D}
\]

(1.10)

The efficiency of energy transfer \( E \) can be calculated either from the fluorescence emission spectrum (\( F \)) or the lifetime measurement (\( \tau \)) of the donor-acceptor system (DA) and of the donor alone (D).

As shown above, the distance dependence of the FRET process is very much apparent as the rate (equation 1.5) and efficiency (equation 1.9 and 1.10) of the energy transfer is contingent on the sixth power of the distance between the donor and acceptor; hence, FRET is often used as a spectroscopic nanoruler. The FRET phenomenon is of great importance not only in photosynthetic systems but it also finds its applications in biological systems for tagging, labeling, and bioimaging.
1.6.3.2 Dexter Energy Transfer

When the donor and acceptor chromophores are in very close proximity (less than 10 Å), wavefunction (charge orbital) overlap and tunneling of electrons can occur which results in an energy transfer. Such energy transfer is called Dexter energy transfer and is oftentimes called short-range electronic energy transfer.\textsuperscript{32} The energy transfer per se is unlike FRET because Dexter energy transfer essentially involves a concerted or simultaneous two electron exchange between the excited donor and the ground state acceptor chromophores as illustrated in Figure 1.11.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{dexter_energy_transfer_diagram.png}
\caption{A Jablonski diagram depicting Dexter energy transfer.}
\end{figure}

The electron at the LUMO level of the excited donor is exchanged with the electron at the HOMO level of the acceptor as a result the acceptor is excited and the donor relaxed back to its ground state.\textsuperscript{19, 33} The electron exchange could occur via singlet-singlet\textsuperscript{34} or triplet-triplet
energy transfers\textsuperscript{32a, 35} although triplet-triplet energy transfer is not commonly observed, it is quite prevalent in metal-organic complexes and quantum dots.

Designing systems for Dexter-type energy transfer is not as easy compare to FRET systems. Even in systems where the distance between the donor and acceptor is short, as long as there is an adequate overlap of the donor emission spectrum and the acceptor absorption spectrum then the energy transfer mechanism could either be through FRET or Dexter energy transfer which is difficult to distinguish. Therefore, in order for Dexter energy transfer to prevail the spectral overlap of the donor and acceptor chromophores should be minimized.\textsuperscript{19}

Since Dexter energy transfer is a short-ranged energy transfer process, the transfer rates can be expressed in an exponential decay form as shown in equation 1.11:\textsuperscript{32d, 36a}

\[ k_{ET}^{Dexter} = \frac{2\pi}{\hbar} K J_{DA}^{norm} e^{-\frac{2R}{L}} \]  

(1.11)

where $K$ is a factor related to the specific orbital interactions of the donor and acceptor, $J_{DA}^{norm}$ is the normalized spectral overlap integral term, $R$ is the distance between the donor and acceptor, and $L$ is the characteristic wavefunction decay length (i.e., average Bohr radius). The $J_{DA}^{norm}$ term can be calculated from the normalized emission of the donor and the normalized absorbance of the acceptor. Furthermore, the transition dipole or oscillator strength of both donor and acceptor is not significant for Dexter energy transfer; therefore, energy transfer from non-phosphorescent triplet states could only proceed via Dexter energy transfer.\textsuperscript{36} However, it should be noted that since wavefunction overlap is important for Dexter energy transfer that the transfer drastically drops with increasing distance.\textsuperscript{37}
1.7 Photoinduced Electron Transfer

Once the absorbed light energy has undergone through a series of energy transfer and funneled into the energy trap, the collected energy is then converted to redox energy through a series of electron transfers in the PS II reaction center in natural photosynthesis. The generated redox energy is then used to oxidized water at PS II and later used to reduce carbon dioxide at the PS I reaction center as discussed in section 1.4.1. The oxidation of water yields four electrons which are then transported to PS I through cytochrome b6f complex in a series of electron transfers. The transported electrons together with NADPH and ATP reduce carbon dioxide and convert into carbohydrates.\(^{5b-f, 16b}\)

Likewise, reaction centers in artificial photosynthetic systems should also exhibit similar electron transfer processes in order to provide redox energy for the multielectron transfer catalysts, both water oxidizing (WOC) and proton reducing catalysts (PRC), to function as described in section 1.4.2. The oxidation of water produces \(\text{O}_2\) gas, four protons (\(\text{H}^+\)), and four electrons, very much similar to the oxidation reaction at PS II. The electrons are then transported to the PRC through a series of electron transfers through the donor-acceptor system which stabilizes the charges and allow the transport of the electrons. In the PRC, two electrons are utilized to reduce protons forming \(\text{H}_2\) gas.\(^{16a, 17, 18}\)

In order to mimic natural photosynthesis, it is necessary to investigate and have a better understanding of photoinduced electron transfer (PET) processes: its principles and mechanisms. By doing so, improvements can be made for the currently studied artificial photosystems, and have a better design and construction for these supramolecular photosystems. The focus in this section will be the electron donor-acceptor systems in the
artificial photosynthetic apparatus because this is where the electron transfer and charge stabilization is facilitated as mentioned above.

1.7.1 Marcus Theory

The potential energies of reactants and products in a chemical reaction can be depicted as parabolas as described by Morse potentials as shown in Figure 1.12. The intersection point of the two parabolas is a good estimate of the transition state and according to the Hammond postulate, the identity or structure of the activated complex resembles the chemical specie that is closest to in energy. Construction of the reaction coordinate diagram using Morse potentials shows that activation free energy, $\Delta G^\dagger$, is the difference between the lowest reactant free energy and the intersection point of the two parabolas; and the reaction free energy change, $\Delta G^0$, is the energy difference between the lowest free energy of the reactant and product.

It was proposed that for thermodynamically controlled reactions as it becomes more exergonic (a large negative $\Delta G^0$), the reaction will proceed faster. As shown in Figure 1.12b and c, as the reaction becomes more exergonic, $\Delta G^0$ also increases, thus, the reaction rate increases. Especially in Figure 1.12c where the activation free energy is equal to the free energy of the reactant, therefore, the reactant can be readily converted into the product.

However, Marcus predicted that for certain chemical reactions when exergonicity is increased further, the reaction rate decreases. As illustrated in Figure 1.12d, when it goes more exergonic, at some point activation free energy will be reintroduced. The reestablishment of the activation free energy causes the rate of the reaction to decrease. The decrease in the reaction rate with increasingly large negative $\Delta G^0$ is called the Marcus inverted region which is
the highlight of the Marcus theory. Experimental evidence of the existence of Marcus inverted region is obtained in electron transfer reactions.

![Reaction Coordinate Diagrams](image)

Figure 1.12. Reaction coordinate diagrams at varying reactant (blue) and product (red) reaction free energies ($\Delta G^0$) depicted as Morse potentials.

1.7.2 Application of Marcus Theory to Electron Transfer

Photoexcitation in electron donor and acceptor systems occurs at approximately $10^{-16}$ seconds, a time too quick for an appreciable nuclei displacement in both donor and acceptor (Franck-Condon Principle); therefore, the chemical identity of the donor and acceptor is retained during and after electron transfer. Likewise, the energy of the electron remains the same which then implies that the orbital energies of both donor and acceptor need to match in order for electron transfer to take place. This can be achieved through the simultaneous geometrical and solvation rearrangements that will afford the donor and acceptor orbitals to
meet at the same energy level. However, due to internal nuclear movements and solvent motions, the energy levels of the donor and acceptor are in constant flux. In order for the energy levels of the donor and acceptor orbitals to match, an energy barrier needs to be overcome and this barrier is called the reorganization energy which will be discussed later in this section.38

According to the Marcus theory, the activation free energy ($\Delta G^\ddagger$) can be calculated from the standard free energy of the reaction ($\Delta G^0$) using the equation:

$$\Delta G^\ddagger = \left( \frac{\Delta G^0 + \lambda}{4\lambda} \right)^2$$  \hspace{1cm} (1.12)

where $\lambda$ is the reorganization energy which takes into account the geometrical rearrangement of the donor-solvent and acceptor-solvent rearrangement or both in order to achieve the same energy levels of their corresponding orbitals.38, 39 The reorganization energy takes into account the inner vibrational $\lambda_i$ and outer solvent component $\lambda_o$ and can be expressed

$$\lambda = \lambda_i + \lambda_o$$  \hspace{1cm} (1.13)

$$\lambda_i = \frac{1}{2} \sum_j k_j (\Delta q_j)^2$$  \hspace{1cm} (1.14)

$$\lambda_o = (ne)^2 \left( \frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} \right) \left( \frac{1}{D_{op}} - \frac{1}{D_s} \right)$$  \hspace{1cm} (1.15)

The internal vibrational contribution $\lambda_i$ primarily involves the stretching motion of the bonds where difference in equilibrium lengths ($\Delta q_j$) and a bond force constant ($k_j$) is considered over the $j$th normal coordinates on both the donor and acceptor sides of the reaction. Meanwhile, the outer solvent shell contribution $\lambda_o$ in a dielectric continuum model includes the number of electrons being exchanged ($n$), the radii of the reactants including coordination shell ($a_1$ and $a_2$),
the distance between the reactants \((R)\), and their optical and static dielectric constants, \((D_{op}
olinebreak\text{ and } D_s, \text{respectively})\).\(^{40}\)

The reaction rate constant \(k_{ET}\) under Marcus theory can be calculated using equation 1.16:

\[
k_{ET} = A_{ET} e^{-\frac{\Delta G^\ddagger}{RT}}
\]

\((1.16)\)

Similar to standard Arrhenius theory, \(A_{ET}\) indicates the frequency of effective association of the donor and acceptor at infinite temperature. For redox reactions, the \(A_{ET}\) value decreases exponentially with increasing edge-to-edge distance \((r)\) between the donor and acceptor due to its decline in effective donor-acceptor association; hence, \(A_{ET}\) can be expressed as \(A_{ET} = Z \kappa(r)\) where \(Z\) has collision frequency units, and \(\kappa(r)\) is the transmission coefficient or the probability that electron transfer happens when the association complex is at the transition state.\(^{41a-b}\)

Additionally, the driving force dependence of \(k_{ET}\) can also be calculated using equation 1.17:

\[
k_{ET} = \frac{k_B T}{h} \exp \left[ -\frac{(\Delta G^0_{ET} + \lambda)^2}{4 \lambda k_B T} \right]
\]

\((1.17)\)

where \(h\) is the Planck’s constant, \(k_B\) is Boltzmann constant \((1.38 \times 10^{-23} \text{ m}^2 \cdot \text{kg} \cdot \text{s}^{-2} \cdot \text{K}^{-1})\), and \(T\) is the absolute temperature.\(^{41c-d}\)

Taking into account the reaction free energy \(\Delta G^0\) and the activation free energy \(\Delta G^\ddagger\) in predicting the rate of electron transfer:\(^{38a, 40}\)

\begin{itemize}
  \item If \(\Delta G^0 = 0\), then \(\Delta G^\ddagger = \lambda/4\): there is no driving force for the reaction to proceed (Figure 1.12a).
\end{itemize}
• If $\Delta G^0 = -\lambda$, then $\Delta G^\dagger = 0$: there is no energy barrier and is called the optimal point where electron tunneling can readily occur and maximum electron transfer rate is expected (Figure 1.12c).

• If $\Delta G^0 > \lambda$, then $\Delta G^\dagger > 0$: energy barrier is reestablished, thus, the electron transfer rate constant decreases (Figure 1.12d) and this is the Marcus inverted plot.

Construction of Marcus plot of reaction rate constant versus reaction free energy ($k_{ET}$ vs $\Delta G^0$) clearly shows the Marcus inverted region as shown in Figure 1.13. As the reaction becomes more exergonic, the reaction rate constant increase; though, there is a threshold. When the exergonicity of the reaction increased further, the rate constant of the reaction will start to decline. The plot of log $k_{ET}$ versus $\Delta G^0$ will also illustrate the Marcus inverted region.

Figure 1.13. Marcus plot of the intramolecular electron transfer from biphenyl anions to different electron acceptors. Adapted from reference 42a.

1.7.3. Single and Multistep Electron Transfer Processes

Electron donor-acceptor systems are one of the most important components in photosynthetic reaction centers both in natural and artificial photosystems since the flow or
transfer of electrons drives photochemical reactions (i.e., water oxidation, carbon dioxide reduction, and etc.). It is important to note that the electron transfer processes in photosynthetic systems are photoinduced which means that prior to electron transfer, light absorption and energy transfer should take place since the absorbed photon jumpstarts the electron transfer, hence, its name photoinduced electron transfer. Figure 1.14 shows a schematic diagram of the photophysical processes occurring in photosystems.

Excitation, energy transfer, and electron transfer are occurring simultaneously in donor-acceptor photosystems. Photoexcitation is the absorption of photons by the chromophores when irradiated with light; thus, chromophores are promoted to their excited states as
discussed in section 1.5 (see Figure 1.14a).\textsuperscript{19} Photoinduced energy transfer on the other hand occurs when an excited chromophore (energy donor) upon its relaxation back to ground state emits a photon and the emitted photon is transfer to a nearby ground state chromophore (energy acceptor) which in turn gets excited as described in section 1.6.3 (see Figure 1.14b).\textsuperscript{21-26} Finally, photoinduced electron transfer occurs when an excited chromophore (electron donor) transfers the excited electron to the low-lying LUMO of nearby chemical specie (electron acceptor), thus, rendering a positive charge on the electron donor and a negative charge on the electron acceptor creating a radical ion pair (see Figure 1.14c).\textsuperscript{19, 38}

In artificial photosynthetic systems, it is ideal to have a fast rate of electron transfer or rate of charge separation and a relatively slow rate of charge recombination.\textsuperscript{15} A variety of electron donor (D) and acceptor (A) chromophores and their different combinations have been employed in order to achieve such parameters. Photophysical and electrochemical properties of the donors and acceptors have also been modified to obtain a long-lived charge-separated state of the donor-acceptor systems. However, simple donor-acceptor systems (assembled either covalently or non-covalently) can only afford so much charge-separated state lifetimes due to the close confinement of the donor and acceptor.\textsuperscript{44} Such electron donor-acceptor system is depicted in Figure 1.15a.

To obtain a relatively long-lived charge-separated state, multimodular donor-acceptor systems have been constructed utilizing either multiple donors or multiple acceptors with varying redox potentials.\textsuperscript{45} For multiple donor systems (D2-D1-A), it is imperative that the position of the donor with the lowest oxidation potential or easiest to oxidize be the farthest from the acceptor. Hence, this will allow a hole transfer process that would result into a
distantly separated radical ion pair, D$^{**}$-D$_1$-A$^*$, as shown in Figure 1.15b.$^{46}$ Since the radical ion pair is far apart the rate of charge recombination is decreased. In a similar manner, for multiple acceptor systems it is important that the acceptor with the lowest reduction potential or easiest to reduce be at the farthest from the donor. This permits electron migration from the initially reduced primary electron acceptor to the secondary electron acceptor rendering a spatially separated radical ion pair, D$^{**}$-A$_1$-A$_2$$^*$.\(^{47}\)

Figure 1.15. Schematic illustration of a) simple, b) multimodular, and c) antenna-donor-acceptor reaction centers. Adapted from reference 15.

In simple and multimodular donor-acceptor systems, the photoexcitation of the donor drives the electron transfer between the donor and acceptor although this only allows a narrow band capturing of light. The introduction of antenna systems maximizes the light harvesting properties of the reaction center as shown in Figure 1.15c. The selected antenna chromophore
should have a spectral overlap with the electron donor in order for energy transfer to take place either through Förster or Dexter energy transfer mechanism (section 1.6.3.1 and 1.6.3.2, respectively). With the utilization of antenna systems, it now permits a wide band capturing of light and the electron transfer is no longer limited to the direct photoexcitation of the electron donor alone since with photoexcitation of the antenna system will also afford the excitation of the electron donor through excitation energy transfer from the antenna chromophore.48

Multimodular antenna-donor-acceptor system provides an ideal artificial photosystem since it maximizes the harvesting of light and it also increases the lifetime of the charge-separated states by slowing down the rate of charge recombination from the distantly separated radical ion pair. Furthermore, electron transfer from the donor and acceptor is no longer restricted from the direct photoexcitation of the donor itself since the photoexcitation of antenna chromophores will also provide the excitation of the donor through excitation energy transfer.

1.8. Analytical Methods for the Characterization of Artificial Photosynthetic Systems

It is essential to determine the photophysical, photochemical, and electrochemical properties of not only the units or components of the artificial photosynthetic system but also the photosystem itself. Obtaining the properties of the individual units enables the selection of the correct chromophore units (energy and electron donors and acceptors) in the construction of the supramolecular photosystem that will allow energy and electron transfer within the antenna-donor-acceptor systems.44-46

The characterization of the photosystem permits us to assess the degree of perturbation of the individual units in the supramolecular construct. Moreover, it will also enable the
evaluation of the rate of charge separation and rate of charge recombination of the radical ion pair, and the lifetime of the charge-separated states. Finally, this will provide important information for the elucidation of the mechanism of the photochemical and electrochemical events occurring in the artificial photosynthetic system.

1.8.1 Steady-State Absorption, Fluorescence Emission, and Phosphorescence Emission Spectroscopy

Steady-state absorption spectroscopy determines the specific absorption bands of the chromophores in the UV and visible spectrum, and with the variation of the molar concentration of the chromophore and recording its corresponding absorbance will provide the molar extinction coefficient of the chromophore. Fluorescence emission and phosphorescence emission spectroscopies measure the emission bands of the chromophore from its excited singlet and excited triplet states, respectively; though, phosphorescence emission is not readily observed in most fluorescent chromophores since the phosphorescence signal is very weak to some chromophores.

The collected UV-visible absorption and fluorescence emission data of the chromophores will allow the calculation the energy of the excited singlet state of the chromophore using equation 1.18. The energy of the excited triplet state can also be determined by equation 1.18 using the phosphorescence emission data. The absorption and emission data will also assess the probability of energy transfer between two or series of chromophores when assembled in the photosystem as shown in Figure 1.9b.

\[ E = \frac{hc}{\lambda} \]  

(1.18)
where $h$ is Planck’s constant ($6.63 \times 10^{-34}$ J·s) and $c$ is speed of light in a vacuum ($3.00 \times 10^{10}$ cm·s$^{-1}$). The resulting energy unit will be in joules (J) which can be converted to electron-volts (eV) since $1 \text{ J} = 6.242 \times 10^{18}$ eV.

The occurrence of energy transfer can be observed from the fluorescence quenching of the energy donor and the increase in emission intensity of the energy acceptor. Although a decrease in emission intensity of the fluorophore does not necessarily guarantee energy transfer since collisional and static quenching could also result in a reduced fluorescence emission intensity.$^{21-27}$

1.8.2 Time-Resolved Fluorescence Emission Measurements

The fluorescence quenching of fluorophores either by collisional or static quenching, or energy transfer is observed from the decrease in fluorescence emission intensity of the energy donor. However, one cannot readily identify the quenching route. Thus, in order to elucidate the quenching mechanism, quantification of the fluorescence quenching is required which can be done by recording the fluorescence lifetime ($\tau$) of the fluorophore through time-correlated single photon counting (TCSPC) which is often referred to as lifetime measurements.$^{49}$

Fluorescence lifetime is the average time the fluorophore resides in the excited state before it returns back to the ground state. Its interaction with its environment (i.e., solvent, quenchers) influences the fluorescence lifetime of a fluorophore.$^{19,\ 26b}$ Determination of fluorescence lifetime is possible since fluorescence emission occurs at $10^{-9}$ second time domain; a time long enough to be recorded by an instrument. Typically most fluorophore lifetimes are about 10 nanoseconds. Fluorescence lifetime is the inverse of the sum of the rate constants of radiative ($k_r$) and non-radiative ($k_{nr}$) processes and can be expressed by equation 1.19:
Fluorescence lifetime can also be obtained from the slope of a plot of log \( I(t) \) vs \( t \) where \( I \) is the fluorescence intensity at a given time \( t \); though it is commonly obtained by fitting the collected data to decay models.

The rate constants \( (k_q) \) of the fluorescence quenching can also be evaluated from the fluorescence lifetime of the reference or control compound and the sample \( (\tau_{\text{ref}} \) and \( \tau_{\text{sample}} \), respectively) using equation 1.20:

\[
k_q = \frac{1}{\tau_{\text{sample}}} - \frac{1}{\tau_{\text{ref}}}
\]

Moreover, fluorescence quantum yield \( (\Phi_F) \) is the ratio of the number of emitted photons to the number of photons absorbed and since the rate constants \( k_r \) and \( k_{nr} \) provide information for the depopulation of the excited state, hence, fluorescence quantum yield can be calculated by equation 1.21:

\[
\Phi_F = \frac{k_r}{k_r + k_{nr}}
\]

In the absence of \( k_r \) and \( k_{nr} \) data, fluorescence quantum yield can be determined through relative or comparative method using a standard material of known fluorescence quantum yield and can be calculated using equation 1.22:

\[
\Phi_F = \Phi_{F(\text{std})} \frac{F \times A_{\text{std}} \times n^2}{F_{\text{std}} \times A \times n_{\text{std}}^2}
\]
In a similar manner, when the fluorescence lifetimes of the reference ($\tau_{\text{ref}}$) and the sample ($\tau_{\text{sample}}$) have been obtained, fluorescence quantum yield can be assessed using equation 1.23:

$$\Phi_F = \frac{1}{\tau_{\text{sample}}} - \frac{1}{\tau_{\text{ref}}}$$

The determined fluorescence quantum yield will indicate the efficiency of the energy transfer process. When fluorescence quantum yield approaches unity, if $k_{nr} \ll k_r$ (equation 1.21), it demonstrates a highly efficient energy transfer or conversion.$^{51}$

1.8.3 Electrochemical Studies

Photosynthesis involves not only chemical but also electrochemical processes through redox reactions. Therefore, the determination of the electrochemical properties of the chromophores and the photosystem is of great importance. The electrochemical properties of these compounds can be determined using cyclic and differential pulse voltammetry (CV and DPV, respectively).$^{48}$ These will provide the number of oxidation and reduction potentials of the redox active compounds though in artificial photosynthesis, the first oxidation and first reduction potentials are the ones of great value since most redox processes in artificial photosynthesis only involves one electron for the transfer processes. Moreover, the first oxidation and first reduction potentials estimates energy gap between the HOMO and LUMO of the chromophores.$^{46}$

It is important to perform cyclic voltammetry not only to determine the redox potentials but to also identify if the oxidation and reduction processes are reversible. This is significant because in electron donor-acceptor systems, charge recombination should also take place in
order for the photosynthetic system to return to its original state and be able to repeat the photosynthetic reactions again. So basically the photosynthetic apparatus functions through a reaction cycle. Additionally, the determined redox potentials will be used to calculate the free energy change for the energy and electron transfer processes using Rehm-Weller approach will be discussed in a later section.44, 46

1.8.4 Spectroelectrochemical Technique

The tandem of electrochemical and spectroscopic techniques will permit great insights in chemical and electrochemical reactions occurring in a chemical system that each individual analytical method won’t be able to provide.52 It is very much helpful in the characterization of artificial photosystems since both photo- and electrochemical reactions are occurring in these photosystems. Furthermore, it offers important preliminary data for the transient absorption spectroscopic studies which will be discussed in detail in the next section.

Prior to performing spectroelectrochemical studies, it is necessary that steady-state absorption and electrochemical analysis have already been conducted on the chromophore of interest in order to determine the UV-vis absorption scanning range, and the redox potential that will be applied.52, 53 The newly developed absorption bands after the application of oxidation or reduction potential represent the oxidized and reduced chemical specie, respectively, when the chromophore undergoes electron transfer in an electron donor-acceptor system, ergo, the radical ion pair.54

Chemical oxidation and reduction can also be used to identify the absorbance of the oxidized electron donor and reduced electron acceptor, respectively. The commonly used chemical oxidant is nitrosonium tetrafluoroborate (NOBF₄)55 while chemical reduction is not
commonly done since chemical reductants are unstable and requires careful handling. However, chemical oxidation and reduction have only limited applications. For chemical species that have high redox potentials, chemical oxidation and reduction are not feasible; therefore, it is suitable to use spectroelectrochemical analysis to find the absorbance of the oxidized and reduced species.

1.8.5 Transient Absorption Spectroscopy

Energy and electron transfer processes both in natural and artificial photosynthetic systems occur at approximately less than 100 femtoseconds (fs) to a couple of nanoseconds (ns) upon photoirradiation and are simultaneously occurring together with internal conversion, fluorescence emission, and intersystem crossing. In order to examine these extremely fast photophysical and photochemical events, an ultrafast technique is employed.56

The emergence of ultrafast laser systems with femtosecond pulse duration permits the investigation of the occurrence of energy and electron transfer processes in donor-acceptor photosystems. With the use of ultrafast spectroscopy, the existence of transient species and their photophysical and photochemical properties can now be studied. Furthermore, energy and electron transfer mechanisms in photosystems can also be elucidated and have a better understanding of the antenna-reaction center photosystems.

Transient absorption spectroscopy utilizes two lasers: the pump pulse which is used to excite the chromophores and thus, allows the population of the excited singlet state; and the probe pulse which is a white light that investigates the ultrafast processes. The transient events originates from the excited singlet state $S_1$ of the chromophores prior to any subsequent photophysical and photochemical phenomena in accordance to Kasha’s Rule as shown in Figure.
1.16. For triplet chromophores or photosensitizers, it will still be initiated by the $S_1$ excited singlet state and will readily undergo intersystem crossing to populate the $T_1$ excited triplet state.\textsuperscript{57}

![Jablonski diagram](image)

Figure 1.16. Modified Jablonski diagram depicting the mechanism of transient absorption spectroscopy. Adapted from reference 57.

In transient absorption spectroscopy, only about 0.1 percent to tens of percent of the molecules is excited by the pump. The probe on the other hand has a low intensity to avoid multiphoton processes when probing. Varying the distance traveled by the pump and the probe (see Figure 1.17) enables the collection of the difference absorption spectrum ($\Delta A$) at each time delay ($\tau$) and allows the construction of a time profile at each wavelength ($\lambda$).\textsuperscript{58} The accumulated $\Delta A$ profile as a function of time and wavelength ($\Delta A(\lambda, \tau)$) holds information on the dynamic processes (i.e., energy transfer, intersystem crossing, electron transfer, hole shift, charge migration, etc.) taking place in the photosynthetic system.\textsuperscript{59}
There are four main contributing transient dynamic processes that can be deduced by the $\Delta A$ spectrum (see Figure 1.18) and these are:

- **Ground-state bleach:** As the sample is excited by the pump pulse and is promoted to the excited state, the number of molecules in the ground state decreases; hence, the ground state absorption is also reduced. The decrease in ground state absorption is manifested as negative bands in the transient absorption spectrum and these are at the same position with the absorption spectral bands obtained by UV-visible absorption.

- **Stimulated emission:** When the photon of the probe pulse induces emission of the photon of the excited molecules, hence, it decays back to the ground state in the same exact direction as the probe pulse photon. The stimulated emission increases the intensity of light that reaches the detector and are therefore registers as a negative signal in the $\Delta A$ spectrum.
• Excited-state absorption: Upon photoirradiation with the pump beam, the sample is promoted to the $S_1$ excited singlet state. These excited molecules further absorb the probe pulse as shown in Figure 1.16 and are exhibited as positive absorption bands in the transient absorption spectrum. The probe pulse is so weak that it has no appreciable effect on the population of the $S_1$ excited singlet state.

• Product absorption: With the photoexcitation of the sample with the pump pulse, it is imperative that photochemical events will take place such as energy and electron transfer especially in antenna-reaction centers of photosynthetic systems. The resulting transient species have their own distinct photophysical properties and will be observed as newly developing positive peaks in the transient absorption spectrum.

![Figure 1.18. Difference absorption spectrum illustrating the different contributing transient events.](image)

As mentioned, these photochemical events are simultaneously occurring and it would be difficult to discern the ground state absorption and stimulated emission from the transient absorption of the excited sample and products. In order to distinguish the components, the
pump pulse is allowed to pass through a mechanical chopper as shown in Figure 1.17 that is synchronized to the amplifier of the detector, while the probe pulse continuously investigates the sample. As result, there is a constant alternating pumped and unpumped sample signals designated as $I(\lambda)_{\text{pumped}}$ and $I(\lambda)_{\text{unpumped}}$, respectively, which are recorded. The difference absorption spectra are then constructed from the collected $I(\lambda)_{\text{pumped}}$ and $I(\lambda)_{\text{unpumped}}$ signals using equation 1.24:\textsuperscript{59}

\[ \Delta A(\lambda) = -\log \frac{I(\lambda)_{\text{pumped}}}{I(\lambda)_{\text{unpumped}}} \]  

(1.24)

The distance traveled by the probe pulse is constantly increased with the delay stage and different time delays ($\tau$) between the pump and probe is recorded and the collection of $I(\lambda)_{\text{pumped}}$ and $I(\lambda)_{\text{unpumped}}$ signals are repeated until the maximum time delay at the delay line is reached. This affords the construction of $\Delta A(\lambda, \tau)$ that provides valuable information regarding the dynamic processes in photosynthetic systems.

Transient absorption spectroscopy is a vital analytical technique in the characterization and investigation of both natural and artificial photosynthetic systems. Its application is paramount for the development of supramolecular constructs for photosynthetic applications. With the elucidation of the photophysical and photochemical mechanisms occurring in the current antenna-reaction center photosystems, it allows a better understanding for the development of highly efficient artificial photosynthetic systems.

1.9 Current Antenna-Reaction Center Mimics for Artificial Photosynthesis

The abundance and easy access of sunlight has drawn a great attention to artificial photosynthesis. Furthermore, the production of carbon-free energy has heightened its appeal
to the scientific community.\textsuperscript{4, 9} However, the greatest challenge is the design and construction of supramolecular photosystems that will efficiently capture light energy and convert it to electricity and fuel.\textsuperscript{17}

1.9.1 Common Chromophores used in Supramolecular Photosystems

The photosynthetic supramolecular assembly requires photoactive compounds that have the ability to harvest light and undergo photophysical and photochemical processes upon photoexcitation. Taking advantage of natural photosynthetic systems and mimicking its antenna-reaction center permits the use of chlorophyll \textit{a} analogues as electron donors in artificial photosystems.\textsuperscript{60} The commonly used chlorophyll \textit{a} analogues are porphyrins (Por),\textsuperscript{45a, 61} phthalocyanines (Pc)\textsuperscript{61d, 61f, 62-64} and naphthalocyanines (Nc)\textsuperscript{61f, 65} along with their reduced-pyrrole ring derivatives such as corroles (Cor),\textsuperscript{61c, 66} subphthalocyanines (SubPc),\textsuperscript{50c-d, 67-69} boron dipyrromethenes (BODIPY or BDP)\textsuperscript{18, 70, 71} and aza-boron dipyrromethenes (azaBODIPY)\textsuperscript{70b, 72, 73} as shown in Figure 1.19. Furthermore, expanded-pyrrole ring\textsuperscript{74} and \textit{\pi}-extended derivatives\textsuperscript{75} have also been used for light-harvesting purposes.

These chromophores are commonly used in artificial photosystems due to their high molar extinction coefficient allowing them to absorb and capture ultraviolet (UV), visible (vis) and near infrared (NIR) light.\textsuperscript{18} Its photophysical and photochemical properties can be easily regulated with the modification and functionalization of its peripheral substituents. Additionally, these chromophores are electroactive and its redox potentials can also be varied when modified and functionalized.\textsuperscript{15} The photophysical and electrochemical properties of these chromophores are listed in Table 1.1.
Figure 1.19. Structures of common chromophores used for artificial photosynthetic systems. BODIPY = boron dipyrromethene, azaBODIPY = aza-boron dipyrromethene, M = 2 or 3 H’s, transition metals (i.e., Mg, Mn, Cu, Zn, Al, Au, etc.), X = F, Cl, Br.

Fullerene, C\textsubscript{60}, is widely used as an electron acceptor due to its low reorganization energy and six almost equally spaced reduction potentials.\textsuperscript{76, 77} Furthermore, the three-dimensional structure of fullerene allows multiple functionalizations where numerous electron donors can be directly attached.\textsuperscript{44, 77a, 78a} Moreover, pyridine or imidazole, and alkylammonium or crown ether functionalized fulleropyrrolidines are also utilized to afford axial coordination
and ion-dipole interaction, respectively, in self-assembled donor-acceptor systems\textsuperscript{15, 48, 78b-c} as shown in Figure 1.20.

Aside from fullerene, naphthalene diimide (NDI)\textsuperscript{79} and perylene diimide (PDI; also called as perylene bisimide)\textsuperscript{44b, 80} are also used as electron acceptors in artificial photosystems owing to its low reduction potentials as listed below which permits both molecules to readily accommodate electrons. In a similar manner with fullerene, both NDI and PDI could either be covalently-linked to electron donors or have been appended with pyridine or imidazole at the N-imide or at the conjugated ring position in self-assembled multimodular photosystems.

Table 1.1. Photophysical and electrochemical properties of the common chromophores used in antenna-reaction center systems.

<table>
<thead>
<tr>
<th>chromophore</th>
<th>absorbance (nm)</th>
<th>emission (nm)</th>
<th>potential (V) vs Fc/Fc$^+$</th>
<th>oxidation</th>
<th>reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>zinc porphyrin</td>
<td>425, 550, 590</td>
<td>600, 650</td>
<td>0.28, 0.62</td>
<td>-1.92, -2.23</td>
<td></td>
</tr>
<tr>
<td>zinc phthalocyanine</td>
<td>350, 615, 680</td>
<td>695</td>
<td>-0.04, 0.74</td>
<td>-1.63</td>
<td></td>
</tr>
<tr>
<td>zinc naphthalocyanine</td>
<td>345, 690, 780</td>
<td>780</td>
<td>-0.18, 0.56</td>
<td>-1.52, -1.94</td>
<td></td>
</tr>
<tr>
<td>free-base corrole</td>
<td>390, 405</td>
<td>650</td>
<td>0.21$^{[a]}$</td>
<td>-1.03$^{[a]}$</td>
<td></td>
</tr>
<tr>
<td>subphthalocyanine</td>
<td>307, 568</td>
<td>582</td>
<td>0.60</td>
<td>-1.51, -2.05</td>
<td></td>
</tr>
<tr>
<td>boron dipyrrromethene</td>
<td>505</td>
<td>515</td>
<td>0.74, 0.92</td>
<td>-1.74</td>
<td></td>
</tr>
<tr>
<td>aza-boron dipyrrromethene</td>
<td>316, 480, 660</td>
<td>685</td>
<td>0.80</td>
<td>-0.79</td>
<td></td>
</tr>
<tr>
<td>fullerene, C$_{60}$</td>
<td>320</td>
<td>720</td>
<td>-0.65, -1.06, -1.52, -1.79$^{[a]}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>naphthalene diimide</td>
<td>342, 360, 381</td>
<td>486</td>
<td>-0.55, -1.00$^{[a]}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>perylene diimide</td>
<td>525</td>
<td>530</td>
<td>-1.00, -1.20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^{[a]}$potential (V) vs SCE

As mentioned above, the electrochemical properties of the chromophores can be modified by varying its substituents. Functionalization with fluorinated substituent lowers the reduction potentials up to 100 mV less than its unfluorinated congener.\textsuperscript{66e, 81, 82} Moreover, varying the metal centers of these chromophores could also alter its electrochemical properties especially with metal ions that afford positively charged metal complexes.\textsuperscript{61b, 66d-e, 83} These
alterations enable these modified chromophores to be employed as primary electron acceptors in multimodular reaction center mimics allowing sequential electron transfer (D-A₁-A₂ in section 1.7.3).\textsuperscript{47}

Figure 1.20. Donor-acceptor systems for artificial photosynthesis illustrating the different modes of interaction in supramolecular assemblies.

1.9.2 Rehm-Weller Approach for Free Energy Calculations

The assembly of artificial photosynthetic systems requires a careful selection of donor and acceptor chromophores to ensure efficient energy and electron transfer. It is important to
take into account the photophysical, photochemical and electrochemical properties of the individual chromophores since this will dictate the sequence of energy and electron transfer processes. The feasibility of the aforementioned processes in the designed antenna-reaction center can be assessed using the Rehm-Weller approach where the free energy of charge separation (ΔG<sub>CS</sub>) and charge recombination (ΔG<sub>CR</sub>) is calculated (equation 1.25 and 1.26, respectively).<sup>48a, 84</sup> An energy level diagram is constructed (as shown in subsequent sections) using the obtained free energies of reaction, thus, providing plausible photoinduced energy and electron transfer (PEnt and PET, respectively) mechanisms of the designed photosystem.<sup>85</sup>

\[
-\Delta G_{CS} = \Delta E_{0,0} - (-\Delta G_{CR})
\] (1.25)

\[
-\Delta G_{CR} = (E_{ox} - E_{red}) + \Delta G_S
\] (1.26)

where \(\Delta E_{0,0}\) is the lowest excited singlet-state energy, \(E_{ox}\) is the first oxidation potential and \(E_{red}\) is the first reduction potential of the electron donor and acceptor, respectively. The \(\Delta G_S\) on the other hand, is the static or stabilization energy which is calculated using the “dielectric continuum model” and expressed in equation 1.27:<sup>86</sup>

\[
-\Delta G_S = -\frac{e^2}{4\pi \varepsilon_0} \left[ \left( \frac{1}{2R_+} + \frac{1}{2R_-} - \frac{1}{R_{D-A}} \right) \frac{1}{\varepsilon_S} - \left( \frac{1}{2R_+} + \frac{1}{2R_-} \right) \frac{1}{\varepsilon_R} \right]
\] (1.27)

where \(e\) is the elementary charge, \(\varepsilon_0\) is vacuum permittivity, \(R_+\) and \(R_\) are the radii of the radical cation and anion, respectively, while \(R_{D-A}\) is the center-to-center distance between the electron donor and electron acceptor, and \(\varepsilon_S\) and \(\varepsilon_R\) are the dielectric constants of the solvents used for the photophysical studies and redox potential measurements, respectively.

The Rehm-Weller approach is an essential tool in evaluating the constructed antenna-reaction center photosystems. It provides vital information on the expediency of the selected
antenna, donor, and acceptor chromophores in establishing energy transfer and stabilizing charge separated states since these will affect the performance of the photosystems. Aside from the type of chromophores chosen for the artificial photosystem, there are different factors that can affect the efficiency of light-to-electricity conversion of the antenna-reaction center. The arrangement and number of chromophoric units (as mentioned in section 1.7.3), mode of assembly (either covalent or non-covalent interaction of the donor-acceptor systems), and the type of molecular connector or spacer between the donor and acceptor chromophores also impact the efficiency of the artificial photosynthetic systems.

In the subsequent sections, the current strides on artificial photosynthetic systems with various antenna, donor, and acceptor chromophores will be surveyed. The literature review will be focusing mainly on porphyrin- and subphthalocyanine-based antenna-reaction center photosystems and will not involve multielectron transfer catalysts (i.e., water oxidizing catalysts and proton reducing catalysts). Modification and functionalization of chromophores to permit near infrared (NIR) absorption rendering NIR-photosensitizers will also be evaluated.

### 1.9.3 Porphyrin-Based Light-Harvesting Systems

Porphyrin is a macrocyclic compound composed of four pyrrole units connected by four bridging sp² carbons, yielding an aromatic and planar conformation. Its high molar extinction coefficient and readily tuneable photophysical and electrochemical properties are of great importance making porphyrin a front-runner in artificial photosynthetic research.免费版

Free-base porphyrins have an intense Soret band absorption at 425nm and weak Q bands at 550, 590 and 660nm, and emits at 650 and 700nm. Upon metalation, the 660nm absorption band disappears with a 50nm-blue-shift in its fluorescence emission bands to 600
and 650nm. The disappearance of the 660nm absorption band and blue-shifted emission bands are oftentimes used as qualitative tests for successful porphyrin metalation. Metalloporphyrins have an advantage over free-base porphyrins since the metal centers permit further functionalization. Depending on the metal center, the porphyrin macrocycle can be decorated with one or two more chromophoric units via metal-ligand axial coordination, thus, expanding the antenna-reaction center supramolecular construct.

Furthermore, the photophysical properties of porphyrins can be tailored by attaching substituents at the meso and/or beta (β) position of the macrocycle as depicted in Figure 1.19. An array of substituents with distinct photophysical properties can be casted, altering the photophysical and electrochemical properties of the supramolecular construct. Furthermore, electron acceptors can also be covalently-linked in the aforementioned positions of the macrocycle. Functionalization of porphyrins with pyridine, imidazole, alkylammonium and crown ether substituents can also be performed for self-assembled donor-acceptor photosystems as shown in Figure 1.20.

1.9.3.1 Zinc Porphyrin-Based Antenna-Reaction Center Mimics

Zinc porphyrin complexes accommodate nitrogen-containing ligands through metal-ligand axial coordination making zinc porphyrins a vital constituent in artificial photosynthesis. Imidazole and pyridine are the common nitrogen-containing ligands appended to various molecules like fullerenes (C₆₀ or C₇₀), naphthalene diimide (NDI), perylene diimide (PDI), phenothiazine (PTZ), tetrathiafulvalene (TTF) to name a few.

Supramolecular constructs composed of zinc porphyrin (ZnP), boron dipyrromethene (BODIPY), triphenylamine (TPA), ferrocene (Fc) and fullerene (C₆₀) units (as shown in Figure
1.21) have been synthesized utilizing metal-ligand axial coordination and ion-dipole interaction for multimodular antenna-reaction center mimics for artificial photosynthetic applications. Varying the arrangement of these units enables the regulation of its photophysical and electrochemical properties permitting the occurrence of photoinduced energy (PEnT) and electron transfer (PET) processes in these photosystems. The functionalized zinc porphyrin units for antenna-reaction center photosystems are listed in Table 1.2.

Stabilization of the charge separated states in donor-acceptor photosystems have been one of the most important parameter in designing antenna-reaction center mimics to achieve long-lived charge separated states. In the designed photosystems, ZnP is the primary electron donor while BODIPY can either act as an antenna system or an electron acceptor depending on the wavelength used in photoexcitation. In a similar fashion, TPA is also used as an antenna and
for charge stabilization. Finally, Fc is utilized as a secondary electron donor owing to its small oxidation potential, hence, stabilizes the charge separated states of the donor-acceptor photosystems.

Table 1.2. Functionalized zinc porphyrin units for the self-assembled supramolecular constructs for artificial photosynthesis.

<table>
<thead>
<tr>
<th>compound</th>
<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
<th>R₄</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
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<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>61e</td>
</tr>
<tr>
<td>9</td>
<td>c</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>87a</td>
</tr>
<tr>
<td>10</td>
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<td>b</td>
<td>b</td>
<td>b</td>
<td>87b</td>
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<td>d</td>
<td>b</td>
<td>d</td>
<td>b</td>
<td>87b</td>
</tr>
<tr>
<td>12</td>
<td>d</td>
<td>d</td>
<td>d</td>
<td>d</td>
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<td>d</td>
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<td>b</td>
<td>88a</td>
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<td>f</td>
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<td>88b</td>
</tr>
<tr>
<td>15</td>
<td>g</td>
<td>g</td>
<td>g</td>
<td>i</td>
<td>89a</td>
</tr>
<tr>
<td>16</td>
<td>h</td>
<td>g</td>
<td>i</td>
<td>g</td>
<td>89b</td>
</tr>
</tbody>
</table>

In a self-assembled dyad of zinc tetraphenylporphyrin (8, ZnTPP) and phenylimidazole appended fulleropyrrolidine (17, C₆₀Im) (used as electron donor and acceptor, respectively) via metal-ligand axial coordination (Scheme 1.1), fluorescence quenching and a decrease in the fluorescence lifetime of 8 were observed which was attributed to electron transfer from ZnTPP to C₆₀Im. The fluorescence lifetime of 8 alone was measured to be 2.10 nanoseconds (ns) and in the presence of 17, it was reduced to 1.70 ns in benzonitrile. The k<sub>CS</sub> and Φ<sub>CS</sub> values from the singlet state (¹ZnP*) was calculated to be 8.60 × 10⁷ s⁻¹ and 0.15, respectively, using equations 1.20 and 1.23, respectively. In order to verify that the decrease in fluorescence lifetime is indeed due to electron transfer, nanosecond transient absorption spectroscopy was employed to the 8:17 solution in benzonitrile and was laser irradiated at 530 nm. An intense band at 700 nm and 840 nm corresponding to the triplet state of C₆₀Im (³C₆₀Im*) and ZnTPP (³ZnP*), respectively, was observed which decayed faster than fullerene anionic radical, C₆₀Im⁻, at
1020nm which by itself establishes the occurrence of electron transfer as depicted in Figure 1.22a. The $k_{CS}^T$ and $k_{CR}^T$ via triplet excited states were determined to be $2.50 \times 10^7$ and $8.40 \times 10^9$ s$^{-1}$, respectively, in benzonitrile.

![Scheme 1.1](image)

Figure 1.22. Transient absorption spectra of 8:17 obtained using 530 nm laser excitation in Ar-saturated (a) benzonitrile and (b) o-dichlorobenzene. Inset: time profiles at a) 700 and 1000 nm, and b) 850 and 1000 nm bands. Adapted from reference 61a.

Fluorescence lifetime measurements and transient absorption studies were also conducted in o-dichlorobenzene. The fluorescence lifetime of the ZnTPP:C$_{60}$Im solution had a biexponential decay fit and were 0.058 ns (50%) and 2.00 ns (50%) obtaining $k_{CS}^S$ and $\Phi_{CS}^S$ values of $1.70 \times 10^{10}$ s$^{-1}$ and 0.97, respectively. The transient absorption studies on the other hand, didn’t exhibit any triplet excited states of ZnTPP and C$_{60}$Im though a fast decaying C$_{60}$Im$^*$ peak was observed. However, the time constant was the same as the nanosecond laser pulse, hence, the $k_{CS}$ and $k_{CR}$ values from the transient studies cannot be obtained with certainty.
The free energy of the reaction was calculated using Rehm-Weller’s approach (section 1.9.2) in order to build an energy level diagram that would elucidate the photophysical and photochemical processes occurring in the donor-acceptor dyad as shown in Figure 1.23. It was determined that for non-coordinating solvent (i.e., o-dichlorobenzene), photoinduced electron transfer proceeds via the singlet excited state of the electron donor while coordinating solvent (i.e., benzonitrile) facilitates intersystem crossing of the electron donor, hence, demonstrating photoelectron transfer via the triplet excited state of the electron donor.\textsuperscript{61e}

In order to enhance the photophysical and electrochemical properties of the ZnTPP photosensitizer, BODIPY was used as an antenna system linked through an ethylene glycol bridge (compound 9)\textsuperscript{87a}, although it was observed that BODIPY can also act as an electron acceptor depending on the wavelength used for photoexcitation (Scheme 1.2).

![Energy level diagrams of ZnTPP:C\textsubscript{60}Im (8:17) donor-acceptor dyad in a) o-dichlorobenzene and b) benzonitrile. Adapted from reference 61e.](image)

When dyad 9 was excited at 502 nm, over 60% quenching of the BODIPY emission at 522 nm was observed with developed ZnP emission bands at 600 and 649 nm, thus, indicating photoinduced energy transfer from BODIPY to ZnP as shown in Figure 1.24b. Fluorescence
lifetime measurement of the BODIPY control and dyad 9 provided 530 and 90 picosecond lifetimes with monoexponential decay, respectively, confirming that indeed BODIPY transfers energy to ZnP and yielding a singlet energy transfer rate constant ($k_{\text{EnT}}$) of $9.2 \times 10^8$ s$^{-1}$. However, when dyad 9 is excited at 550 nm, quenching of the ZnP emission bands at 600 and 649 nm were observed (Figure 1.24c). Additionally, fluorescence lifetime measurements of pristine ZnP and dyad 9 also showed a decrease of the ZnP lifetime from 1.92 ns to 1.20 ns. These results suggest electron transfer from ZnP to BODIPY owing to BODIPY’s relatively low reduction potential at -1.33 V vs Fc/Fc$. However, the calculated rate of electron transfer and quantum yield ($3.10 \times 10^8$ s$^{-1}$ and 0.38, respectively) indicated a less likely electron transfer process from ZnP to BODIPY in dyad 9.

Nanosecond transient absorption studies of dyad 9 upon laser irradiation at 550 nm showed an intense absorption band at 460 nm along with broad bands at 700-850 nm which is assigned to $^3\text{ZnP}^*$. An absorption band at 625 nm had also developed which could be attributed to $\text{ZnP^{**}}$, although it overlaps with the broad $^3\text{ZnP}^*$ bands, thus, the peak at 625 nm cannot be ascertained to originate from $\text{ZnP^{**}}$ (see Figure 1.254a). Upon the addition of excess 17 to dyad 9 and irradiation at 500 nm, absorption bands at 700 and 850 nm corresponding to $^3\text{C}_6\text{Im}^*$ and $^3\text{ZnP}^*$ were observed, respectively. Moreover, a band at 1020 nm was seen confirming the occurrence of electron transfer self-assembled antenna-reaction center mimic. The calculated $k_{\text{CS}}$ and $k_{\text{CR}}$ were $4.70 \times 10^9$ s$^{-1}$ and $2.00 \times 10^8$ s$^{-1}$, respectively, from the 1020 nm time profile (Figure 1.25b inset).
The Free energy of the reaction was calculated and the constructed energy level diagram (Figure 1.26) showed that a preliminary energy transfer from \(^1\text{BODIPY}^*\) to ZnP yielded \(^1\text{ZnP}^*\) in which the presence of C\(_{60}\)Im, resulted in an electron transfer rendering BDP-ZnP':C\(_{60}\)Im' radical ion pair. In the self-assembled antenna-reaction center triad (9:17), the presence of BODIPY stabilized the charge separated states by decreasing the rate of charge recombination from \(8.40 \times 10^9\) s\(^{-1}\) (8:17 dyad) to \(2.00 \times 10^8\) s\(^{-1}\).
Figure 1.25. Nanosecond transient absorption spectra of a) dyad 9 and b) 9:17 after 550 and 500 nm laser irradiation, respectively, in Ar-saturated o-dichlorobenzene. Inset: time profiles at a) 625, and b) 1020 nm bands. Adapted from reference 87a.

Figure 1.26. Energy level diagram depicting the different photophysical and photochemical processes occurring in the self-assembled 9:17 antenna-reaction center mimic after BODIPY photoexcitation. Solid, and thin and broken arrows indicate the major and minor events occurring, respectively. Adapted from reference 87a.

Since energy transfer from BODIPY to ZnP and charge stabilization was established in the self-assembled 9:17 photosystem, ZnP was further decorated with multiple BODIPY units connected through amide bonds. ZnP was appended with one, two, and four BODIPY units (designated as compounds 10, 11, and 12, respectively) with the premise that increasing the number of BODIPY substituents will promote more stabilization of the charge separated states.
It was observed that as the number of BODIPY unit increases, its absorbance at 505 nm also increases with a 1-2 nm red-shift for compound 12 (shown in Figure 1.27a). Quenching of the BODIPY emission along with weak emission bands at 600 and 650 nm at 495 nm excitation were also obtained (Figure 1.27b) indicating energy transfer from BODIPY to ZnP (same with compound 9). Energy transfer from singlet BODIPY was further confirmed with the excitation spectra holding the monochromator at 662 nm corresponding to the ZnP emission (Figure 1.27c). ZnP and BODIPY excitation bands were noted; BODIPY band increases with increasing number of BODIPY units.

Figure 1.27. Steady-state a) absorption, b) fluorescence emission (\( \lambda_{\text{exc}} = 505 \text{ nm} \)), and c) excitation spectra (held at 662 nm emission monochromator) of (i) 10, (ii) 11, (iii) 12, and (iv) BODIPY in o-dichlorobenzene. Adapted from reference 87b.

The rate constants for energy transfer, \( k_{\text{EnT}} \), were assessed from the transient absorption spectra in o-dichlorobenzene and was determined to be \( 2.08 \times 10^{10}, 2.27 \times 10^{10}, \) and \( 6.25 \times 10^{10} \text{ s}^{-1} \) for compound 10, 11, and 12, respectively. The increasing \( k_{\text{EnT}} \) values were expected due to the increasing number of BODIPY substituents. Moreover, electron transfer rate constants of 10:17 in o-dichlorobenzene were evaluated to be \( k_{\text{CS}} = 1.61 \times 10^{10} \text{ s}^{-1} \) and \( k_{\text{CR}} = 2.50 \times 10^{8} \text{ s}^{-1} \). Electron transfer in 11:17 and 12:17 photosystems was difficult to discern since the transient absorption bands were weak due to its low solubility in the said solvent.
The calculated free energy of reaction of compounds 10, 11, and 12 with 17 shows a very similar energy level diagram as 9:17 shown in Figure 1.26. Appending multiple BODIPY units to ZnP allowed a faster rate of energy transfer, however, stabilization of the charge separated states was difficult to assess due to the weak transient absorption bands acquired.

Supramolecular self-assembled photosystems via ion-dipole interaction using ammonium and crown ether moieties were employed to investigate its effects with the stabilization of the charge separated states in ZnP-BODIPY systems. The antenna-reaction center mimics were composed of crown ether appended ZnP-BODIPY dyads and an ammonium functionalized fulleropyrrolidine, compound 18. The crown ether moiety was either appended to the ZnP or BODIPY component of the dyad (compounds 13 and 14, respectively) to further evaluate charge stabilization in the said photosystems as seen in schemes 3 and 4, respectively.

Absorption spectra of dyad 13 revealed the Soret and Q bands of ZnP at 431, 550, and 602 nm, and the BODIPY band at 495 nm. Fluorescence emission spectra of 13, excited at 495 nm, showed quenching of the BODIPY emission with ZnP emission bands at 614 and 662 nm suggesting energy transfer from BODIPY to ZnP as expected in ZnP-BODIPY dyads (Figure 1.28a and b). The energy transfer efficiency was estimated to be about 97%.
Dyad 14 on the other hand, revealed a 2-3 nm red-shift of the ZnP absorption bands while a 5 nm red-shift on the BODIPY absorption band. Additionally, excitation of 14 at 510 nm displayed similar features with the emission spectra of 13 implying a similar energy transfer phenomena (Figure 1.28c and d). Due to the spatial variation of 14 where when self-assembled with 18, the electron acceptor will be closer to the BODIPY moiety, hence, excitation at 430 nm was investigated. When 14 was excited at 430 nm quenching of ZnP emission bands at 605 and 653 nm were observed which indicates the occurrence of energy transfer and/or electron transfer processes.

![Figure 1.28. Steady-state a) absorption and b) fluorescence (λ\text{exc} = 495 nm) spectra of (i) 13, (ii) 18, (iii) BODIPY, and (iv) ZnP-crown ether control compounds in benzonitrile excited; c) absorption and d) fluorescence (λ\text{exc} = 510 nm) spectra if (i) 14, (ii) ZnP, and (iii) BODIPY-crown ether in benzonitrile. Adapted from references 88a (a and b) and 88b (c and d).](image)

Transient absorption studies of 13:18 in benzonitrile excited at 410 nm, afforded an absorption band around 1000 nm which is from the C\textsubscript{60} anion radical providing \(k_{CS}\) and \(k_{CR}\)
values of $5.00 \times 10^{10}$ and $4.35 \times 10^{4}$ s$^{-1}$, respectively. A $k_{\text{ET}}$ value of $1.67 \times 10^{10}$ s$^{-1}$ was evaluated from the transient absorption studies of 13 in benzonitrile excited at 410 nm.

Using the same solvent, femtosecond transient absorption studies of 14 at 430 nm excitation was performed. Transient absorption bands at the 600-700 nm region corresponding to ZnP$^{\bullet\bullet}$ was observed confirming electron transfer from ZnP to BODIPY in dyad 14 (Figure 1.29a); and modest electron transfer rate constants were determined: $k_{\text{CS}} = 1.20 \times 10^{12}$ s$^{-1}$ and $k_{\text{CR}} = 1.17 \times 10^{10}$ s$^{-1}$ demonstrating a very fast electron transfer phenomena. Laser excitation of 14 at 510 nm depicted the same features since the energy transfer is complemented by the electron transfer at this excitation wavelength (Figure 1.29b).

Figure 1.29. Femtosecond transient absorption spectra of 14 excited at a) 430 nm and b) 510 nm in benzonitrile (inset: time profiles at a) 460 and b) 630 nm bands); c) femtosecond and d) nanosecond transient absorption spectra of 14:18 in benzonitrile excited at 430 nm (inset: time profiles at c) 460 and 700 nm, and d) 1000 nm bands). Adapted from reference 88b.
Femtosecond transient absorption studies of 14:18 excited at 430 nm did not render any C$_{60}$ anionic radical band at 1000 nm. However, upon employing nanosecond transient absorption, a band at 1000 nm appeared stipulating that the electron transfer process occurs via triplet excited state (Figure 1.29c and d). The evaluated $k_{CS}$ and $k_{CR}$ values were $1.50 \times 10^5$ and $1.03 \times 10^4$ s$^{-1}$, respectively.

Evaluation of the reaction free energy of the self-assembled antenna-reaction center mimics of 13:18 and 14:18 provided energy level diagrams depicting the photophysical and photochemical processes as illustrated in Figure 1.30a and b, respectively. Photoexcitation of the 13:18 photosystem at 495 nm initially excited the BODIPY moiety of 13. Then singlet-singlet energy transfer from $^1$BODIPY$^*$ to ZnP was observed, thus, BODIPY serves as an antenna system in the said dyad. The resulting $^1$ZnP$^*$ facilitated electron transfer yielding the C$_{60}^*$:ZnP$^{**}$-BODIPY radical ion pair which then recombined and decayed back to its ground state ($k_{CS} = 5.00 \times 10^{10}$ and $k_{CR} = 4.35 \times 10^4$ s$^{-1}$). The 14:18 photosystem on the other hand could be photoexcited at either 430 or 510 nm. It was observed that at 510 nm irradiation, a similar energy transfer phenomena with 13 occurred. However, when irradiated at 430 nm, the initially excited ZnP allowed electron transfer from ZnP to BODIPY rendering the ZnP$^{**}$-BODIPY$^*$ radical ion pair which was also observed with dyad 9. With the addition of 18, it was observed that the formation of the C$_{60}^*$ was promoted by the $^3$C$_{60}^*$ established from the charge recombination of the ZnP$^{**}$-BODIPY$^*$ radical ion pair, rendering a longer-lived charge separated state with $k_{CS}$ and $k_{CR}$ values of $1.50 \times 10^5$ and $1.03 \times 10^4$ s$^{-1}$, respectively.
Figure 1.30. Energy level diagrams illustrating the photophysical and photochemical events occurring in self-assembled a) 13:18 and b) 14:18 antenna-reaction center mimics. Solid, and thin and broken arrows indicate the major and minor events occurring, respectively. Adapted from references 88a and b, respectively.

To further probe the effect of antenna systems in stabilizing charge separated states, triphenylamine (TPA) was utilized, especially that it has a strong UV absorption band around 307 nm. Additionally, ferrocenene (Fc) was also introduced as a secondary electron donor in the ZnP-based photosystem to afford a much long-lived charge separated states. Pentads 15
and 16 were synthesized to investigate the effect of the aforementioned conditions (scheme 1.5 and 1.6, respectively).

**Scheme 1.5**

![Scheme 1.5](image)

**Scheme 1.6**

![Scheme 1.6](image)

Figure 1.31a shows the absorption spectra of 15 and 16 revealing absorption bands at 307 and 328 nm corresponding to the appended TPA and fulleropyrrolidine moieties, respectively. Soret and Q bands of ZnP were also observed though absorption bands of 16 were red-shifted by 5-10 nm relative to 15. Ferrocene on the other hand has a low molar extinction coefficient, thus, ferrocene absorption band was not observed in 16. Fluorescence spectra of 15 and 16 excited at 555 nm displayed quenching of the ZnP emission, though 16 was quenched further as shown in Figure 1.31b. Quenching of 16 is could be attributed to the possible electron transfer of Fc to ZnP. The antenna effect of TPA was confirmed when 15 was excited at 307 nm (TPA absorbance) and ZnP emission bands were observed (Figure 1.31c).

**Figure 1.31.** Steady-state a) absorption and b) fluorescence ($\lambda_{exc} = 555$ nm) spectra of (i) 15, (ii) 16, and (iii) Fc-(TPA)$_2$ZnP; c) fluorescence spectra of (i) 15, (ii) (TPA)$_2$ZnP, (iii) (TPA)$_3$H$_2$P-C$_{60}$, and (iv) (TPA)$_3$H$_2$P excited at 307 nm. All solutions were in o-dichlorobenzene. Adapted from references 89b (a and b) and 89a (c).
Time-resolved fluorescence studies of the 15 in benzonitrile gave a 0.17 ns lifetime. The calculated $k_{CS}$ and $\Phi_{CS}$ values were $5.20 \times 10^9$ s$^{-1}$ and 0.90, respectively. The (TPA)$_2$ZnP control compound was used as a reference with a lifetime of 1.72 ns in benzonitrile.

Transient absorption studies of 15 and 16 in benzonitrile were performed to investigate the electron transfer processes in the photosystems and to assess the rate constants for charge separation and recombination. Femtosecond and nanosecond transient absorption spectra of 15 laser irradiated at 430 and 532 nm, respectively, displayed a broad transient peak at 770 nm which is characteristic of a delocalized cationic radical in [(TPA)$_2$ZnP]$^{++}$, and a band at 1000 nm corresponding to C$_{60}^*$. These results confirm the occurrence of electron transfer in the said photosystem as shown in Figure 1.32. The evaluated $k_{CS}^T$ and $k_{CR}^T$ values were $1.30 \times 10^7$ and $1.00 \times 10^6$ s$^{-1}$, respectively.

Figure 1.32. a) Femtosecond and b) nanosecond transient absorption spectra of 15 in Ar-saturated benzonitrile laser irradiated at 430 and 532 nm, respectively. Inset: time profiles at a) 1000 and b) 1300 nm. Adapted from references 89b and 89a, respectively.

Figure 1.33a shows the femtosecond transient spectra of 16 irradiated at 430 nm having similar features with 15. A transient peak at 640 nm appeared corresponding to ZnP$^{++}$ and a 1000 nm band for the formation of C$_{60}^*$. However, in the femtosecond spectra the 640 nm
band disappeared at 2500 ps while the 1000 nm band persisted longer suggesting a charge migration or a hole shift process stabilizing the charge separated states. The $k_{CS}$ and $k_{HS}$ values were assessed from the rise and decay of the 640 nm peak and were determined to be $2.40 \times 10^{10}$ and $2.52 \times 10^9$ s$^{-1}$, respectively. Utilizing nanosecond transient absorption studies, the rate constant of charge recombination was evaluated to be $1.18 \times 10^5$ s$^{-1}$ which is slower than the $k_{CR}$ value of 15 implying charge stabilization of the charge separated, Fc$^{++}$-(TPA)$_2$ZnP-C$_{60}$*, in the presence of Fc.

![Figure 1.33](image)

**Figure 1.33.** a) Femtosecond and b) nanosecond transient absorption spectra of 16 in Ar-saturated benzonitrile laser irradiated at 430 nm. Time profiles at a) 640 and 1000 nm, and b) 1000 nm (inset). Adapted from reference 89b.

The energy level diagram of 15 from calculated reaction free energy (Figure 1.34a) illustrates that the initial photoexcitation of the TPA substituents permit energy transfer to ZnP yielding $^1$ZnP* excited singlet state. The resulting $^1$ZnP* could either initiate electron transfer producing the [(TPA)$_2$ZnP]$^{++}$-C$_{60}$* charge separated states ($k_{CS} = 5.20 \times 10^9$ s$^{-1}$). It could further undergo intersystem crossing to yield $^3$ZnP* which could also initiate electron transfer via triplet excited state. The resulting $k_{CS}^{T}$ and $k_{CR}^{T}$ values were $1.30 \times 10^7$ and $1.00 \times 10^6$ s$^{-1}$,
respectively. The charge was stabilized from the delocalization of the cationin radical in the \((\text{TPA})_2\text{ZnP}\) moiety.

Free energy calculations of \(16\) affords the energy level diagram in Figure 1.34b depicting the photophysical and photochemical processes occurring in the said antenna-reaction center mimics. In a similar manner with \(15\), initial photoexcitation of the TPA substituents allow energy transfer to ZnP rendering the \(^1\text{ZnP}^*\) excited singlet state which then initiates electron transfer to \(\text{C}_{60}\) resulting in the \(\text{Fc}-[(\text{TPA})_2\text{ZnP}]^{**}\text{-}\text{C}_{60}^*\) radical ion pair. Due to the low oxidation potential of Fc, hole shift or transfer process is favored yielding to a spatially separated \(\text{Fc}^{**}(\text{TPA})_2\text{ZnP-}\text{C}_{60}^*\) radical ion pair. The \(k_{CS}\) and \(k_{CR}\) values were calculated to be \(2.40 \times 10^{10}\) and \(1.18 \times 10^5\) s\(^{-1}\), respectively, with a \(k_{HS}\) value of \(2.52 \times 10^9\) s\(^{-1}\). The \(k_{CR}\) value of \(16\) is a magnitude slower than \(15\) indicating a much better charge stabilization with the employment of a secondary electron donor.

![Figure 1.34](image)

Figure 1.34. Energy level diagrams depicting the different photophysical and photochemical events occurring in the antenna-reaction center mimics of pentads a) \(15\) and b) \(16\). Solid, and thin and broken arrows indicate the major and minor events occurring, respectively. Adapted from references 89a and b, respectively.
The presence of antenna systems and secondary electron donors in zinc porphyrin-based antenna-reaction center mimics allows the stabilization of the charge separated states. Moreover, the antenna systems afford a broad band light capturing ability of the photosystems. It also permits charge delocalization in the case of TPA which stabilizes the radical ion pair.\textsuperscript{89a} Chromophores of low oxidation potentials (i.e., ferrocene) are suited to function as secondary electron donors enabling either electron migration\textsuperscript{88b} or hole transfer\textsuperscript{89b} processes producing spatially separated radical ion pairs of slower rate of charge recombination, hence, longer lifetimes.

1.9.3.2 Aluminum(III) Porphyrin-Based Antenna-Reaction Center Mimics

There is a steadily growing appeal of metallating porphyrins with aluminum(III) due the unique characteristics that aluminum(III) renders to porphyrins. Aluminum(III) is an oxophilic\textsuperscript{90} metal cation forming stable axial covalent bonds with alcohols,\textsuperscript{91a-b} carboxylic acids,\textsuperscript{91c} and phosphinates.\textsuperscript{91d} Moreover, its redox properties are moderate but can be easily tuned through the utilization of different substituents.\textsuperscript{92} Finally, it has a sixth binding site that entertains external ligands to coordinate.\textsuperscript{93} These unique properties of aluminum(III) enables further functionalization of porphyrins, hence, expanding their photophysical and electrochemical properties for artificial photosynthetic applications.

Aluminum(III) porphyrin-based antenna-reaction center mimics have been synthesized employing the aforementioned properties of the aluminum(III) metal center. The covalently-linked and/or self-assembled artificial photosystem is composed of aluminum(III) porphyrin (AlP) which served as the primary electron donor; ferrocene (Fc), phenothiazine (PTZ), and tetrathiafulvalene (TTF) are used as secondary electron donors; and \( p \)-benzoquinones (BQ),
anthraquinones (AQ), naphthalenediimide (NDI) and fullerene (C₆₀) as the electron acceptors.

Figure 1.35 shows the structures of the aluminum(III) porphyrin-based antenna-reaction center mimics.

Figure 1.35. Structures of the aluminum(III) porphyrin-based antenna-reaction center mimics.

Aluminum(III) porphyrin (19) has a strong Soret band at 419 nm and weak Q bands at 548 and 587 nm; and has fluorescence emission bands at 594 and 646 nm. Electrochemical studies conducted in 0.1 M tetrabutylammonium perchlorate (TBAP) o-dichlorobenzene revealed its first oxidation potential at 0.38 V vs Fc/Fc⁺ and two reduction potentials at -1.70
and 2.07 V vs Fc/Fc⁺. The blue-shifted absorption and emission bands, and slight difference in its redox properties is due to the aluminum(III) metalation of the porphyrin moiety.

Benzoquinones (BQ) are good electron acceptors owing to its low reduction potential as listed in Table 1.3. The intermolecular interaction of 19 with these benzoquinones results in a pseudo-first order electron transfer reaction. The electron transfer reaction was confirmed from appearance of a broad absorption band in the 600-800 nm region corresponding to AIP⁺⁺ in the transient absorption studies of 19:20g in benzonitrile shown in Figure 1.36a. A close inspection of Figure 1.36a shows that upon laser excitation at 559 nm, absorption bands at 490 nm is developed corresponding to ³AlP*. As the 490 nm band relaxes, a new band at 410 nm is formed which was designated to BQ⁻. This indicates that the electron transfer occurs via the triplet excited state of AIP which is a pseudo-first order electron transfer process.⁴¹d

In order to determine the second-order electron transfer rate constants, increasing concentration of [BQ] was plotted against the pseudo-first order rate constants obtained from transient absorption studies of 19:BQ. The slope of the linear plot gives the second-order rate constant listed also in Table 1.3.

### Table 1.3. Reduction potential of the BQ electron acceptors and the second-order rate constants, $k_{ET}$, for the electron transfer from 19 to BQ. Adapted from reference 41d.

<table>
<thead>
<tr>
<th>BQ</th>
<th>$E_{red}$ (V vs SCE)</th>
<th>$k_{ET}$ [M⁻¹·s⁻¹]</th>
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<td>20a</td>
<td>-0.96</td>
<td>⎯</td>
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<tr>
<td>20b</td>
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<tr>
<td>20g</td>
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<td>$5.6 \times 10^9$</td>
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</tbody>
</table>

ᵃnot measured due to its extremely negative $-\Delta G_{ET}$ value.
The rate of intramolecular electron transfer in covalently-linked donor-acceptor system dyad 21 was investigated. Quenching of the AlP emission bands suggest the occurrence of either energy or electron transfer from AlP to AQ in the 21. Evaluation of the excited singlet states of AlP and AQ revealed that the energy of $^1$AQ* is higher than $^1$AlP*, thus, energy transfer is not plausible. Therefore, the quenching of the AlP emission bands is due to electron transfer.

Figure 1.36. a) Transient absorption spectra of 19:20g in deaerated benzonitrile at 298 K irradiated at 599 nm; b) time profiles at 410 (dotted line) and 490 nm (solid line); c) Decay time profiles at 500 nm of 19:20a in deaerated benzonitrile; and d) plot of the pseudo-first order rate constant ($k_{obs}$) vs molar concentration of 20a. Adapted from reference 41d.

The electron transfer rate constant from $^1$AlP* in 21 was assessed from transient absorption studies and was determined to be $1.3 \times 10^{10}$ s$^{-1}$. Intersystem crossing from $^1$AlP* to
\(^3\)AlP* was estimated to be a slow process at a rate of \(4.0 \times 10^8\) s\(^{-1}\) and decays at \(2.9 \times 10^3\) s\(^{-1}\).

Relaxation of \(^3\)AlP* in 19 was calculated to be \(8.3 \times 10^3\) s\(^{-1}\).

Figure 1.37 shows the evaluation of the reaction free energy of the donor-acceptor system 21 revealed that electron transfer is initiated by the \(^1\)AlP* at a \(k_{ET}\) of \(1.3 \times 10^3\) s\(^{-1}\) which then recombines at \(k_{BET} = 2.6 \times 10^{11}\) s\(^{-1}\) from calculations. The photosystem then relaxes back to its ground state through \(^3\)AlP* at a \(k_{T-T}\) of \(2.9 \times 10^3\) s\(^{-1}\).

Figure 1.37. Energy level diagram of the donor-acceptor photosystem 21. Adapted from reference 41d.

In order to stabilize the charge separated states in the donor-acceptor photosystem, Fc was employed as a secondary electron donor. Furthermore, the BQ and AQ electron acceptors were replaced with \(C_\text{60}\) since \(C_\text{60}\) is a better electron acceptor owing to its low reorganization energy and low reduction potential. Thus, triad 22 along with its control compounds Fc-AlP (22a) and AlP-\(C_\text{60}\) (22b) were synthesized and characterized in order to determine the degree of charge stabilization.\(^94\) Scheme 1.7 shows the structures of the compounds 22, 22a, and 22b, and the possible photophysical and photochemical events.
Optical absorption studies showed the Soret and Q bands of porphyrin at 416 and 547 nm, respectively. Additional absorption bands at 256 and around 700 nm were observed from fullerene as shown in Figure 1.38a. Ferrocene has an electronic transition at 442 nm but not quite intense due to its low molar absorptivity. Quenching of the porphyrin emissions at 600 and 650 nm were also observed in the fluorescence spectra (Figure 1.38b) which is attributed to the occurrence of electron transfer processes.

Figure 1.38. Steady-state a) absorption and b) fluorescence ($\lambda_{exc} = 550$ nm) spectra of Fc (wine-red), C$_{60}$COOMe (black), 19 (red), 22b (blue), 22a (green), and 22 (magenta) in dichloromethane and o-dichlorobenzene, respectively. Inset: 600-750 nm region illustrating C$_{60}$ absorption. Adapted from reference 94.

Fluorescence lifetime measurements of 22 and the control compounds afforded the calculation of the $k_q^S$ values which could be evaluated as the rate of charge separation, $k_{CS}^S$, of
the photosystems. The obtained $k_q$ values for 22b and 22 were $4.60 \times 10^9$ and $1.46 \times 10^{10}$ s$^{-1}$, respectively. The rates of charge recombination, $k_{CR}$, were assessed from the nanosecond transient studies of 22b and 22 shown in Figure 1.39.

![Figure 1.39. Nanosecond transient absorption spectra of a) 22b and b) 22 in Ar-saturatured o-dichlorobenzene laser irradiated at 532 nm. Inset: time profiles at 1020 nm. Adapted from reference 94.](image)

The transient absorption spectra of 22b and 22 revealed similar peaks at 480 and 820 nm corresponding to the triple excited state of the AlP moiety. A peak at 1020 nm was also observed designated to C$_{60}^\bullet$- confirming electron transfer in the said photosystems. The determined $k_{CR}$ values from the time profiles of C$_{60}^\bullet$ at 1020 nm were $2.54 \times 10^7$ and $5.70 \times 10^7$ s$^{-1}$ for 22b and 22, respectively, which is counterintuitive to charge stabilization in the presence of Fc.

The constructed energy level diagram shown in Figure 1.40 demonstrates the possible photophysical and photochemical events happening in triad 22. Photoexcitation of the photosystem promotes the AlP moiety to its singlet excited state which initiates electron transfer yielding the radical ion pair Fc-AlP$^{\bullet\bullet}$-C$_{60}^\bullet$. The radical ion pair could either proceed to produce the spatially separated Fc$^{\bullet\bullet}$-AlP-C$_{60}^\bullet$ radical ion pair, or recombine and populate the
$^3$Fc*. The latter is most likely the reason for the fast charge recombination in 22 since weak electronic coupling between the unpaired electrons in the radical ion pair permits faster charge recombination. Furthermore, population of the $^3$Fc* could occur in the triad since it has a lower energy than the radical ion pair, thus, further accelerates the charge recombination in 22.

Figure 1.40. Energy level diagram of 22. Adapted from reference 94.

Since the substitution of AlP at the meso position didn’t provide any charge stabilization; hence, functionalization at the axial position with a secondary electron donor was investigated. Two phenothiazine molecules, each appended to pyridine to allow axial ligation with the aluminum(III) metal center, were employed as secondary electron donors while maintaining the position of the electron acceptor C$_{60}$. Scheme 1.8 shows the structures of the multimodular self-assembled donor-acceptor systems 23 and 24.$^{95}$ In the pyridine-appended phenothiazine ligands, when R = H it is designated as PTZpy, and when R = SCH$_3$ it is designated as TPTZpy for photosystems 23 and 24, respectively.

Figure 1.41 shows the absorption spectra of the components of the self-assembled photosystems 23 and 24 displaying strong Soret and weak Q bands of the porphyrin moiety at 416 and 547 nm, respectively. Moderately strong fullerene absorption bands at 275 and 325
nm along with weak bands at 430 and 700 nm were also observed. Phenothiazine ligands showed UV absorption peaks at 256 and 314 nm for PTZpy, and 266 and 322 nm for TPTZpy. Figure 1.41. Absorption spectra of PTZpy (red), TPTZpy (green), C\textsubscript{60}COOMe (blue), 19 (magenta), and 22b (wine) in dichloromethane. Inset: 600-750 nm region illustrating C\textsubscript{60} absorption. Adapted from reference 95.

Time-resolved fluorescence studies of 23, 24, and the control compounds showed a decrease in the lifetime of 22b in the presence of the phenothiazine ligands. Values of the resulting fluorescence lifetime are listed in Table 1.4. The obtained quenching rate constants, \( k_q \), are evaluated as the \( k_{CS} \) of the photosystems.

Table 1.4. Fluorescence emission bands (\( \lambda_F \)), lifetimes (\( \tau \)), and quenching rate constants (\( k_q \)). Adapted from reference 95.

<table>
<thead>
<tr>
<th>sample</th>
<th>( \lambda_F ) /nm</th>
<th>( \tau )/ps (amplitude)</th>
<th>( k_q )/s\textsuperscript{-1}[a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>594, 646</td>
<td>7050 (1.00)</td>
<td>---</td>
</tr>
<tr>
<td>PTZpy:19</td>
<td>610, 663</td>
<td>7000 (1.00)</td>
<td>( 1.0 \times 10^6 )</td>
</tr>
<tr>
<td>TPTZpy:19</td>
<td>610, 663</td>
<td>6900 (1.00)</td>
<td>( 3.1 \times 10^6 )</td>
</tr>
<tr>
<td>22b</td>
<td>594, 646</td>
<td>2900 (0.10), 210 (0.90)</td>
<td>( 4.6 \times 10^9 )</td>
</tr>
<tr>
<td>py:22b</td>
<td>607, 662</td>
<td>2820 (0.11), 205 (0.89)</td>
<td>( 4.7 \times 10^9 )</td>
</tr>
<tr>
<td>23</td>
<td>609, 662</td>
<td>2550 (0.12), 198 (0.88)</td>
<td>( 4.9 \times 10^9 )</td>
</tr>
<tr>
<td>24</td>
<td>609, 665</td>
<td>2120 (0.08), 182 (0.92)</td>
<td>( 5.4 \times 10^9 )</td>
</tr>
</tbody>
</table>

[a]Calculated using equation 1.20.
Transient absorption studies were conducted to evaluate the rate constants for charge recombination, $k_{CR}$, of the 23 and 24 photosystems. As shown in Figure 1.42, transient absorption peaks at 500 and 820 nm corresponding to $^3$AlP* appeared along with a strong band at 700-720 nm for the $^3$C$_{60}$*. The prominent peak at 600 nm is from PTZ** seen in both 23 and 24 indicating the participation of phenothiazine in the electron transfer process (Figures 1.42a and b, respectively). Transient absorption band at 1020 nm characteristic of the C$_{60}$* was also observed. The $k_{CR}$ values were assessed from the time profile of the 1020 nm peak and were calculated to be $1.00 \times 10^7$ and $1.20 \times 10^7$ s$^{-1}$ for 23 and 24, respectively, which are slower than that of 22b ($k_{CR} = 2.54 \times 10^7$ s$^{-1}$). This in deed shows that phenothiazine serving as the secondary donor, did stabilize the charge separated states of the radical ion pair.

![Figure 1.42. Nanosecond transient absorption spectra of a) 23, b) 24, c) py:22b, and d) 22b in Ar-saturated o-dichlorobenzene laser irradiated at 532 nm. Inset: time profiles at 1020 nm. Adapted from reference 95.](image)
Construction of the energy level diagram shown in Figure 1.43 illustrates that the electron transfer process is initiated by the population of the $^{1}\text{AlP}^{*}$ yielding $\text{D-}^{1}\text{AlP}^{*-}\text{C}_6\text{O}^{*}$. The phenothiazine moiety then undergoes hole transfer/shift to render a distantly separated radical ion pair $\text{D}^{**}-\text{AlP}\text{-C}_6\text{O}^{*-}$ with lifetimes of 100 and 83 ns for 23 and 24, respectively. Though $\text{PTZ}^{**}-\text{AlP}\text{-C}_6\text{O}^{*-}$ (23) has a higher energy than $\text{D-}^{1}\text{AlP}^{*-}\text{C}_6\text{O}^{*}$, charge stabilization was still apparent which could have undergone in a different route than 24.

![Energy level diagram](image)

Figure 1.43. Energy level diagram of 23 and 24 depicting the photophysical and photochemical events occurring in the self-assembled multimodular donor-acceptor system. Adapted from reference 95.

Effects of the length of the spacer or linking bridge in the donor-acceptor system was also investigated in the aluminum(III) porphyrin-based multimodular donor-acceptor photosystem. Naphthalenediimide (NDI) was employed as the electron acceptor covalently linked to AlP using a benzoate linker similar to the previous AlP photosystems. Tetrathiafulvalene was appended to pyridine with (TTF-Ph-py) and without phenyl spacer (TTF-
py) was used as the secondary donor that axially coordinated to AlP. The structure of the multimodular donor-acceptor photosystem is shown in scheme 1.9.79a

Optical absorption studies of the components of 26 and 27 shown in Figure 1.44 revealed the typical Soret and Q bands of porphyrin at 415 and 547 nm, respectively. Weak absorption bands at 342, 360, and 381 nm were from the NDI moiety. The TTF-py registered peaks at 304 and 432 nm while TTF-Ph-py peaks were at 299 and 427 nm.

![Absorption spectra](image)

Figure 1.44. Absorption spectra of 19 (dashed line), NDI-Ph (dotted line), and 25 (solid line) in dichloromethane. Inset: absorption spectra of TTF-py and TTF-Ph-py. Adapted from reference 79a.

To estimate the extent of the hole and electron transfer in 26 and 27, systematic time-resolved fluorescence studies was conducted for the aforementioned photosystems and its control compounds. The resulting fluorescence lifetimes are listed in Table 1.5. Rate constants of the fluorescence quenching, $k_q$, were calculated from the fast, major components in lifetimes with biexponential decay fit. The obtained $k_q$ were used to establish the rate of electron transfer, $k_{ET}$, in the donor-acceptor systems. For 26 and 27, the $k_{ET}$ values were $5.57 \times 10^9$ and $4.45 \times 10^9$ s$^{-1}$, respectively, which are much faster than 25 ($1.00 \times 10^9$ s$^{-1}$) indicating the
participation of TTF-py and TTF-Ph-py in the electron transfer process. From the evaluated $k_{\text{ET}}$ values in dichloromethane, it suggests that electron transfer initially takes place between TTF and AlP yielding TTF*-AlP*: this occurs at $k_{\text{ET}} = 4.12 \times 10^9 \text{ s}^{-1}$. Afterwards, an electron migration occurs producing the radical ion pair TTF*-AlP-NDI* at $k_{\text{ET}} = 1.13 \times 10^9 \text{ s}^{-1}$ ($\tau = 880 \text{ ps}$). However, $k_{\text{ET}}$ values in benzonitrile propose that the initial electron transfer occurs between AlP and NDI to produce AlP*-NDI*, then hole transfer occurs yielding TTF*-AlP-NDI*. The fluorescence lifetimes indicate that the electron transfer process is solvent dependent and further studies are needed in order to confirm the route of electron transfer.

Table 1.5. Fluorescence lifetimes ($\tau$) and quenching rate constants ($k_q$) of 26, 27, and its control compound in dichloromethane and benzonitrile. Adapted from reference 79a.

<table>
<thead>
<tr>
<th>sample</th>
<th>solvent</th>
<th>$\tau$/ns (amplitude, %)</th>
<th>$k_q/ \times 10^9 \text{ s}^{-1}$[a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>dichloromethane</td>
<td>5.70 (100)</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>benzonitrile</td>
<td>6.10 (100)</td>
<td>---</td>
</tr>
<tr>
<td>py:19</td>
<td>dichloromethane</td>
<td>5.66 (100)</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>benzonitrile</td>
<td>6.62 (100)</td>
<td>---</td>
</tr>
<tr>
<td>25</td>
<td>dichloromethane</td>
<td>5.45 (21), 0.852 (79)</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>benzonitrile</td>
<td>6.64 (22), 0.283 (78)</td>
<td>3.38</td>
</tr>
<tr>
<td>py:25</td>
<td>dichloromethane</td>
<td>5.53 (24), 0.763 (78)</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>benzonitrile</td>
<td>6.55 (28), 0.268 (76)</td>
<td>3.58</td>
</tr>
<tr>
<td>26</td>
<td>dichloromethane</td>
<td>4.44 (8), 0.174 (92)</td>
<td>5.57</td>
</tr>
<tr>
<td></td>
<td>benzonitrile</td>
<td>6.25 (28), 0.231 (72)</td>
<td>4.18</td>
</tr>
<tr>
<td>27</td>
<td>dichloromethane</td>
<td>3.99 (8), 0.216 (92)</td>
<td>4.45</td>
</tr>
<tr>
<td></td>
<td>benzonitrile</td>
<td>6.11 (20), 0.256 (80)</td>
<td>3.75</td>
</tr>
<tr>
<td>TTF-py:19</td>
<td>dichloromethane</td>
<td>4.75 (18), 0.233 (82)</td>
<td>4.12</td>
</tr>
<tr>
<td></td>
<td>benzonitrile</td>
<td>6.22 (74), 0.623 (26)</td>
<td>1.45</td>
</tr>
<tr>
<td>TTF-Ph-py:19</td>
<td>dichloromethane</td>
<td>4.08 (34), 0.293 (57)</td>
<td>3.24</td>
</tr>
<tr>
<td></td>
<td>benzonitrile</td>
<td>6.33 (63), 0.706 (37)</td>
<td>1.27</td>
</tr>
</tbody>
</table>

[a]Calculated using equation 1.20.

Transient electron paramagnetic resonance (EPR) studies were conducted and it was determined that the initial electron transfer of photosystems 26 and 27 is between AlP and NDI. EPR studies were also used to determine the rate constants of the charge recombination in the
said photosystems. Figure 1.45 shows the signal decay of 27 where at an earlier time, both the singlet ($\Psi_2$ and $\Psi_3$) and triplet ($\Psi_1$ and $\Psi_4$) electron transfer states are populated. However, at a later time, $\Psi_2$ and $\Psi_3$ are depopulated since singlet recombination rate, $k_S$, is faster than the triplet recombination rate, $k_T$. The recorded lifetimes of the singlet and triplet electron transfer states were 350 ns and 8.5 $\mu$s for 27, respectively. In 26, the recombination of the singlet electron transfer state was measured to be 200 ns which are expected since it doesn’t have any phenyl spacer between pyridine and TTF; however, the triplet electron transfer state was at 12 $\mu$s which is longer than 27. This could be due to the difference in triplet relaxation.

Figure 1.45. Signal decay and qualitative model of charge recombination in 27. Adapted from reference 79a.

Calculation of the free energy of reaction and construction of the energy level diagram shown in Figure 1.46, illustrate the photophysical and photochemical events occurring in photosystems 26 and 27. Photoexcitation of AlP to afford $^1$AlP* drives the electron transfer between AlP and NDI yielding AlP**-NDI*. It further undergoes hole transfer generating the
TTF*-AlP-NDI* radical ion pair with singlet lifetimes of 200 and 350 ns for photosystems 26 and 27, respectively.

![Energy level diagram for the self-assembled multimodular donor-acceptor systems 26 and 27. Adapted from reference 79a.](image)

Figure 1.46. Energy level diagram for the self-assembled multimodular donor-acceptor systems 26 and 27. Adapted from reference 79a.

Aluminum(III) porphyrin-based antenna-reaction center mimics permits further functionalization of the porphyrin template, aside from the substitution at the meso and β positions of the macrocyle, by utilizing the sixth coordination site of the aluminum(III) metal center for pyridine or imidazole appended chromophores. The investigation on the effect of the length and type of spacer used in photosystems similar to 23-27, is an interesting topic due to the electronic coupling it offers from to the vertical arrangement of the secondary electron donor and electron acceptor. Only a hand-full of studies have been done in aluminum(III) porphyrin for artificial photosynthetic applications, hence, there is ample opportunities for the improvement and expansion of the said antenna-reaction center mimic.
1.9.4 Subphthalocyanine-Based Light-Harvesting Systems

Subphthalocyanines (SubPc) are the smallest homologues of phthalocyanines composed of three \( N \)-fused diiminoisoindoline units constructed around a central boron atom. It has a 14 \( \pi \)-electron aromatic core with a two-dimensional nonplanar structure that presents unique photophysical and redox properties. Its versatile structure allows substitution at the \( \alpha \) and \( \beta \) positions at the periphery of the subphthalocyanine macrocycle as shown in Figure 1.47. Moreover, functionalization at the central boron atom through axial substitution affords further tuning of its photophysical and redox properties while preserving the electronic characteristics of the macrocycle.

![Figure 1.47. Structures and acronyms for the types of substituted subphthalocyanines: D (dodecasubstituted), U (unsymmetrically trisubstituted), H\(_\alpha\) (hexasubstituted at the \( \alpha \) positions), H\(_\beta\) (hexasubstituted at the \( \beta \) positions), and N (subnaphthalocyanine). Adapted from reference 67a.](image)

Modulation of the redox properties of subphthalocyanine allows it to be employed as either an electron donor or acceptor in antenna-reaction center photosystems.\(^{68b,96}\)

Furthermore, substitution at the \( \alpha \) and/or \( \beta \) positions of the macrocycle enables tuning of not
only its electrochemical properties but also its photophysical properties which will be discussed later in this section. The substituted and axially functionalized subphthalocyanine-based multimodular donor-acceptor systems for artificial photosynthetic applications are listed in below.

Table 1.6. Modified subphthalocyanine-based antenna-reaction centers photosystems.

<table>
<thead>
<tr>
<th>compound</th>
<th>type</th>
<th>R peripheral</th>
<th>X axial</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>D</td>
<td>H</td>
<td>Cl</td>
<td>69a</td>
</tr>
<tr>
<td>29</td>
<td>D</td>
<td>H</td>
<td>OPh</td>
<td>68b</td>
</tr>
<tr>
<td>30</td>
<td>D</td>
<td>H</td>
<td>p-OPh-Fc</td>
<td>68b</td>
</tr>
<tr>
<td>31</td>
<td>D</td>
<td>H</td>
<td>m-OPh-Fc</td>
<td>68b</td>
</tr>
<tr>
<td>32</td>
<td>D</td>
<td>H</td>
<td>N-PDI[c]</td>
<td>96</td>
</tr>
<tr>
<td>33</td>
<td>D</td>
<td>F</td>
<td>N-PTZ[c]</td>
<td>96</td>
</tr>
<tr>
<td>34</td>
<td>D</td>
<td>H</td>
<td>p-OPh-t-Bu</td>
<td>69a</td>
</tr>
<tr>
<td>35</td>
<td>H[β]</td>
<td>SEt[a]</td>
<td>Cl</td>
<td>69b</td>
</tr>
<tr>
<td>36</td>
<td>H[β]</td>
<td>SBz[a]</td>
<td>Cl</td>
<td>69bb</td>
</tr>
<tr>
<td>37</td>
<td>H[α]</td>
<td>SPh[a]</td>
<td>Cl</td>
<td>69a</td>
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<tr>
<td>38</td>
<td>N</td>
<td>Nc</td>
<td>Cl</td>
<td>69a</td>
</tr>
<tr>
<td>39</td>
<td>D</td>
<td>F</td>
<td>m-OPh-C_60</td>
<td>68a</td>
</tr>
<tr>
<td>40</td>
<td>U</td>
<td>I</td>
<td>m-OPh-C_60</td>
<td>68a</td>
</tr>
<tr>
<td>41</td>
<td>H[β]</td>
<td>catechol[b]</td>
<td>m-OPh-C_60</td>
<td>68a</td>
</tr>
<tr>
<td>42</td>
<td>U</td>
<td>N(Ph)_2</td>
<td>m-OPh-C_60</td>
<td>68a</td>
</tr>
<tr>
<td>39a</td>
<td>D</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40a</td>
<td>U</td>
<td>I</td>
<td>OPh</td>
<td>68a</td>
</tr>
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<td>41a</td>
<td>H[β]</td>
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<td>OPh</td>
<td>68a</td>
</tr>
<tr>
<td>42a</td>
<td>U</td>
<td>N(Ph)_2</td>
<td>OPh</td>
<td>68a</td>
</tr>
</tbody>
</table>

[a] linked directly by a C-S covalent bond, [b] C-O covalent bonds, and [c] a single B-N covalent bond

The redox properties of SubPc having its first oxidation and reduction potentials at 1.06V and -1.04 V vs SCE, respectively, allows it to function as an electron acceptor in the presence of an easily oxidizable chromophore like Fc in dyads 30 and 31. In order to investigate the photophysical and photochemical events in the dyads, a systematic analysis is conducted. In the absorption spectra, the Soret band of SubPc appeared at 309 nm with a strong Q band at
566 nm shown in Figure 1.48. This indicates that there is negligible electronic interaction between the SubPc and Fc entities in the said dyads. Fluorescence spectra showed quenching of the SubPc emission at 578 nm which could be due to energy or electron transfer. The latter is the most probable reason since energy transfer from SubPc to Fc is energetically unfavorable. This however, proposes that electron transfer is initiated by $^1$SubPc*.

![Figure 1.48](image)

Figure 1.48. a) Absorption and b) fluorescence spectra ($\lambda_{exc} = 525$ nm) of dyads 30, 31, and its control compounds in benzonitrile. Adapted from reference 68b.

Femtosecond transient absorption studies of 29 revealed pronounced bleaching at 564 nm corresponding to the depletion of the singlet ground state which decayed at 1.70 ns (Figure 1.49a). Peaks at 564 and 620 nm were observed on the transient absorption spectra of 30 which decayed with a rate constant of $8.8 \times 10^{10}$ s$^{-1}$ which is much faster than 29 suggesting electron transfer, though formation of Fc$^{**}$ and SubPc$^{**}$ is difficult to establish due to the low molar extinction coefficients of the said radical ion pair. Transient absorption spectra of 31 gave similar features to that of 30 shown Figures 1.49b and c, respectively. The obtained rate of charge separation from Fc to $^1$SubPc* was $1.20 \times 10^{11}$ s$^{-1}$ which is faster than 30. This is rationalized from the short distance between Fc and SubPc in 31 than in 30. Nanosecond
transient absorption spectra of 30 a peak at 450 nm appeared which is attributed to $^3$SubPc* decaying at $7.1 \times 10^4$ s$^{-1}$. Bleaching at around 570 nm was also observed.

![Figure 1.49](image)

Figure 1.49. Differential transient absorption spectra of a) 29, b) 30, and c) 31 obtained upon femtosecond flash photolysis ($\lambda_{exc} = 440$ nm) in benzonitrile; d) nanosecond transient absorption spectra of 30 in benzonitrile ($\lambda_{exc} = 570$ nm). Inset: time profiles at 600 (a, b, and c) and 450 nm (d). Adapted from reference 68b.

Free energy of reaction was calculated using Rehm-Weller approach to elucidate the photophysical and photochemical events of dyad 30 and 31. Figure 1.50 shows the constructed energy level diagram and it depicts electron transfer from Fc to $^1$SubPc* producing Fc$^{**}$-SubPc* efficiently. The generated radical ion pair rapidly decays back to its ground states.
Subphthalocyanine donor-acceptor conjugates linked directly through a single B-N bond were synthesized. Electron poor (PDI) and electron rich (PTZ) moieties were convalently linked to the SubPc forming dyads 32 and 33, respectively. Additionally, the SubPc unit in 33 was substituted with fluorine to improve its electron acceptor properties. Therefore, in dyad 32 the SubPc is the electron donor while in 33, SubPc is the electron acceptor illustrating the versatility of SubPc's electrochemical properties.96

Absorption studies showed very little changes in the SubPc absorbance of 32 while a 5 nm red-shift of the Q band was observed with 33. Fluorescence studies showed quenching of both dyads though more quenching was observed with 33. Fluorescence lifetime of 32 in THF provide two time constants: 6 and 1.5 ns. The long-lived component is comparable to the unquenched PDI control compound leaving the short-lived component assigned to the SubPc moiety. Fluorescence lifetime values of 33 on the other hand, were too short to be detected by the instrument.
In order to probe the electron transfer processes in the dyads, femtosecond transient absorption was employed. Figure 1.51a illustrating the transient absorption spectra of 32 revealed the population of $^1$SubPc* (maxima: 615, 755, 800 and 1100 nm; minima: 575 nm) and $^1$PDI* (maxima: 475, 700 and 1000 nm; minima: 440 nm), and both have decay lifetimes of 28.5 ± 0.8 ps in THF. The deactivation of the both $^1$SubPc* and $^1$PDI* did not result in formation of the SubPc**-PDI** radical ion pair though it populated the $^3$PDI*. It was concluded that SubPc**-PDI** is semistable and that back electron transfer is significantly faster than the forward electron transfer.

![Differential absorption spectra obtained upon femtosecond flash photolysis ($\lambda_{exc} = 550$ nm) of a) 32 and b) 33 in THF. Adapted from reference 96.](image)

Transient absorption spectra of 33 revealed $^1$SubPc* peaks which rapidly decayed at 1.1 ± 0.1 ps compare to 32. This suggests intramolecular electron transfer in 33, however, formation of PTZ** at 520 nm difficult to establish since it is masked by the features related to
SubPc*. Multiwavelength analysis of the PTZ**/SubPc* fingerprints provided a back electron transfer dynamics of $16 \pm 2$ ps in THF.

The tunability of SubPc’s electronic structure was further examined by employing a variety of electron rich thioakyl substituents at the $\alpha$ and $\beta$ positions of the macrocycle ($35$, $36$, $37$), and expanding the of $\pi$-conjugation of the benzene rings through benzoannulation ($38$). The synthesized SubPc derivatives and their maximum absorption are listed below.

Table 1.7. UV-visible spectra of the modified subphthalocyanines. Adapted from references 69a and b.

<table>
<thead>
<tr>
<th>compound</th>
<th>$\lambda_{max}$/nm (log $\varepsilon$/M$^1$-cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>564 (7.01), 546 (sh), 510 (sh), 303 (3.83)</td>
</tr>
<tr>
<td>34</td>
<td>563 (4.97), 546 (sh), 515 (sh), 305 (4.62)</td>
</tr>
<tr>
<td>35</td>
<td>592 (4.77), 546 (sh), 362 (4.14), 296 (4.55)</td>
</tr>
<tr>
<td>36</td>
<td>601 (4.78), 555 (sh), 386 (4.21), 304 (4.52)</td>
</tr>
<tr>
<td>37</td>
<td>644 (4.87), 576 (sh), 294 (4.72)</td>
</tr>
<tr>
<td>38</td>
<td>656 (4.47), 594 (sh), 328 (4.5), 293 (4.72)</td>
</tr>
</tbody>
</table>

sh = shoulder

For compounds 28 and 34, the substitution of the axially linked chlorine with an alkyl group didn’t afford any significant changes in the UV-visible absorption spectra, thus, suggesting that the electronic characteristic of the SubPc core is preserved with the variation of axial substituents. On the other hand, introduction of six electron donating thioalkyl groups at the $\alpha$ and $\beta$ positions of the SubPc macrocycle has a greater impact on its electronic structure. This is manifested by the large and low-energy shift of the Q band. Benzoannulation of the SubPc core also results in a large red-shift of the Q band indicating the reduction of the HOMO-LUMO energy gap in the macrocycle.

The electronic properties of the SubPc macrocycle were further modulated for artificial photosynthetic applications. The antenna-reaction center photosystems were composed of an
array of substituted SubPc’s and C₆₀ electron acceptor. The periphery of the SubPc electron donor was functionalized by fluorine (39), iodine (40), catechol (41), and diphenylamino groups (42) while the boron central atom was covalently bonded to meso-phenoxyl appended fulleropyrrolidine. The SubPc analogues without the C₆₀ electron acceptor (39a-42a) were also synthesized as control compounds.68a

Results from the absorption, fluorescence (both steady-state and time-resolved), and phosphorescence studies of control compounds 39a-42a are listed in Table 1.8. It was shown that 42a is greatly affected by the peripheral substitution of SubPc with N, N-diphenylamine as illustrated by the red-shifted Q band at 618 nm. Moreover, fluorescence quenching was also apparent in the SubPc compounds, especially with 40a which was expected due to the presence of iodine atoms which promote intersystem crossing populating the SubPc triplet excited state, ³SubPc*.

Table 1.8. Optical studies of 39a-42a in toluene. Adapted from reference 68.a.

<table>
<thead>
<tr>
<th>measurement</th>
<th>39a</th>
<th>40a</th>
<th>41a</th>
<th>42a</th>
</tr>
</thead>
<tbody>
<tr>
<td>λₐᵇˢ, nm</td>
<td>573</td>
<td>571</td>
<td>570</td>
<td>618</td>
</tr>
<tr>
<td>λᵢ, nm</td>
<td>585</td>
<td>585</td>
<td>585</td>
<td>650</td>
</tr>
<tr>
<td>Φᵢ</td>
<td>0.40</td>
<td>0.08</td>
<td>0.49</td>
<td>0.15</td>
</tr>
<tr>
<td>τᵢ, ns</td>
<td>1.66</td>
<td>0.51</td>
<td>1.76</td>
<td>1.5</td>
</tr>
<tr>
<td>λᵢᵖ, nm[s]</td>
<td>835</td>
<td>835</td>
<td>844</td>
<td>&gt;850</td>
</tr>
</tbody>
</table>

[a] in methylcyclohexane, 2-methyltetrahydofuran, ethyl iodide (2:1:1 v/v)

Transient absorption studies were performed in order to investigate the photophysical events in the SubPc derivatives. The resulting kinetics data are tabulated in Table 1.9. Laser irradiation of 40a at 532 nm populated the singlet SubPc as manifested by the strong absorption band at 650 nm shown in Figure 1.52a which lasted beyond the picosecond measurement. Nanosecond flash photolysis at 532 nm showed a well-developed peak at 460
nm corresponding to $^3$SubPc* (Figure 1.52b). Similar results were also observed on the other SubPc derivatives validating the intersystem crossing processes observed in the steady-state and time-resolved optical studies of the said SubPc derivatives.

Table 1.9. Transient absorption studies of 39a-42a and one-electron oxidized SubPc in toluene. Adapted from reference 68.a.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>39a</th>
<th>40a</th>
<th>41a</th>
<th>42a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Singlet excited state maximum, nm</td>
<td>660</td>
<td>650</td>
<td>675</td>
<td>730</td>
</tr>
<tr>
<td>Singlet excited state lifetime, ns</td>
<td>1.73</td>
<td>0.59</td>
<td>1.81</td>
<td>1.26</td>
</tr>
<tr>
<td>Singlet excited state rate constant, s$^{-1}$</td>
<td>$5.8 \times 10^8$</td>
<td>$1.7 \times 10^9$</td>
<td>$5.5 \times 10^8$</td>
<td>$7.9 \times 10^8$</td>
</tr>
<tr>
<td>Triplet excited state maximum, nm</td>
<td>460</td>
<td>460</td>
<td>480</td>
<td>550</td>
</tr>
<tr>
<td>Triplet excited state lifetime, μs</td>
<td>28</td>
<td>32</td>
<td>36</td>
<td>40</td>
</tr>
<tr>
<td>Radical cation maximum$^{[a]}$</td>
<td>620</td>
<td>620</td>
<td>620</td>
<td>685</td>
</tr>
</tbody>
</table>

$^{[a]}$in dichloromethane

Figure 1.52. Differential absorption spectra obtained upon a) picosecond and b) nanosecond flash photolysis ($\lambda_{exc} = 532$ nm) of 40a in nitrogen saturated toluene at time delay 25 ps and 50 ns, respectively. Adapted from reference 68a.

Optical studies of the SubPc-C$_{60}$ dyads 39-42 revealed further quenching of the SubPc fluorescence emission which proposes electron transfer. Thus, transient absorption studies
were conducted in the said dyads to probe the photophysical and photochemical events. The gathered fluorescence lifetimes and kinetics data are listed below.

Table 1.10 Photophysical parameters (steady-state and transient) of SubPc-C\textsubscript{60} dyads 39-42 in toluene. Adapted from reference 68a.

<table>
<thead>
<tr>
<th>measurement</th>
<th>39</th>
<th>40</th>
<th>41</th>
<th>42</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\lambda_F), nm</td>
<td>588</td>
<td>592</td>
<td>588</td>
<td>655</td>
</tr>
<tr>
<td>(\Phi_F) (SubPc)</td>
<td>1.2 \times 10^{-3}</td>
<td>9.6 \times 10^{-4}</td>
<td>3.1 \times 10^{-3}</td>
<td>1.1 \times 10^{-3}</td>
</tr>
<tr>
<td>(\Phi_F) (C\textsubscript{60})</td>
<td>5.04 \times 10^{-4}</td>
<td>1.0 \times 10^{-3}</td>
<td>2.8 \times 10^{-3}</td>
<td>7.8 \times 10^{-4}</td>
</tr>
<tr>
<td>(\tau_F), ns (SubPc)</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.25</td>
</tr>
<tr>
<td>(\tau_F), ns (C\textsubscript{60})</td>
<td>1.44</td>
<td>1.17</td>
<td>1.27</td>
<td>0.52</td>
</tr>
<tr>
<td>singlet excited state lifetime (SubPc), ns</td>
<td>0.05</td>
<td>0.041</td>
<td>0.04</td>
<td>0.25</td>
</tr>
<tr>
<td>singlet excited state rate constant, s\textsuperscript{-1}</td>
<td>2.0 \times 10^{10}</td>
<td>2.4 \times 10^{10}</td>
<td>2.5 \times 10^{10}</td>
<td>4.0 \times 10^{9}</td>
</tr>
<tr>
<td>singlet excited state lifetime (C\textsubscript{60}), ns</td>
<td>1.39</td>
<td>1.25</td>
<td>1.25</td>
<td>---\textsuperscript{[a]}</td>
</tr>
<tr>
<td>triplet excited state quantum yield (SubPc)</td>
<td>0.48</td>
<td>0.43</td>
<td>0.45</td>
<td>radical pair state</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]}masked by the strong SubPc features

Time-resolved transient absorption spectra of 40 revealed a broad peak at 650 nm corresponding to \(^1\text{SubPc}^*\) as determined from the previous transient studies of the 40\textsubscript{a} control compound (Figure 1.53a). However, the \(^1\text{SubPc}^*\) decays at 2.4 \times 10^{10} s\textsuperscript{-1} which is almost a magnitude faster than 40\textsubscript{a}. Aside from the peak at 650 nm, a new transient peak appeared at 880 nm which is assigned to \(^1\text{C}_{60}^*\), decaying at 1.25 ns which is faster than the C\textsubscript{60} control. Thus, this indicates intersystem crossing though no characteristic \(^3\text{C}_{60}^*\) was observed since it was masked by the strong \(^3\text{SubPc}^*\) features at higher time delays as shown in Figure 1.53b. Similar features were obtained from the transient absorption spectra of 39 and 41.
From the gathered fluorescence lifetime and kinetics data, it was determined that in compounds 39-41 upon photoexcitation affords $^1\text{SubPc}^*$ where it undergoes singlet-singlet energy transfer to C$_{60}$ yielding $^1\text{C}_{60}^*$. Consequentially, the singlet excited $^1\text{C}_{60}^*$ then undergoes intersystem crossing to populate the $^3\text{C}_{60}^*$. Finally, triplet-triplet energy transfer from $^3\text{C}_{60}^*$ to $^3\text{SubPc}^*$ occurs.

Figure 1.53. Differential absorption spectra obtained upon picosecond flash photolysis ($\lambda_{\text{exc}}=532$ nm) of 40 in nitrogen saturated toluene at time delay a) 50 and b) 2500 ps, respectively. Adapted from reference 68a.

The fluorescence lifetimes of 42 on the other, indicates a different fluorescence quenching pathway than the other SubPc-C$_{60}$ dyads since it has the least lifetime values. Time-resolved transient absorption spectra revealed peaks at 685 and 1000 nm corresponding to SubPc•• and C$_{60}$••, respectively, as shown in Figure 1.54. These results suggest electron transfer occurring in 42 and the radical ion pair had a life time of 145 and 101 ns in tetrahydrofuran and o-dichlorobenzene, respectively. Benzonitrile gave a destabilizing trend of the radical ion pair.

The functionalized SubPc-C$_{60}$ dyads 39-42 proved that substitution at the SubPc core does affect the electronic properties of SubPc. The effect could range from singlet-singlet or triplet-triplet energy transfer to electron transfer. In dyad 42, the presence of $N,N$-diphenylamine at the SubPc core not only reduces the HOMO-LUMO gap of the SubPc’s
molecular orbitals as seen from the red-shift of the Q band but it also serves as a charge stabilizing entity in the dyad.

Figure 1.54. Differential absorption spectra obtained upon nanosecond flash photolysis ($\lambda_{exc} =$ 532 nm) of 42 in nitrogen saturated benzonitrile at 50 ns time delay. Adapted from reference 68a.

Subphthalocyanines are proven to have versatile photophysical and electrochemical properties as shown from the different peripheral substituents employed, modulating the visible absorption bands and fluorescence lifetimes of the subphthalocyanine-based antenna-reaction mimics. Its ability to function as an electron donor or acceptor, or even as an antenna system provides great advantages for artificial photosynthetic applications.

1.10 Scope of Present Work

Artificial photosynthesis is one of the answers to solve the global energy crisis and to mitigate the current condition of the earth. Although extensive research has been conducted to improve the artificial photosynthetic systems, there is still a great deal of work that needs to be done. Different strategies have been used for the design and construction of multimodular donor-acceptor photosystems. Modulation of the photophysical and photochemical properties of its components have been investigated through functionalization, employment of various substituents and varying substitution positions.
The goal of the current research is to provide insights into the photophysical and photochemical events occurring in various antenna-reaction center mimics for artificial photosynthetic applications, through characterization and elucidation of photodynamic mechanisms using different well-established analytical methods. The photosystems of interest are based from chlorophyll analogues, specifically zinc- and aluminum(III)-metallated porphyrins, and subphthalocyanines that absorb and capture light energy, and use this energy to initiate electron transfer in the donor-acceptor systems. To maximize the light capturing ability, antenna systems are utilized which excites the electron donors indirectly via photoinduced energy transfer. Stabilization of the charge separated states was obtained by employing secondary electron donors in the design and construction of multimodular donor-acceptor photosystems. Furthermore, the different strategies (i.e., covalent and non-covalent donor-acceptor interaction) used for the construction of artificial photosynthetic systems were also investigated. It is our hope that the results of this research will be used to better understand the photophysical and photochemical events occurring in donor-acceptor photosystems; hence, this knowledge will be used to devise and develop better artificial photosynthetic apparatuses of high quantum efficiency.

Chapter 1 presents the importance of artificial photosynthesis not only to resolve the current and future energy demand but also to mitigate the up and coming global climate change catastrophe if the present condition of the earth is not improved. Moreover, the first chapter provides the important guiding principles about photoinduced energy and electron transfer processes which governs the construction of multimodular donor-acceptor
photosystems. Finally, chapter 1 describes the current donor-acceptor conjugates that have comparable components with the photosystems of interest.

Chapter 2 provides the chemicals used for the synthesis of the multicomponent donor-acceptor photosystems. Furthermore, it also describes the analytical methods and instrumentation used for the characterization and investigation of photodynamic events occurring in the photosystems of interest: zinc and aluminum(III) porphyrin-, and subphthalocyanine-based antenna-reaction center mimics.

Chapter 3 illustrates the importance to antenna systems in maximizing light absorption by the use of BODIPY which upon photoexcitation transfers energy to zinc porphyrin. The significance of secondary electron donors in the stabilization of charge separated states, either via electron migration or hole transfer, is also presented. Furthermore, it also shows the impact of employing multiple secondary electron donors and the length of the linker towards charge transfer; depicted by the direct substitution of one and two ferrocene moieties in the beta position/s of the zinc porphyrin macrocycle, and by the use of two phenyl spacer, respectively.

In chapter 4, the elegant structure of aluminum(III) porphyrin-based photosystems, utilizing the sixth coordination site of the aluminum metal center to afford the vertically positioned multicomponent donor-acceptor systems, are showcased. The length of the spacer between the electron donor and acceptor is varied in order to investigate its effect in the rates of charge separation and charge recombination. Modulation of the porphyrin macrocycle to customize its function is also presented as in the second photosystem where the fluorinated porphyrin is used as an electron acceptor due to its low electron density. Moreover, metalation
of porphyrin with gold(III) render a positive charge on the macrocycle, lowering further its electron density, hence, served as an electron acceptor as well.

Chapter 5 exhibits the novelty of subphthalocyanine-based donor-acceptor systems for artificial photosynthesis. In the first SuPc photosystems, it displays the influence of spacers on the electronic coupling of subphthalocyanine and the phenothiazine secondary electron donors. The coupling of subphthalocyanine and phenothiazine affects the charge stabilization of the radical ion pair which is elaborated in the said chapter. Furthermore, it also demonstrates the effect of thioalkyl substituents in the modulation of the photophysical properties of subphthalocyanine-fullerene dyads towards charge separation and recombination.

Finally, chapter 6 summarizes the results of the aforementioned multimodular antenna-reaction center mimics. Its validity for artificial photosynthetic applications is also evaluated.
CHAPTER 2
MATERIALS AND PHYSICAL METHODS

This chapter provides the list of chemicals and solvents employed at various stages of the research work. Discussion of the general synthetic procedures used for the synthesis of porphyrin, subphthalocyanine, and fulleropyrrolidine derivatives are presented in each respective chapter. The zinc porphyrin, aluminum (III) porphyrin, and subphthalocyanine series of compounds were synthesized by Dr. Eranda Maligaspe, Dr. Prasanth Poddutoori, and Dr. Chandra KC, respectively. Furthermore, a brief description of the analytical methods employed is discussed as well.

2.1 Materials

Buckminsterfullerene, C_{60} (+99.95%) was from SES Research, (Houston, TX). All the reagents were from Aldrich Chemicals (Milwaukee, WI) or Alfa-Aeser, while the bulk solvents utilized in the syntheses were from Fischer Chemicals (Plano, TX). The supporting electrolyte, tetra-n-butylammonium perchlorate, (n-Bu₄N)ClO₄, used in electrochemical studies was from Fluka Chemicals (Ronkonkoma, NY).

2.2 Physical Methods

2.2.1 Spectral Measurements

The UV-visible and near-IR spectral measurements were carried out with a Shimadzu 2550 UV-Vis spectrophotometer or Jasco V-670 spectrophotometer. The steady-state fluorescence emission was monitored by using a Varian (Cary Eclipse) Fluorescence Spectrophotometer or a Horiba Jobin Yvon Nanolog spectrofluorometer equipped with PMT (for UV-visible) and InGaAs (for near-IR) detectors. A right angle detection method was used.
for fluorescence measurements at room temperature. All the solutions were purged prior to spectral measurements using nitrogen gas. The $^1$H NMR studies were carried out on a Bruker 400 MHz spectrometer. Tetramethylsilane (TMS) was used as an internal standard.

2.2.2 Electrochemical Studies

Differential pulse voltammetry were recorded on a Princeton Applied Research potentiostat/galvanostat Model 263A using a three electrode system. A platinum button electrode was used as the working electrode, while a platinum wire served as the counter electrode and an Ag/Ag$^+$ electrode was used as the reference electrode. Ferrocene/ferrocenium redox couple was used as an internal standard. All the solutions were purged prior to electrochemical and spectral measurements with nitrogen gas.

2.2.3 Time-Resolved Fluorescence Emission Spectroscopy

The fluorescence lifetimes were measured with the Time Correlated Single Photon Counting (TCSPC) option with nano-LED excitation sources on the Nanolog. A right angle detection method was used for both steady-state and time-resolved emission measurements at RT. All the solutions were purged prior to spectral measurements by using argon gas.

2.2.4 Transient Absorption Measurements

2.2.4.1 Femtosecond Transient Absorption Spectroscopy

Femtosecond transient absorption spectroscopy experiments were performed using an Ultrafast Femtosecond Laser Source (Libra) by Coherent incorporating diode-pumped, mode locked Ti:Sapphire laser (Vitesse) and diode-pumped intra cavity doubled Nd:YLF laser (Evolution) to generate a compressed laser output of 1.45 W. For optical detection, a Helios transient absorption spectrometer coupled with femtosecond harmonics generator both
provided by Ultrafast Systems LLC was used. The source for the pump and probe pulses were derived from the fundamental output of Libra (Compressed output 1.45 W, pulse width 100 fs) at a repetition rate of 1 kHz. 95% of the fundamental output of the laser was introduced into harmonic generator which produces second and third harmonics of 400 and 267 nm besides the fundamental 800 nm for excitation, while the rest of the output was used for generation of white light continuum. In the present study, the second harmonic 400 nm excitation pump was used in all the experiments. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. Data analysis was performed using Surface Xplorer software supplied by Ultrafast Systems. All measurements were conducted in degassed toluene at 298 K.

2.2.4.2 Nanosecond Laser Flash Photolysis

The studied compounds were excited by a Opolette HE 355 LD pumped by a high energy Nd:YAG laser with second and third harmonics OPO (tuning range 410-2200 nm, pulse repetition rate 20 Hz, pulse length 7 ns) with the powers of 1.0 to 3 mJ per pulse. The transient absorption measurements were performed using a Proteus UV-Vis-NIR flash photolysis spectrometer (Ultrafast Systems, Sarasota, FL) with a fibre optic delivered white probe light and either a fast rise Si photodiode detector covering the 200-1000 nm range or a InGaAs photodiode detector covering 900-1600 nm range. The output from the photodiodes and a photomultiplier tube was recorded with a digitizing Tektronix oscilloscope. Data analysis was performed using Surface Xplorer software supplied by Ultrafast Systems.

2.2.4.3 Transient Electroparamagnetic Resonance Spectroscopy

Transient EPR time/field data sets were recorded in collaboration with Dr. Art van der Est and Dr. Prashanth K. Poddutoori, Brock University using a modified Bruker EPR 200D-SRC X-
band spectrometer (Bruker Canada, Milton ON, Canada). Light excitation at 532 nm was achieved using 10 ns pulses from a Nd:YAG laser at a repetition rate of 10 Hz. EPR samples were prepared by dissolving the porphyrin complex under study in the o-DCB to a concentration of $\sim 10^{-4}$ M. The solutions were purged with N2 and then placed in a sealed flat cell.

2.3 Computational Studies

The computational calculations were performed in collaboration with Dr. Melvin E. Zandler, Wichita State University. These calculations were obtained by B3LYP methods with GAUSSIAN 03 software package. The HOMO and LUMO orbitals were generated using GaussView program.

Other computational studies were conducted in collaboration with Dr. Paul A. Karr, Wayne State College. The geometry and electronic structures of the supramolecular assemblies were predicted by performing DFT calculations using Gaussian 09:ASL64L-G09RevD.01 and all structures were constructed and visualized through GaussView: 5.0.9. The Becke Three Parameter Hybrid Functional utilizing the Lee-Yang-Parr non-local correlation expression (B3LYP) was chosen as the DFT method.
CHAPTER 3

ZINC PORPHYRIN-BASED SELF-ASSEMBLED MULTIMODULAR ANTENNA-REACTION CENTER MIMICS

3.1 A Supramolecular Tetrad Featuring Covalently Linked Ferrocene-Zinc Porphyrin-BODIPY Coordinated to Fullerene: A Charge Stabilizing, Photosynthetic Antenna-Reaction Center Mimic*

3.1.1 Introduction

The ever increasing energy demands, and the rising concern over environmental pollution and climate changes due to burning of fossil fuels\cite{1} have driven researcher to look into renewable forms of energy.\cite{2-4} Towards this, development of artificial photosynthetic systems capable of producing energy by utilizing sunlight is highly desirable since solar energy has the potential to fulfill the worldwide energy needs in an environmentally benevolent manner.\cite{1} Towards this, extensive efforts have been devoted to develop artificial photosynthetic reaction centers, which can mimic both the antenna and reaction center functionalities of natural photosystems.\cite{5-19} Both covalently linked and supramolecularly assembled donor-acceptor systems have been elegantly designed, and occurrence of photoinduced energy and electron transfer leading into the generation of charge separated states have been accomplished. Generally, porphyrins and phthalocyanines as photosensitizing electron donors\cite{20-21} and fullerenes as electron acceptors\cite{22-23} have been primarily employed, while a variety of photo/redox active entities have been utilized as secondary electron donors or energy funneling antenna molecules.\cite{5-19} The presence of secondary electron donors resulted in the generation of long-lived charge-separated states by a sequential electron...

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transfer mechanism while the presence of energy funneling antenna molecules provided better utilization of solar light (broad band capture).

In artificial photosynthesis models, covalently linked ferrocene-zinc porphyrin (such as Fc-ZnP in Scheme 3.1.1), self-assembled to fullerene functionalized with a ligand functionality (such as C$_{60}$Im in Scheme 3.1.1) is a well-known example for charge stabilization via a stepwise electron transfer-hole migration mechanism.$^{[24-25]}$ This is in contrast to simple donor-acceptor dyads, for example C$_{60}$Im:ZnP (see Scheme 3.1.1 for structure of ZnP) where only a single-step photoinduced electron transfer is witnessed upon photoexcitation of ZnP.$^{[26]}$ Interestingly, when ZnP is covalently linked to BODIPY$^{[27]}$ (such as ZnP-BODIPY in Scheme 3.1.1) and coordinated to C$_{60}$Im forms model to visualize antenna-reaction center functionality.$^{[28]}$ That is, in the assembled systems of C$_{60}$Im:ZnP-BODIPY, selective excitation of BODIPY results in efficient singlet-singlet energy transfer to the ZnP entity to produce $^1$ZnP$^*$ within the triad. The $^1$ZnP$^*$ thus produced promoted electron transfer to produce ZnP$^{*+}$:ImC$_{60}$$^-$$^*$-charge separated states.

Scheme 3.1.1. Structure of the newly synthesized Fc-ZnP-BODIPY and the control compounds, investigated in the present study.
In the present study, we have combined the electron transfer-hole shift and antenna-reaction center concepts in a single model compound by covalently linking ferrocene (hole shift entity) and BODIPY (energy transfer entity) to the opposite sides of zinc porphyrin (see Scheme 3.1.1 for structure), and self-assembled $C_{60}$Im to the ZnP center to create a novel artificial photosynthetic system that is capable of utilizing broader spectrum of light (by antenna effect, process 2 in Figure 3.1.1), followed by charge separation (process 3 in Figure 3.1.1), and charge stabilization (via hole shift, process 4 in Figure 3.1.1), as shown in Figure 3.1.1. The outcome of these findings as revealed from the spectral (optical absorbance and emission), electrochemical, computational, and photochemical (from femtosecond and nanosecond transient spectroscopy) studies is reported.

Figure 3.1.1. Proposed photochemical events in the supramolecular Fc-(ZnP:Im$C_{60}$)-BODIPY tetrad featuring a zinc porphyrin (ZnP) as primary electron donor, BODIPY as energy transferring antenna, ferrocene (Fc) as charge stabilizing hole-shift agent, and fullerene (C$_{60}$Im) as terminal electron acceptor. Abbreviations: EnT – excited energy transfer, ET = excited electron transfer, HS – hole shift and CR = charge recombination. The photochemical events are shown as 1, 2, according to their appearance upon selective excitation of the BODIPY entity of the supramolecular assembly.
3.1.2 Results and Discussion

3.1.2.1 Synthesis of Fc-ZnP-BODIPY triad

The synthesis of the Fc-ZnP-BODIPY triad was carried out according to Scheme 3.1.2. The details are given in the experimental section. Briefly, the precursors, 4-ferrocenylaniline (Fc-NH₂) and 1-(difluoroboryl)-2-[(Z)-(3,5-dimethyl-2H-pyrrol-2-ylidene)-(4-aminophenyl)methyl]-3,5-dimethyl-1H-pyrrole (NH₂-BODIPY) and H₂-5,15-Di(p-carboxyphenyl)-10,20-di(p-tolyl) porphyrin (HOOC-H₂P-COOH) were prepared using literature methods^[29] with few minor modifications. Next, acid chloride of HOOC-H₂P-COOH was obtained by treating dicarboxylic acid with SOCl₂ followed by reacting the porphyrin acid chloride with equimolar mixtures of Fc-NH₂ and NH₂-BODIPY in the presence of pyridine as base in toluene to obtain Fc-H₂P-BODIPY, followed by chromatographic purification. The Fc-H₂P-BODIPY thus prepared was metallated using zinc acetate to obtain the Fc-ZnP-BODIPY triad. The syntheses of control compounds, Fc-ZnP and ZnP-BODIPY were also carried out using a similar procedure, but using mono carboxylic acid functionalized free-based porphyrin, followed by zinc insertion. The compounds were stored in dark prior performing spectral and transient measurements.
Scheme 3.1.2. Synthetic methodology adopted for Fc-ZnP-BODIPY triad.

3.1.2.2 Optical Absorption and Fluorescence Studies

Figure 3.1.2a shows the absorbance spectrum of Fc-ZnP-BODIPY triad along with the control compounds in o-dichlorobenzene (o-DCB). The Soret band of ZnP at 425 nm and visible bands at 550 and 590 nm along with BODIPY band at 505 nm were observed. Position of these
bands was not significantly different from the control compounds (shift < ± 2 nm). The absorbance due to ferrocene entity was hidden in the 320 nm band with the ZnP and BODIPY bands in the spectral range. These results indicate little or no intrasupramolecular interactions between the entities of the triad. Importantly, at the wavelength of BODIPY absorption at 505 nm, no significant absorbance of ZnP or Fc was observed. These results point out the possibility of selective excitation of the energy transferring antenna entity, BODIPY, in the supramolecular assembly.\cite{28} Figure 3.1.2b shows the fluorescence spectrum of Fc-ZnP-BODIPY triad along with the control compounds in o-DCB. At the excitation wavelength of 500 nm corresponding to BODIPY absorbance, an emission from $^1$BODIPY* at 520 nm was observed. The control compounds, ZnP and Fc-ZnP revealed no emission in this wavelength range or at the emission wavelengths of ZnP (< 2 % at 605 and 650 nm). Interestingly, for Fc-ZnP-BODIPY triad and ZnP-BODIPY dyad, the BODIPY emission was found to be quenched over 95% of the original intensity accompanied by two news bands at 605 and 650 nm, corresponding to ZnP emission. These results indicate occurrence of singlet-singlet energy transfer from $^1$BODIPY* to ZnP to produce $^1$ZnP*. The energy transfer in ZnP-BODIPY dyad is consistent with our previous studies.\cite{28b} Further, excitation spectrum recorded by holding the emission monochromator to 650 nm corresponding to ZnP emission and scanning the excitation monochromator, revealed peaks not only that of ZnP excitation but also of BODIPY excitation (see Figure 3.1.S1 in the supporting information). These results reveal occurrence of efficient energy transfer in the Fc-ZnP-BODIPY triad and ZnP-BODIPY dyad.
Figure 3.1.2. (a) Absorption and (b) emission spectrum ($\lambda_{\text{exc}} = 500$ nm) of Fc-ZnP-BODIPY, ZnP-BODIPY, BODIPY, Fc-ZnP and ZnP (8 µM each) in N$_2$ saturated o-DCB.

Next supramolecular assembly of Fc-ZnP-BODIPY triad with C$_{60}$Im via metal-ligand axial coordination was studied. Figure 3.1.3a shows spectral changes during the titration of C$_{60}$Im to a solution of Fc-ZnP-BODIPY triad in o-DCB. The observed spectral changes were consistent with ZnP binding to nitrogenous bases.$^{[26]}$ That is, red-shifted Soret and visible bands of ZnP were observed, however, with no changes in the peak maxima of BODIPY suggesting the latter’s lack of interactions with the added C$_{60}$Im in solution. An isosbestic point at 419 nm was also observed indicating the existence of an equilibrium process in solution. The binding constant was obtained by analyzing the data using Benesi-Hildebrand plot,$^{[30]}$ as shown in inset of Figure 3.1.3a. The calculated binding constant ($K$), was found to be $4.5 \times 10^4$ M$^{-1}$ not significantly different from C$_{60}$Im binding to ZnP ($K = 1.2 \times 10^4$ M$^{-1}$), Fc-ZnP ($K = 2.3 \times 10^4$ M$^{-1}$) and ZnP-BODIPY ($K = 3.0 \times 10^4$ M$^{-1}$) in o-DCB.$^{[26a, 25a, 28a]}$ Further, the emission spectrum of the Fc-ZnP-
BODIPY triad was also monitored during the course of the titration. As shown in Figure 3.1.3b, emission bands of both BODIPY and ZnP were found to be quenched. In a control experiment, emission of BODIPY was monitored with increasing addition of C$_{60}$Im where no significant quenching of $^1$BODIPY* was observed. On the other hand, when pristine ZnP was titrated with C$_{60}$Im, efficient quenching of $^1$ZnP* was observed both in $\sigma$-DCB. These results indicate occurrence of additional excited state processes involving the C$_{60}$Im:ZnP segment of the supramolecular tetrad assembly.\textsuperscript{[31]} Changing the solvent to toluene also revealed similar spectral features, however, with slight improved singlet-singlet energy transfer efficiencies.

![Figure 3.1.3](image.png)

Figure 3.1.3. (a) Absorbance and (b) fluorescence spectrum ($\lambda_{exc} = 500$ nm) of Fc-ZnP-BODIPY triad (8 $\mu$M) with increasing addition of C$_{60}$Im (0.2 eq. each) in $\sigma$-DCB.

3.1.2.3 Computational and Electrochemical Studies

The structure of the supramolecular tetrad, Fc-(ZnP:ImC$_{60}$)-BODIPY, was optimized using B3LYP/6-31G* method\textsuperscript{[32]} to visualize its stable geometry. Figure 3.1.4 shows two possible structures, although additional structures are possible due to flexible metal-ligand coordinate
bond which would place the C₆₀lm in different places with respect to the Fc-ZnP-BODIPY geometry. In agreement with our earlier studies,[²⁵a] the most stable structure was found to be the one in which fullerene is close to the ferrocene unit as shown in Figure 3.1.4a. An alternate structure was built and optimized in which the C₆₀lm unit was close to the BODIPY segment. The former structure was slightly stable by 2.56 × 10⁻³ Hartrees. For the optimized structure shown in Figure 3.1.4a, the center-to-center distances (R_{Ct-Ct}) between ZnP-C₆₀, Fc-ZnP and ZnP-BODIPY were 13.0, 16.9, and 18.7 Å while corresponding the edge-to-edge distances were 9.6, 4.3, and 12.3 Å, respectively. The closest distance between ferrocene and C₆₀ entities was about 3.7 Å indicating their close proximity. Such close proximity between the final charge resting entities would facilitate charge recombination (vide infra).

Figure 3.1.4. B3LYP/6-31G* optimized structures of supramolecular tetrad (Fc-(ZnP:ImC₆₀)-BODIPY) assembled by coordinating C₆₀lm to Fc-ZnP-BODIPY triad. Two structures, one in which the C₆₀ is close to ferrocene and another in which the C₆₀ is close BODIPY are shown.

Figure 3.1.5 shows cyclic voltammograms of the Fc-ZnP-BODIPY triad and the tetrad assembled upon coordinating C₆₀lm to Fc-ZnP-BODIPY triad in o-DCB containing 0.1 M
(TBA)ClO₄. The site of electron transfer of the individual redox couples for this rather intricate system involving four redox active entities was deduced from careful control experiments involving pristine Fc, ZnP, BODIPY, Fc-ZnP and ZnP-BODIPY. During the anodic excursion of the potential of the Fc-ZnP-BODIPY triad, an one-electron reversible oxidation of ferrocene located at -0.03 V and first oxidation corresponding to ZnP located at 0.27 V vs. Fc/Fc⁺ were observed. Two additional oxidations located at 0.58 and 0.79 vs. Fc/Fc⁺, corresponding to the second oxidation of ZnP and first oxidation of BODIPY, were also observed (not shown); the latter being an irreversible process. Similarly during cathodic excursion of the potential, two reductions at -1.72 and -1.88 V vs. Fc/Fc⁺ were observed; the former being an overlap of two one-electron processes. By comparison with reduction potentials of control compounds, the first process was ascribed to the overlap of first reductions of BODIPY and ZnP entities while the second process was due to the second reduction of ZnP entity.

![Cyclic voltammograms of Fc-ZnP-BODIPY triad (dashed) and Fc-(ZnP:ImC₆₀)-BODIPY tetrad (solid line) in o-DCB containing 0.1 M (TBA)ClO₄. Scan rate = 100 mV/s.](image)

Figure 3.1.5. Cyclic voltammograms of Fc-ZnP-BODIPY triad (dashed) and Fc-(ZnP:ImC₆₀)-BODIPY tetrad (solid line) in o-DCB containing 0.1 M (TBA)ClO₄. Scan rate = 100 mV/s.

For the Fc-(ZnP:ImC₆₀)-BODIPY tetrad, there was no shift in the oxidation potential corresponding to Fc entity while the first oxidation of ZnP revealed a cathodic shift of 60 mV as
a result of coordination of imidazole entity to the Zn metal center. On the negative side, additional processes corresponding to fullerene reduction were also observed. That is, two one-electron reduction processes, at -1.16 and -1.54 V vs. Fc/Fc⁺ were observed. At higher negative potentials, the ZnP reduction revealed a small anodic shift.

By using the electrochemical, computational, and excited singlet energy data, the free-energies of charge-separation ($\Delta G_{CS}$) were calculated using equations 1 by Rehm-Weller’s approach.[33]

$$\Delta G_{CS} = \Delta E_{0-0} - (E_{ox} - E_{red}) + \Delta G_S$$

where $E_{ox}$ is the first one-electron oxidation potential of the donor porphyrin, $E_{red}$ is the first one-electron reduction potential of the C$_{60}$Im, $\Delta E_{0-0}$ is the energy of the lowest excited state of ZnP (2.04 eV), $\Delta G_S$ refers to the solvation energy, calculated by using the ‘Dielectric Continuum Model’ according to the following equation,

$$\Delta G_s = \frac{e^2}{4\pi\varepsilon_0}[\frac{1}{2R_+} + \frac{1}{2R_-} - \frac{1}{R_{CC}}](1/\varepsilon_0)$$

Values of $R_+ = 4.8$ Å, $R_- = 4.2$ Å, $R_{CC}$ is center-to-center distance from modeling were used. $\varepsilon_0$ and $\varepsilon_s$ refer to vacuum permittivity and dielectric constant of o-DCB, respectively.

Such calculations revealed photoinduced electron transfer from the $^1$ZnP$^*$ to coordinated fullerene to generate Fc-($^{1}$ZnP$^{*}$:ImC$_{60}^{-}$)-BODIPY to be exothermic by $\sim$-0.80 eV while that for the formation of Fc$^+$-(ZnP:ImC$_{60}^{*}$)-BODIPY, the free-energy change was -0.51 eV. Energies corresponding to other states are shown pictorially and discussed in the next section.
3.1.2.4 Energy Level Diagram depicting Excited State Events

Figure 3.1.6 shows the energy level diagram depicting different photochemical processes originating from the singlet excited states of BODIPY and ZnP entities of the tetrad. Although intricate due to the presence of four photo-/redox-active species, it has been possible to identify and dissect key photochemical processes. From the steady-state fluorescence, efficient singlet-singlet energy transfer in Fc-ZnP-BODIPY triad is witnessed similar to that reported earlier for the ZnP-BODIPY dyads.[28] The excited supramolecular tetrad, Fc-(ZnP:ImC60)-1BODIPY*, produced by selective excitation of BODIPY (hv’a) would undergo singlet-singlet energy transfer to produce Fc-(1ZnP*:ImC60)-BODIPY in competition with intersystem crossing (ISC-2) to populate Fc-(ZnP:ImC60)-3BODIPY* or a charge separation process (CS5) to yield Fc-(ZnP**:ImC60)-BODIPY++. The Fc-(1ZnP*:ImC60)-BODIPY produced either as a product of energy transfer from the previous step or by direct excitation of the ZnP Soret or visible bands (hv’a), could undergo one of the following processes: (i) intersystem crossing (ISC-1) to populate Fc-(3ZnP*:ImC60)-BODIPY, (ii) charge separation (CS1) to produce Fc-(ZnP**:ImC60*-)-BODIPY radical ion pair, (iii) charge separation (CS2) to produce Fc-(ZnP**:ImC60)-BODIPY** radical ion pair, or (iv) charge separation (CS3) to produce Fc+--(ZnP**:ImC60)-BODIPY ion pair. Based on energy considerations, formation of Fc-(ZnP**:ImC60*-)-BODIPY radical ion pair through CS1 is the most probable process (shown in thicker arrow). Additionally, the Fc-(ZnP**:ImC60*-)-BODIPY could undergo a hole-shift process (HS) to produce Fc+--(ZnP:ImC60*-)-BODIPY ion pair. Other photochemical events also involve direct excitation of the fullerene entity of the tetrad to form Fc-(ZnP:1ImC60*)-BODIPY which could undergo electron transfer to produce Fc-(ZnP**:ImC60*-)-BODIPY radical ion pair (CS4) in competition with intersystem crossing to
populate $\text{Fc}^-(\text{ZnP}^\cdots:3\text{ImC}_{60}^\cdots)$-BODIPY radical ion-pair. Additionally, $\text{Fc}^+(\text{ZnP}^\cdots:3\text{ImC}_{60}^\cdots)$-BODIPY ion pair produced from CS3 would undergo electron migration (EM) to yield $\text{Fc}^+(\text{ZnP}:\text{ImC}_{60}^\cdots)$-BODIPY ion pair. The $\text{Fc}^+(\text{ZnP}^\cdots:3\text{ImC}_{60}^\cdots)$-BODIPY radical ion-pair, formed either from CS1, CS4 or EM, could undergo a hole shift (HS) to produce $\text{Fc}^+(\text{ZnP}:\text{ImC}_{60}^-)$-BODIPY radial ion pair. Finally, $\text{Fc}^+(\text{ZnP}:\text{ImC}_{60}^-)$-BODIPY and $\text{Fc}^+(\text{ZnP}^\cdots:3\text{ImC}_{60}^-)$-BODIPY radical ion-pairs could return to the ground state through charge recombination (CR1 and CR2). Please note that the energy level diagram in nonpolar toluene would be much different revealing high energy (150 – 200 mV) for the charge separated states due to less energy of solvation. In such a case, occurrence of CS3 could be ruled out as supported by the steady-state measurements (vide supra). Additionally, the energy levels of both $\text{Fc}^+(\text{ZnP}^\cdots:3\text{ImC}_{60}^-)$-BODIPY and $\text{Fc}^+(\text{ZnP}^\cdots:3\text{ImC}_{60}^\cdots)$-BODIPY radical ion-pairs would be higher than that of $\text{Fc}^-(\text{ZnP}^\cdots:3\text{ImC}_{60}^\cdots)$-BODIPY and $\text{Fc}^+(\text{ZnP}^\cdots:3\text{ImC}_{60})$-BODIPY levels in nonpolar toluene. In order to establish these photochemical events in the tetrad, transient absorption measurements using femtosecond and nanosecond pump-probe techniques were performed in o-DCB and toluene, as discussed in the next section.
Figure 3.1.6. Energy level diagram showing the different photochemical events of the supramolecular Fc-(ZnP:ImC60)-BODIPY tetrad after excitation of either the BODIPY (λ_{exc} = 505 nm) or ZnP (λ_{exc} = Soret or visible band) entities in o-DCB. Abbreviations: k stands for different kinetic processes. EnT = excited energy transfer, ET = excited electron transfer, HS – hole shift, EM = electron migration, CS = charge separation, ISC = intersystem crossing, and CR = charge recombination. Thick arrow – most probable process, and thin and dotted arrow – less likely process. Fc-(ZnP:1ImC60*)-BODIPY is abbreviated as 1ImC60* for simplicity.

3.1.2.5 Femtosecond and Nanosecond Transient Absorption Studies

Figure 3.1.7 shows the femtosecond transient spectral changes observed at different time intervals for Fc-ZnP-BODIPY triad in o-DCB and toluene. At the excitation wavelength of 400 nm, due to higher absorption cross section, ZnP was mainly excited as evidenced from the instantaneous population (< 1 ps) of S_{1}-S_{n} transition with a peak maxima in the 460 nm range; similar to that observed for pristine ZnP (Figure 3.1.S2 in the supporting information). In the higher wavelength region, two depleted signals at the 550 and 590 nm range related to the
ground state absorption of the Q-bands were observed. Spectral signature in the 850-900 nm range corresponding to $^1$ZnP* was also observed. A weak signal at 510 nm, corresponding to ground state depletion of excited BODIPY was also observed. Since intensity of this band was much lower than the transient bands of excited ZnP, no singlet-singlet energy transfer that would occur within few ps was monitored. In a control experiment, as shown in Figure 3.1.S3 in the supporting information, at the Soret excitation of the triad, the ZnP Q(0,0) emission located in the 600 nm range was found to be quenched over 55% in o-DCB and 40% in toluene compared to pristine ZnP. Interestingly, this quenching for the Q(0,1) band located in the 650 nm range was almost negligible for the triad in toluene. However, for ZnP-BODIPY this change was less than 10% in both solvents. These results suggest occurrence of one or both of the following processes, at least in polar o-DCB for the triad.

$$\text{Fc}-^1\text{ZnP}^*\text{-BODIPY} \rightarrow \text{Fc}^+\text{-ZnP}^*\text{-BODIPY}$$  \hspace{1cm} (3)

$$\text{Fc}-^1\text{ZnP}^*\text{-BODIPY} \rightarrow \text{Fc-ZnP}^+\text{-BODIPY}^-$$  \hspace{1cm} (4)

The formation of Fc$^+$-ZnP$^+$-BODIPY radical ion-pair would result in new transient band in the 600 nm range corresponding to ZnP$^+$,[25a] while identification of Fc$^+$ would be a difficult task due to its very low molar extinction coefficient.[24] On the other hand, the formation of Fc-ZnP$^{**}$-BODIPY* radical ion-pair would result in a new transient band in the 650-700 nm range corresponding to ZnP$^{**}$,[26] while a positive identification of BODIPY* would be difficult due to lack of diagnostic bands of the radical anion in the monitored spectral range, although, this process is energetically the favored one. Although subtle, a close examination of the transient spectra shown in o-DCB reveals a transient band in the 600 nm range corresponding to the
formation of ZnP*, suggesting reaction 3 could be the quenching mechanism in the Fc-ZnP-BODIPY triad at least in o-DCB at the excitation wavelength.

Figure 3.1.7. Femtosecond transient absorption spectra of Fc-ZnP-BODIPY triad ($\lambda_{exc} = 400$ nm of 100 fs pulse width) at the indicated time intervals in N$_2$ purged (a) o-DCB and (b) toluene solutions.

Figure 3.1.8 shows the femtosecond transient spectra of the Fc-(ZnP:ImC$_{60}$)-BODIPY tetrad in the investigated solvents. In o-DCB, immediately upon excitation, bands in the 460 nm region and 910 nm region corresponding to $S_1$-$S_n$ transitions of ZnP and C$_{60}$Im, respectively (see Figure 3.1.55 in the supporting information) were observed. The decay of the 460 nm was accompanied by the growth of 480 nm band corresponding to $^3$ZnP* within the tetrad. Additionally, transient bands corresponding to the formation of the initial Fc-(ZnP$^+$:ImC$_{60}^-$)-BODIPY radical ion-pair state was clearly witnessed. That is, transient band at 1000 nm corresponding to the formation of ImC$_{60}^-$ and 650 nm corresponding to the formation of ZnP$^{++}$ were observed. However, we could not confirm whether $^1$ZnP* or $^1$ImC$_{60}$* or both of these species are involved in generating the charge separated species. The time constants for the growth of the ImC$_{60}^-$ band were found to be 16.8 ps that resulted into $k_{CS}$ value of $5.95 \times 10^{10}$ s$^{-1}$. Importantly, the decay rate of ZnP$^{++}$ was found to be slightly faster than that of the decay rate of ImC$_{60}^-$ indicating a hole shift to the neighboring ferrocene entity. Further, the decay of
ImC$_{60}$$^\cdot$$^-$ and $^3$ImC$_{60}^\cdot$ transient peaks were accompanied by growth of a new weak band with maxima at 707 nm with a shoulder band at 825 nm, characteristic of triplet fullerene.[10d] Since the energy level of the charge separated state is lower than that of $^3$C$_{60}^\cdot$ in polar $\sigma$-DCB, it is likely that the population of the $^3$C$_{60}^\cdot$ is via intersystem crossing of $^3$ImC$_{60}^\cdot$.

Figure 3.1.8. Femtosecond transient absorption spectra of the Fc-(ZnP:ImC$_{60}$)-BODIPY tetrad ($\lambda_{exc}$ = 400 nm of 100 fs pulse width) at the indicated time intervals in N$_2$ purged (a) $\sigma$-DCB and (b) toluene. Figure c and d show the time profile of the 1000 nm band in $\sigma$-DCB and toluene, respectively.

Interestingly, in toluene different spectral features were observed. That is, peak corresponding to $S_1$-$S_n$ transitions of ZnP was observed in the 460 nm, however, such peak for ImC$_{60}$ in the 900-950 nm region was rather bleak. The decay of the 460 nm peak was accompanied by a growing shoulder band at 485 nm revealing formation of $^3$ZnP$^\cdot$. Importantly, evidence for charge separation was secured by the appearance of transient peaks at 1020 nm corresponding to ImC$_{60}$$^\cdot$$^-$ and 680 nm corresponding to ZnP$^{\cdot\cdot}$. The time constants for the growth of the ImC$_{60}$$^\cdot$$^-$ band were found to be 31.5 ps that resulted into $k_{CS}$ value of $3.17 \times 10^{10}$.
s\(^{-1}\). The decay of the \(\text{ImC}_{60}^{•−}\) band was accompanied by a strong new band in the 700 nm region corresponding to \(3\text{ImC}_{60}^{*}\) formation. As predicted from the earlier discussed energy level diagram, these observations suggest charge recombination results in populating the \(3\text{C}_{60}^{*}\) which might be in competition with a hole shift reaction. Importantly, the part of the signal corresponding to \(\text{ImC}_{60}^{•−}\) persisted beyond 3 ns, the time window of our instrument in both solvents.

![Figure 3.1.9](image)

Figure 3.1.9. Nanosecond transient absorption spectra of the Fc-(ZnP:ImC\(_{60}\))-BODIPY tetrad (\(\lambda_{\text{exc}} = 430\) nm of 7 ns pulse width) at the indicated time intervals in Ar purged (a) o-DCB and (b) toluene. Figures (c) and (d) show the time profile of the 1040 nm band in o-DCB and toluene, respectively.

In order to spectrally identify \(3\text{ZnP}^{*}\) and \(3\text{C}_{60}^{*}\), and to evaluate persistent survival of the \(\text{ImC}_{60}^{•−}\) beyond the 3 ns as a result of hole-shift process or charge separation resulting from the possible \(3\text{ZnP}^{*}\), nanosecond transient absorption spectral studies were performed. As shown in Figure 3.1.9, the triplet states of ZnP and ImC\(_{60}\) were obvious with peaks in the 480 nm corresponding to \(3\text{ZnP}^{*}\) and at 700 nm corresponding to \(3\text{C}_{60}^{*}\). In the near-IR region of 1000
nm, a peak corresponding to ImC₆₀⁻ was also observed. In toluene, the decay of ImC₆₀⁻ peak was monoexponential resulting into a $k_{CR}$ value of $1.44 \times 10^5$ s⁻¹. However, in o-DCB this decay was bi-exponential resulting into $k_{CR}$ values of $2.12 \times 10^5$ s⁻¹ and $6.31 \times 10^4$ s⁻¹, respectively. The biexponential decay in o-DCB could be as a result of different geometries of the tetrad (Figure 3.1.4), or independent contributions from the excited singlet ($^1$ZnP* or $^1$C₆₀*) and triplet ($^3$ZnP*) originated electron transfer which was too close to resolve in toluene. Importantly, persistence of the radical ion-pair for 7-15 µs, depending upon solvent and nature of excited species involved in electron transfer (singlet or triplet), were accomplished indicating charge stabilization as a result of hole-shift in the present multi-modular photosynthetic antenna-reaction center model compound. The $k_{CR}$ values are more than two orders of magnitude lower compared to that reported earlier for Fc-ZnP:ImC₆₀ triads,[26a] revealing better charge stabilization.

3.1.3 Summary

A novel photosynthetic model compound integrating both an antenna (BODIPY) and a secondary electron donor (ferrocene) to the primary donor-acceptor pair (zinc porphyrin-fullerene) was newly synthesized and characterized, and the photochemical events were elucidated as shown in Figure 3.1.1. Systematic spectral, computational and electrochemical studies were performed to evaluate the role of each entity in the photochemical reactions. The energy level diagram, although intricate involving several competitive reactions, helped identifying dominant photochemical events under the experimental conditions. Consequently, selective excitation of BODIPY resulted in efficient energy transfer to the ZnP. The $^1$ZnP* formed either as a result of singlet-singlet energy transfer or direct excitation, and the $^1$ImC₆₀*
from direct excitation, depending upon the solvent conditions, revealed ultrafast electron
transfer to the fullerene entity resulting in Fc-(ZnP**:ImC_{60}**) \text{-} \text{BODIPY} radical ion-pair.
Subsequent hole-shift to the ferrocene entity resulted in Fc\textsuperscript{+}-(ZnP:ImC_{60}**) \text{-} \text{BODIPY} radical ion-
pair with spatially separated radical cation and anion species in competition with populating
the \textsuperscript{3}C_{60}**. Nanosecond transient studies revealed that the radical ion-pair persisted for 7-15 \, \mu s,
depending upon the solvent and the nature of excited state species (singlet or triplet generated
charge separated state) prior to returning to the ground state revealing charge stabilization and
better utilization of solar light by the present model compound.

3.1.4 Supporting Information

Figure 3.1.S1. Excitation spectrum of the Fc-ZnP-BODIPY triad in \text{o-DCB}. The spectrum was
recorded by holding the emission monochromator to 650 nm corresponding to ZnP emission
and scanning the excitation monochromator wavelength.
Figure 3.1.S2. Femtosecond transient spectra of ZnTTP in (a) o-DCB and (b) toluene upon excitation using 400 nm laser.

Figure 3.1.S3. Fluorescence spectrum of ZnP (black line), ZnP-BODIPY (green line), Fc-ZnP-BODIPY (red line) in (a) o-DCB and (b) toluene. The samples were excited at their respective Soret band wavelength position.
Figure 3.1.S4. Femtosecond transient absorption spectra of the ZnP:ImC₆₀ dyad (λₑₓᶜ = 400 nm of 100 fs pulse width) at the indicated time intervals in N₂ purged (a) o-DCB and (b) toluene. Figure c and d show the time profile of the 1000 nm band in o-DCB and toluene, respectively.

Figure 3.1.S5. Femtosecond transient spectra of fullerene, C₆₀ upon excitation using 400 nm laser in toluene.
Figure 3.1.S6. MALDI-mass spectrum of Fc-H$_2$P-BODIPY triad.

Figure 3.1.S7. MALDI-mass spectrum of Fc-ZnP-BODIPY triad.
Figure 3.1.S8. $^1$H-NMR spectrum of (a) Fc-H$_2$P-BODIPY and (b) Fc-ZnP-BODIPY in CDCl$_3$.

Figure 3.1.S9. $^{13}$C-NMR spectrum of Fc-ZnP-BODIPY in CDCl$_3$. 
3.2 Charge Separation in Supramolecular Ferrocene(s)-Zinc Porphyrin-Fullerene Triads: A Femtosecond Transient Absorption Study*

3.2.1 Introduction

Understanding the mechanistic details and evaluation of kinetic information of photoinduced charge separation in artificial photosynthetic donor-acceptor conjugates is important for light energy harvesting, both in terms of efficiency and the cost of production.1-24 Consequently, studies on photoinduced electron transfer in multi-modular molecular and supramolecular donor-acceptor systems have seen a rapid growth in recent years mainly to address the mechanistic details of electron transfer as applicable towards light energy harvesting,25-33 and also, to the development of molecular optoelectronic devices.34 In the construction of such donor-acceptor systems, fullerenes35 and porphyrins36 have traditionally been utilized as constituents owing to their rich and well-understood redox, optical, and photochemical properties. Fullerenes (C_{60} and C_{70}) in donor-acceptor dyads are known to accelerate forward electron transfer (k_CS) and slow down backward electron transfer (k_CR), due to their small reorganization energy in electron transfer reactions.37-38 Consequently, a number of metallotetrapyrrole-fullerene donor-acceptor systems have been synthesized and studied to probe the effect of molecular topology, and distance and orientation effects on the charge separation and recombination processes.1-24

In an effort to further stabilize the charge separated states, recently, elegantly designed multi-modal polyads (viz., triads, tetrads, pentads, etc.) have also been synthesized and studied.1-24 In some of these systems, using photosynthetic reaction center concepts,33 distinctly separated donor-acceptor radical ion pairs are generated upon initial electron

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transfer by charge migration reactions along the well-tuned redox gradients. In these studies, covalently or self-assembled ferrocene-porphyrin-fullerene triads are one of the well-studied polyads.\textsuperscript{39-40} Among the different strategies, one of the designs developed in our laboratory involved utilizing covalently linked ferrocene(s)-zinc porphyrin self-assembled via metal-ligand axial coordination to zinc center (Figure 3.2.1).\textsuperscript{40a} Here, zinc porphyrin was functionalized with one or two ferrocene entities with different spacer units. Also, fulleropyrrolidine having a pyridine or phenylimidazole coordinating ligands was employed as an electron acceptor. The different ligands on fullerene varied the ZnP-fullerene donor-acceptor distance about 2.3 Å. In these triads, it was possible to establish photoinduced electron transfer leading to charge stabilization using time-resolved fluorescence and nanosecond transient studies.

![Figure 3.2.1: Structure of the donors (1 to 4) and acceptors (5 and 6) utilized to form supramolecular dyads (1:5 or 1:6) and triads (binding of 2, 3, or 4 to 5 or 6) via metal-ligand axial coordination of zinc porphyrin. The symbol ‘:’ refers to metal-ligand axial coordination bond.](image-url)
As shown in Scheme 3.2.1, in the triads, the initial electron transfer from the singlet excited zinc porphyrin (\(^1\text{ZnP}^*\)) could involve ferrocene (route 1) or fullerene (route 2) to yield the respective \(\text{Fc}^+\text{-ZnP}^{**}:\text{C}_{60}\) or \(\text{Fc}-\text{ZnP}^{**}\cdot\text{C}_{60}^+\) intermediate radical ion-pair species, respectively. The former would undergo an electron migration to fullerene (route 3) to yield \(\text{Fc}^+\text{-ZnP}:\text{C}_{60}^-\) as the final charge separated species while the latter would undergo a hole shift involving neighboring ferrocene (route 4) to yield the same final charge separated species with distantly separated cation and radical anion species. In our previous work\(^{40a}\) based on steady-state and time-resolved fluorescence studies, we proposed route 1 as the initial step involved in the triads formed by \(\text{2 or 4}\) coordinated to fullerene (\(\text{5 or 6}\)), while route 2 as the initial step involved in the triads formed by \(\text{3}\) coordinated to fullerene (\(\text{5 or 6}\)), but couldn’t offer any spectroscopic evidence to support this claim. In the present study, we have accomplished this task by performing systematic studies using femtosecond transient absorption in toluene, as discussed in the following sections.

![Scheme 3.2.1](image_url)

Scheme 3.2.1. Routes for formation of \(\text{Fc}^+\text{-ZnP}:\text{C}_{60}^+\) charge separated state from \(\text{Fc}^{-1}\text{ZnP}^*\cdot\text{C}_{60}\) in the investigated supramolecular triads.
3.2.2 Results and Discussion

The ferrocene-zinc porphyrin and fulleropyrrolidine derivatives were synthesized according to our previous procedure.\textsuperscript{40a} Purity of these compounds were checked by thin-layer chromatography and were stored in dark to avoid any photodecomposition. Freshly prepared solutions, degassed using argon, were used in spectral investigations.

Figure 3.2.2a shows the normalized absorption spectrum of the porphyrin and fullerene derivatives in toluene. Appended ferrocene had no significant effect on the peak maxima of both Soret and visible bands, however, slight broadening of the spectrum was observed. The spectrum of ImC\textsubscript{60} (6) reveals considerable absorption in the 400 nm region with peak maxima at 324 and 432 nm. Similar spectral features were observed for PyC\textsubscript{60}, 5. This suggests that at the 400 nm excitation wavelength where our femtosecond transient spectrometer operates, both ZnP (about 60-70 \%) and fullerene (about 30-40 \%) are getting excited. Figure 3.2.2b shows the fluorescence spectrum of the porphyrin derivatives, excited at 550 nm corresponding to the visible band. The 0,0 emission band of zinc porphyrin in compound 3 in which the ferrocene and porphyrin are held together by a phenyl amide bond was quenched nearly 40\%, however, in compounds 2 and 4, having direct linkage, the quenching was over 95\% in toluene. As reported earlier,\textsuperscript{40a} in o-dichlorobenzene (DCB), this quenching was over 70\% for 3 and over 98\% for compounds 2 and 4. These results indicate occurrence of efficient excited state events in 2 and 4, and to a lesser extent in 3.

\textsuperscript{40a}
Figure 3.2.2. Normalized absorption and fluorescence spectrum ($\lambda_{\text{exc}} = 550$ nm) of zinc porphyrin, 1 and ferrocene-zinc porphyrin derivatives (2-4) and phenylimidazole functionalized fullerene, 6 in N$_2$ saturated toluene.

The binding of fullerenes, 5 and 6 to zinc porphyrins 1-4 was studied in DCB in which red-shifted Soret and visible bands accompanied by one or more isosbestic points, expected for penta-coordinated zinc porphyrin complex, were observed.$^{41}$ Job’s plots confirmed 1:1 stoichiometry for these dyads. The binding constants, $K$ evaluated by constructing Scatchard plot of the absorbance data, are given in Table 3.2.1. The magnitude of these values suggest moderate level of binding. Generally, $K$ for 6 binding to a given zinc porphyrin is higher than that observed for the binding of 5 to the same zinc porphyrin derivative. Introducing one or
two ferrocene entities on the zinc macrocycle improved the binding by 2-3 times compared to that observed for pristine ZnP binding of 5 or 6.\textsuperscript{40a}

Table 3.2.1. Binding constants for axial coordination of fullerene ligands to ferrocene-zinc porphyrin dyads in DCB at 298 K.

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>K, M(^{-1}) \textsuperscript{,a}</th>
<th>Pyridine</th>
<th>PyC(_{60}), 5</th>
<th>ImC(_{60}), 6</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(7.8 \times 10^3)</td>
<td>(7.2 \times 10^3)</td>
<td>(11.6 \times 10^3)</td>
<td>61e</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>(7.7 \times 10^3)</td>
<td>(26.8 \times 10^3)</td>
<td>(29.6 \times 10^3)</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>(5.3 \times 10^3)</td>
<td>(20.5 \times 10^3)</td>
<td>(22.6 \times 10^3)</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>(5.8 \times 10^3)</td>
<td>(23.4 \times 10^3)</td>
<td>(24.6 \times 10^3)</td>
<td>97</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Error = \(+10\%\).

Table 3.2.2 summarizes the free-energy data for various charge separated states discussed in Scheme 3.2.1 originated from the initial singlet excited state of zinc porphyrin. The electrochemical redox potentials and key geometry factors deduced from B3LYP/3-21G(*) geometry optimization studies of the dyads and triads were adapted from our previous study.\textsuperscript{40a} It may be mentioned here that in the optimized structures, the fullerene entity was closer to the ferrocene entity, perhaps due to the electron deficient and electron rich nature of the respective entities. Consequently, the measured edge-to-edge distance (Table 3.2.2) in most of the cases were within the van der Waals interacting distances. The free-energy calculations were performed according to Rehm-Weller approach\textsuperscript{42} using oxidation potential of the donor and reduction potential of the acceptor, and spectroscopic data, according to the following equation.

\[ \Delta G_{cs}^0 = E_{1/2}(D^{*+}/D) - E_{1/2}(A/A^{*}) - \Delta E_{0-0} \]  \hspace{1cm} (1)
where $E_{1/2}(D^{**}/D)$ is the first one-electron oxidation potential of the donor porphyrin or ferrocene, $E_{1/2}(A/A^\ast)$ is the first one-electron reduction potential of the C$_{60}$ electron acceptor, $\Delta E_{0-0}$ is the energy of the 0-0 transition energy gap between the lowest excited state and the ground state, being 2.04 eV for zinc porphyrin. The solvation energy is omitted in these calculations for simplicity.

Table 3.2.2. Electrochemical half-wave potentials (vs. Fc/Fc') of the Fc-ZnP:C$_{60}$ triads in o-dichlorobenzene, 0.1 M (TBA)ClO$_4$, geometric parameters from B3LYP/3-21G(*) calculations, and free-energy change associated for different radical ion-pairs formation from the initial singlet excited zinc porphyrin (redox potential data and computational distances were taken from Ref. 40a).

<table>
<thead>
<tr>
<th>Compound</th>
<th>ZnP$^{0/+}$</th>
<th>Fc$^{0/+}$</th>
<th>C$_{60}$$^{0/+}$</th>
<th>ZnP$^{0/-}$</th>
<th>R$_{cc}$$^1$</th>
<th>R$_{cc}$$^2$</th>
<th>R$_{ee}$$^1$</th>
<th>$\Delta G_{cs}$$^d$</th>
<th>$\Delta G_{cs}$$^e$</th>
<th>$\Delta G_{HSf}$$^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:6$^c$</td>
<td>0.29</td>
<td>-0.01</td>
<td>-1.10</td>
<td>-1.91</td>
<td>12.3</td>
<td>--</td>
<td>--</td>
<td>-0.12</td>
<td>-0.65</td>
<td>-0.30</td>
</tr>
<tr>
<td>2:6$^c$</td>
<td>0.21</td>
<td>-0.03</td>
<td>-1.17</td>
<td>-1.93</td>
<td>12.1</td>
<td>10.4</td>
<td>2.6</td>
<td>-0.09</td>
<td>-0.66</td>
<td>-0.24</td>
</tr>
<tr>
<td>3:5</td>
<td>0.28</td>
<td>-0.01</td>
<td>-1.14</td>
<td>-1.91</td>
<td>9.98</td>
<td>16.8</td>
<td>3.7</td>
<td>-0.12</td>
<td>-0.62</td>
<td>-0.29</td>
</tr>
<tr>
<td>3:6$^c$</td>
<td>0.27</td>
<td>-0.01</td>
<td>-1.13</td>
<td>-1.91</td>
<td>13.0</td>
<td>16.9</td>
<td>3.8</td>
<td>-0.12</td>
<td>-0.64</td>
<td>-0.28</td>
</tr>
<tr>
<td>4:6$^c$</td>
<td>0.23</td>
<td>-0.01</td>
<td>-1.19</td>
<td>-1.94</td>
<td>13.0</td>
<td>10.5</td>
<td>2.8</td>
<td>-0.10</td>
<td>-0.62</td>
<td>-0.24</td>
</tr>
</tbody>
</table>

- $a$ - center-to-center distance between ZnP and C$_{60}$ entities
- $b$ - center-to-center distance between ZnP and ferrocene entities
- $c$ - edge-to-edge distance (through-space) between ferrocene and fullerene entities
- $d$ - for formation of Fc$^+-$ZnP$^{**}$:C$_{60}$ radical ion-pair from $^1$ZnP$^*$
- $e$ - for formation of Fc-ZnP$^{**}$:C$_{60}$$^\ast$ radical ion-pair from $^1$ZnP$^*$
- $f$ - for formation of Fc$^+-$ZnP:C$_{60}$$^\ast$ from Fc-ZnP$^{**}$:C$_{60}$$^\ast$ radical ion-pair

An energy level diagram revealing the possible photochemical events was constructed by utilizing the calculated energy of each radical ion-pair from Table 3.2.2, and the reported singlet and triplet energies ($E^S = 2.04$ for ZnP and 1.75 eV for C$_{60}$; $E^T = 1.55$ eV for ZnP and 1.50 eV for C$_{60}$) of the sensitizers, as shown in Figure 3.2.3. It is important to note that the
formation of Fc⁺-ZnP⁺:C₆₀ radical ion-pair is only possible from ¹ZnP* \((k_{CS1})\) and not from ¹C₆₀* while formation of Fc-ZnP⁺⁺:C₆₀⁺⁺ radical ion-pair is possible from both ¹ZnP* \((k_{CS2})\) and ¹C₆₀* \((k_{CS3})\) or even from their triplet excited states, ³ZnP* and ³C₆₀* (shown in dashed arrows), resulted after the sensitizers had undergone an intersystem crossing process \((k_{ISC})\). The final charge separated state, Fc⁺⁻-ZnP:C₆₀⁺⁺, could be formed either by an electron migration process involving Fc⁺⁻-ZnP⁺⁺:C₆₀ \((k_{EM})\) or a hole shift process involving Fc-ZnP⁺⁺:C₆₀⁺⁺ \((k_{HS})\). These processes are in competition with Fc⁺⁻-ZnP⁺⁺:C₆₀ and Fc-ZnP⁺⁺:C₆₀⁺⁺ radical ion-pairs relaxing directly to the ground state. In the present donor-acceptor conjugates, singlet-singlet energy transfer from the ¹ZnP* to the ground state C₆₀ is considered to be noncompetitive due to latter’s lack of absorption in the emission region of zinc porphyrin (575-700 nm). A similar argument could be applied for singlet-singlet energy transfer involving ³ZnP* to the ground state ferrocene.

Femtosecond transient absorption studies were performed to unravel electron transfer pathways in these triads. In the present study, photochemically more stable toluene has been used instead of DCB. In such a case, the energy of the various charge separated states would be 100-200 mV higher than that shown in Figure 3.2.3. However, it is important to note that the energy levels of both Fc-ZnP⁺⁺:C₆₀⁺⁺ and Fc⁺⁻-ZnP:C₆₀⁺⁺ would be lower than both ³ZnP* and ³C₆₀*, not affecting the electron transfer path that has been originally established in DCB.
Figure 3.2.3. Energy level diagram showing the different photochemical events of the supramolecular triad composed of ferrocene, zinc porphyrin and fullerene entities ($\lambda_{\text{exc}} = 400$ nm) in DCB. Abbreviations: $k$ stands for different kinetic processes. HS = hole shift, CS = charge separation, ISC = intersystem crossing, and CR = charge recombination. Thick and solid arrows – most probable process, and dashed arrow – less likely process.

Prior performing transient absorption studies, spectroelectrochemical studies were performed to characterize one-electron reduced, and one- and two-electron oxidized products of a ferrocene-zinc porphyrin dyad (2) to help characterizing photochemical electron transfer products. During one-electron oxidation to form $\text{Fc}^+\text{-ZnP}$ (applied potential = 0.63 V vs. Ag/AgCl), no significant changes were observed indicating lack of strong absorption of ferrocenium cation in the visible region. However, during the second electron oxidation (applied potential = 0.90 V vs. Ag/AgCl), the Soret and Q bands of ZnP decreased in intensity with the appearance of new peaks at 374, 414, 448(sh), 610, 667, and 873 nm corresponding to the formation of $\text{Fc}^+\text{-ZnP}^{**}$ species in which the spectral changes in the visible region are mainly of that of ZnP$^{**}$ (Figure 3.2.4a). These spectral changes were found to be reversible with the
appearance of an isosbestic point at 443 nm. Figure 3.2.4b shows the spectral changes associated during one-electron reduction of dyad, 2 at an applied potential of -1.36 V vs. Ag/AgCl. The Soret band located at 425 nm and the Q-band at 550 nm decreased in intensity accompanied by new bands at 314, 440, 514, 576, 619 and 660 nm corresponding to the formation of Fc-ZnP•. Isosbestic points at 433 and 564 nm were observed indicating the existence of only one equilibrium process.

Figure 3.2.4. Spectral changes observed for compound 2 during (a) second oxidation corresponding to the formation of Fc+-ZnP++ and (b) first reduction corresponding to the formation of Fc-ZnP• species in DCB containing 0.2 M (TBA)ClO₄. Please note that first oxidation corresponding to the formation of Fc+-ZnP revealed no significant spectral changes in the monitored spectral window. Figure inset are spectra in the visible region enlarged vertically by a factor of 10.
The overall peak positions and shapes were similar to that reported for radical anion and radical cation of ZnP in literature with some differences due to the presence of directly linked ferrocene and experimental solution conditions.

3.2.2.1 Femtosecond Transient Absorption Studies

First, the probe zinc porphyrin, 1 and the dyads, 2-4 were investigated in toluene using 400 nm laser of 100 fs pulse width. As shown in Figure 3.2.5a, excitation of 1 instantly populated the $S_1$ and $S_2$ states of the porphyrins with maximum in the ~ 447 nm region. At higher wavelength region, a depleted signal in the Q-band region of zinc porphyrin (550 nm), opposite mimic of the ground state absorption of the Q-band was observed. In addition, depleted bands at 590 and 648 nm, corresponding to stimulated emission of zinc porphyrin were also observed. Interestingly, in the near-IR region, an additional peak at 1288 nm was observed. The decay rate of this peak was close to that of excited lifetime of $^1$ZnP* (1.85 ns) suggesting that this peak is indeed due to the singlet excited state of zinc porphyrin. Decay of singlet peaks were accompanied by new peaks at 465 and 845 nm corresponding to the triplet excited state of zinc porphyrin. The spectral features for Fc-ZnP dyad, 2 are shown in Figure 3.2.5b. The instantaneously formed singlet features decayed faster than that observed for the ZnP probe in addition to a new peak at 685 nm at early time scales corresponding to ZnP•-. Also, no clear peak of triplet zinc porphyrin at higher time scales was observed. The time profile of ZnP•- shown in Figure 3.2.5b inset shows the charge separation and recombination processes to be very fast. The measured rate of charge separation, $k_{CS}$, and rate of charge recombination, $k_{CR}$, by analyzing the decay curves, were found to be $7.90 \times 10^{11}$ s$^{-1}$ and $2.67 \times 10^{10}$ s$^{-1}$, respectively.
Figure 3.2.5. Femtosecond transient absorption spectra of (a) 1, (b) 2, (c) 3 and (d) 4 in toluene at the excitation wavelength of 400 nm. Figure inset in b and d shows time profile of the 680 nm peak corresponding to ZnP•-

For dyad 3, in which the zinc porphyrin and ferrocene are held a phenylamide linker, the spectral features resembled close to that of the probe, 1. However, in agreement with the steady-state fluorescence results, the rate of decay of the singlet state monitored at 460 nm was in between that of 1 and 3 (see Figure 3.2.6), suggesting occurrence of slow electron transfer due to increased distance between the ferrocene and porphyrin entities. The spectral features of ZnP•- at 680 nm were rather weak, and under these conditions, $k_{CS}$ and $k_{CR}$ were found to be difficult to establish. As predicted, for compound 4 with two ferrocene entities connected to zinc porphyrin, the transient spectral features were similar to that of dyad 2. That
is, rapid decay of singlet peaks with the appearance of ZnP$^*$ at 680 nm, were observed. The measured $k_{CS}$ and $k_{CR}$ by analyzing the decay of 680 nm peak, were found to be $8.64 \times 10^{11}$ s$^{-1}$ and $3.20 \times 10^{10}$ s$^{-1}$, respectively, slightly higher than that observed in 2 due to the presence of two ferrocene units. It may be mentioned here that the measured $k_{CS}$ values for 2 and 3 were nearly an order of magnitude smaller than that reported by Kubo et. al.$^{46}$ for directly linked ferrocene-zinc porphyrin dyads (no phenyl spacer; ferrocene directly linked to the meso-position) due to close proximity of the entities ($k_{CS} > 10^{12}$ s$^{-1}$).

Figure 3.2.6. Time profile of the 460 nm peak representing decay of zinc porphyrin singlet excited state in pristine zinc porphyrin and ferrocene-zinc porphyrin dyads in toluene.

Femtosecond transient studies of 1:5 and 1:6 dyads is reported in our recent publication where photoinduced electron transfer leading to ZnP$^{**}$:C$_{60}^*$ radical ion-pair was established.$^{41b}$ In this case, it was possible to spectrally characterize both ZnP$^{**}$ in the 660-680 nm range and C$_{60}^*$ in the 1020 nm range. The measured $k_{CS}$ for these dyads by monitoring the growth of C$_{60}^*$ was found to be $7.90 \times 10^9$ s$^{-1}$ and $5.7 \times 10^9$ s$^{-1}$, respectively, for 1:5 and 1:6 dyads. Figure 3.2.7 shows femtosecond transient spectra of 2:5 and 2:6 triads in toluene along with the time profiles of key transient peaks. The spectral features at 1 ps were similar to that observed for
the dyad, 2. That is, the instantly formed singlet ZnP developed the characteristic peak of ZnP• at 680 nm suggesting that the initial charge separation in these triads follow route 1 in Scheme 3.2.1. The time constant for the formation of ZnP• was 1.24 ps for 2:5 and 1.29 ps for 2:6 dyads which resulted a $k_{CS}$ values of $8.06 \times 10^{11}$ s$^{-1}$ and $7.75 \times 10^{11}$ s$^{-1}$, respectively for the 2:5 and 2:6 triads. In addition, there was a broad peak in the 850-910 nm range characteristic of singlet excited fulleropyrrolidine. With time, a new band at 1020 nm characteristic of $C_{60}^{•-}$ radical anion appeared (time constant = 24.4 and 33.68 ps, respectively, for 2:5 and 2:6 triads) while the peak of ZnP•+ radical cation expected at 650 nm range was hidden with other spectral bands in this wavelength region. The rate of electron migration, $k_{EM}$, from the initial ZnP• to $C_{60}$ was found to be $7.65 \times 10^{11}$ s$^{-1}$ and $7.45 \times 10^{11}$ s$^{-1}$, respectively for the 2:5 and 2:6 triads. The $k_{EM}$ rates were found to be higher than the $k_{CS}$ rates reported for 1:5 and 1:6 dyads, being $7.90 \times 10^{9}$ s$^{-1}$ and $5.7 \times 10^{9}$ s$^{-1}$, respectively. The fact that $k_{EM}$ in the triads is faster than $k_{CS}$ in the dyads suggest that electron migration from ZnP• to $C_{60}$ to produce the final charge separated state, Fc$^{•-}$-ZnP:$C_{60}^{•-}$ is the main electron transfer route (process 1 followed by 3 in Scheme 3.2.1) in 2:5 and 2:6 triads. Appearance of a new band at 720 nm corresponding to triplet $C_{60}$ was also observed (see Figure 3.2.7d and h for time profiles). This could be a product of intersystem crossing of $^{1}C_{60}^{•}$ since the energy of Fc-ZnP$^{•+}:C_{60}^{•-}$ radical ion-pair is lower than that of $^{3}C_{60}^{•}$ and $^{3}ZnP^{•}$ states as shown in Figure 3.2.3. As shown in Figure 3.2.7d and h, decay of the fullerene anion radical persisted beyond the 3 ns time window of our instrument.
Figure 3.2.7. Femtosecond transient absorption spectra of (a) 2:5 (0.05 mM each) and (b) 2:6 (0.05 mM each) in toluene at the excitation wavelength of 400 nm. Figures b, c and d show the time profile of the 680, 726 and 1020 nm bands of 2:5. Figures f, g and h show the time profile of the 680, 722 and 1020 nm bands of 2:6.

Figure 3.2.8 shows the transient spectra of the 3:5 and 3:6 triads along with the time profile of key transient bands. Similar to pristine 3, peaks corresponding to $^1\text{ZnP}^*$ decayed at a much slower rate than that observed for pristine 2 or the 2:5 and 2:6 triads. Spectral evidence for the formation of ZnP$^*$ in the 680 nm range was bleak. These observations suggest that process 1 in Scheme 3.2.1 is not the main initial electron transfer route and route 2 could be the predominant one. Importantly, evidence for the formation of charge separated state was obtained with the characteristic peak of C$_{60}^-$ radical anion at 1020 nm. The expected, short-
lived as a result of hole migration to Fc, ZnP** band was overlapped with other bands in the 650-680 nm range. Assuming route 2 is the initial electron transfer step, \( k_{CS} \) values of \( 6.16 \times 10^{10} \text{ s}^{-1} \) and \( 2.83 \times 10^{10} \text{ s}^{-1} \), respectively for the \( 3:5 \) and \( 3:6 \) triads which were slightly higher than that obtained for \( 1:5 \) and \( 1:6 \) dyads. Additionally, \( k_{CS} \) for \( 3:5 \) was higher than that for \( 3:6 \) due to close disposition (see Table 3.2.2 for donor-acceptor distances). A new band in the 720 nm range was also developed with time which was attributed to the formation of \( ^3C_{60}^\ast \) from the initially formed \( ^1C_{60}^\ast \). Additionally, for both of these triads, due to the occurrence of hole shift to Fc to yield final Fc*-ZnP:C\(_{60}\) radical ion-pair, the decay of fullerene radical anion persisted beyond 3 ns as shown in Figure 3.2.8c and f, respectively, for \( 3:5 \) and \( 3:6 \) triads.

![Figure 3.2.8. Femtosecond transient absorption spectra of (a) \( 3:5 \), and (b) \( 3:6 \) in toluene at the excitation wavelength of 400 nm. Figures b and c show the time profile of the 710 and 1020 nm bands of \( 3:5 \). Figures e and f show the time profile of the 723 and 1020 nm bands of \( 3:6 \).]
As shown in Figure 3.2.9, the femtosecond transient spectral features of triads 4:5 and 4:6 were similar to those of corresponding 2:4 and 2:6 triads. That is, the singlet ZnP transient bands decayed with the initial appearance of ZnP$^*$ at 680 nm suggesting route 1 in Scheme 3.2.1 to produce Fc$^+$-ZnP$^*$-C$_{60}$ is the main quenching pathway. By monitoring the growth of this band, $k_{CS}$ values of $7.16 \times 10^{11}$ s$^{-1}$ and $6.54 \times 10^{11}$ s$^{-1}$, respectively, for the 4:5 and 4:6 triads were obtained. The rapid decay of ZnP$^*$ resulted in the appearance of C$_{60}^*$ peak at 1020 nm implying electron migration from the initially formed ZnP$^*$ to C$_{60}$ to produce Fc$^+$-ZnP-C$_{60}$ is the main route. The calculated rate of electron migration, $k_{EM}$, from the initial ZnP$^*$ to C$_{60}$ was found to be $7.38 \times 10^{11}$ s$^{-1}$ and $6.16 \times 10^{11}$ s$^{-1}$, respectively for the 4:5 and 4:6 triads. These values are higher than those obtained for charge separation in the 1:5 and 1:6 dyads at least by an order of magnitude suggesting route 1 followed by route 3 in Scheme 3.2.1 is the main electron transfer path in these triads also. Between 4:5 and 4:6, $k_{EM}$ value was higher for 4:5 due to close disposition of fullerene entity compared to that in 4:6 (see Table 3.2.1 for donor-acceptor distances). Additionally, a new band in the 720 nm range appeared with time which was attributed to the formation of C$_{60}^*$ from the initially formed C$_{60}^*$. Similar to the triads formed by 2 and 3 with 5 and 6, due to the formation of Fc$^+$-ZnP:C$_{60}$ radical ion-pair, the decay of fullerene radical anion persisted beyond 3 ns as shown in Figure 3.2.9c and f, respectively, for 4:5 and 4:6 triads.
Figure 3.2.9. Femtosecond transient absorption spectra of (a) 4:5, and (b) 4:6 in toluene at the excitation wavelength of 400 nm. Figures b, c and d show the time profile of the 680, 710 and 1020 nm bands of 4:5. Figures f, g and h show the time profile of the 685, 710 and 1020 nm bands of 4:6.

3.2.3 Summary

Primary electron transfer from the $^1$ZnP* to either ferrocene or fullerene in the supramolecular Fc-ZnP-C$_{60}$ triads was established from femtosecond transient absorption studies in toluene. As speculated from our previous study, formation of initial Fc$^+$-ZnP$^*$:$^{1}$C$_{60}$ radical ion-pair in the case of closely spaced, covalently linked ferrocene-zinc porphyrin, while formation of initial Fc-ZnP$^*$:$^{1}$C$_{60}$ radical ion-pair in the case of covalently linked ferrocene-zinc porphyrin with higher separation distance, has been established in the present study. These radical ion-pair yielded the final Fc$^+$-ZnP:C$_{60}$$^*$ radical ion-pair either via an electron migration (in
the case of 2:5, 2:6, 4:5 and 4:6 triads) or hole shift (in the case of 3:5 and 3:6 triads). In agreement with our previous study, due to distant separation of cation and radical anion species, the radical ion-pair persisted beyond 3 ns, the time window of our instrument (the final radical ion-pair persisted over 100-200 ns in DCB\textsuperscript{40b}). The present study demonstrates the effect of the distance between ferrocene and zinc porphyrin entities in the supramolecular triads formed by axial coordination of fullerene on the primary and secondary electron transfer events.
CHAPTER 4

ALUMINUM(III) PORPHYRI-BASED AXIALLY SELF-ASSEMBLED
MULTIMODULAR ANTENNA-REACTION CENTER MIMICS

4.1 Axially Assembled Photosynthetic Reaction Center Mimics Composed of Tetrathiafulvalene, Aluminum(III) Porphyrin and Fullerene Entities*

4.1.1 Introduction

In photosynthesis solar energy conversion is achieved by a multi-step electron transfer reaction in which the initial charge separation between chlorophyll and pheophytin (or between two chlorophyll molecules) is stabilized by a series of subsequent electron transfer steps that separate the two unpaired electrons. \(^1-5\) Sequential electron transfer, as found in photosynthetic reaction centers, is a necessary design principle for achieving a high quantum yield of long-lived, light-induced charge separation because the initial electron transfer step must be fast enough to successfully compete with other decay processes that would otherwise lead to dissipation of the absorbed light energy. In a single donor-acceptor pair it is not possible to optimize forward electron transfer without increasing the rate of charge recombination. Thus, further electron transfer steps are required to achieve long-lived charge separation. There are many reports of supramolecular complexes designed to perform light-induced charge separation\(^6-15\) but achieving highly efficient light-induced sequential electron transfer in such systems remains a significant challenge.\(^8,11,16,17\)

Porphyrin (Por) derivatives are commonly used as both optical and redox active components in such complexes\(^18-22\) because their redox potentials and other properties can be easily tuned by changing substituents on the periphery and/or the element in the center of the

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Por ring and because they absorb light over a wide spectral range, which ensures more efficient use of the solar spectrum. A crucial factor in the function of any electron transfer system is the electronic coupling between the donors and acceptors, which depends to a large extent on their spatial arrangement and whether the bonds between them promote exchange coupling. The influence of the length, bonding and conformation of the bridges have been studied in porphyrin-based systems in which the components are linked via bridges to the periphery of the Por ring. However, there are fewer studies of these factors in complexes with the components linked axially via the central element of the Por ring. In the natural reaction centers the chlorophylls are generally bound to the protein via axially ligation, often by histidine, and the axial ligands are important for controlling factors such as the free energy change and electronic coupling that govern electron transfer. For artificial complexes, an added advantage of the axial arrangement is that the placement of the donor and acceptor units on opposite faces of the porphyrin ensures that they are spatially well separated and that unwanted interactions are minimized. This arrangement is difficult to achieve with transition metal porphyrins, which often only allow for coordination of one axial ligand, and attachment of two different ligands via coordination bonds, is difficult to control. Hence, examples of step-wise or cascade electron transfer in such systems remain extremely rare.

The problem of attaching electron transfer components axially can be addressed by using porphyrins that contain main group elements at the center of the porphyrin ring. For example, aluminum(III) porphyrins (AlPors) form axial covalent bonds with alcohols, carboxylic acids and phosphinates resulting a 5-coordinate metal center. Moreover, the high Lewis acidity of Al allows coordination by Lewis bases to form 6-coordinate complexes with the
covalent ligand on one face of the porphyrin and the coordination bond on the opposite face. Recently, we reported examples of supramolecular triads in which a naphthalenediimide (NDI) derivative was attached covalently via an ester linkage and a bridging group to AlPor in the axial position and a tetrathiafulvalene (TTF) derivative was coordinated via a pyridine group to the opposite face of the porphyrin.\textsuperscript{55} Optical and electron paramagnetic resonance (EPR) data showed that excitation of porphyrin leads to sequential, two-step electron transfer to generate the charge separated state TTF\textsuperscript{+}–NDI\textsuperscript{−}. However, the lifetime of the charge separation was short (<10 ns) unless a nematic liquid crystalline solvent was used. This observation suggests that the stabilization of the charge separation is limited by the reorganization energy.

In fullerene (C\textsubscript{60}) derivatives delocalization of the charge over the C\textsubscript{60} dodecahedron stabilizes the unpaired electron and has been shown to result in low reorganization energy.\textsuperscript{56-61} This combination of properties has led to a number of studies of reaction-center mimics based on Por and C\textsubscript{60} conjugates\textsuperscript{11, 16, 62-68} many of which perform sequential electron transfer.\textsuperscript{8, 11, 16, 26-30} We have previously reported on several triads in which C\textsubscript{60} was bound axially to AlPor and a secondary donor ferrocene (Fc) or phenothiazine (PTZ) was placed on the opposite face of the Por from the C\textsubscript{60}.\textsuperscript{45, 46} These complexes undergo sequential electron transfer but the properties of Fc and PTZ are problematic. In the case PTZ the driving force for secondary electron transfer is very low and with Fc, the iron atom of Fc promotes fast recombination.
Here we report a series of new triads, in which the secondary donor is a tetrathiafulvalene (TTF) derivative, with the general formula TTF-Ph$_n$-py$\rightarrow$AlPor-Ph$_m$-C$_{60}$. The structures of the triads are shown in Figure 4.1.1. The optical and magnetic properties of the TTF$^+$ radical cation and C$_{60}$$^-$ radical anion make it possible to easily detect the formation and decay of TTF$^+$-AlPor-C$_{60}$$^-$ by both transient absorption and transient EPR (TREPR) spectroscopy. Using this combination of techniques the kinetics and spin selectivity of the electron transfer and the electronic coupling within the complexes can be evaluated. We have studied the dependence of these properties on the donor-acceptor distance by varying the number of phenyl rings in the bridge between TTF and AlPor, and we show that there is an optimal length.
to the bridging groups for formation and stabilization TTF**-AlPor-C60**. The stabilization of the charge separation by sequential electron transfer is relatively modest increasing the lifetime of C60** from ~40 ns to ~100 ns. However, the transient EPR data indicate that in a magnetic field the back-reaction is strongly spin selective and the triplet lifetime of the secondary radical pair is at least an order of magnitude longer than the singlet lifetime.

4.1.2 Results and Discussion

4.1.2.1 Synthesis

The details of the preparation and characterization of the components of the dyads and triads are given in the supporting information, Schemes S1 and S2. Briefly, the new dyads, AlPor-Ph2-C60 and AlPor-Ph3-C60, were prepared by condensation of tetraphenylporphyrinato-aluminum(III)hydroxide (AlPor-OH) with C60-Ph2-COOH and C60-Ph3-COOH, respectively in quantitative yields, Scheme 4.1.S3. Structural characterization of the newly synthesized dyads was carried out with FAB-MS, NMR and absorption techniques. Synthesis and characterization of dyad AlPor-Ph-C60 and reference porphyrin AlPor-Ph and also pyridine appended tetrathiafulvalene derivatives (TTF-py and TTF-Ph-py) have been reported elsewhere. Scheme 4.1.S4 shows the coordination of TTF-Phn-py (n = 0, 1) with AlPor-Phm-C60 (m = 1, 2, 3) which affords the linear axial triads shown in Figure 4.1.1. Formation of the triads was monitored by NMR, UV-VIS absorption and steady-state fluorescence spectroscopy. Characteristic up field shifts of the pyridine protons in the NMR spectra (see supporting information Figure 4.1.S5 & 4.1.S6) confirm that coordination occurs via the pyridine group.
4.1.2.2 Characterization by UV-Visible Spectroscopy

The UV/vis absorption spectra of the components of the triads measured are shown in Figure 4.1.2a and the data are summarized in Table S1. The AlPor unit absorbs between 375-700 nm with the characteristic intense Soret band at ~415 nm and weak Q-bands at ~550 nm and 580 nm. The functionalized C₆₀ derivatives (C₆₀·Ph₂-COOH, C₆₀·Ph₃-COOH) absorb in the ultra-violet region between 230-375 nm. There are noticeable differences in the ultra-violet region (270-360 nm) of the dyads, where the absorption is predominantly due to the phenyl ring. As expected, the absorbance between 270-360 nm increases as with number of the phenyl rings present in the dyads. The spectrum of the dyad is essentially a superposition of the spectra of the corresponding reference compounds. However, as reported previously and as has been observed in related porphyrin-fullerene complexes, the weak long- wavelength absorbance of AlPor·Ph·C₆₀ is stronger than that of AlPor·Ph, C₆₀·COOMe, a 1:1 mixture of AlPor·Ph and C₆₀·COOMe and dyads with longer bridging groups AlPor·Ph₂·C₆₀ and AlPor·Ph₃·C₆₀ (see Figure 4.1.S3). Overall, the spectra indicate that the porphyrin and fullerene units in AlPor·Phₘ·C₆₀ (ₘ = 1-3) do not interact strongly but the difference at longer wavelength suggests that a weak charge-transfer interaction, which decreases with increasing distance, may exist. The py-appended TTF derivatives, used to construct the self-assembled supramolecular triads, have relatively weak and very broad absorption bands (Figure 4.1.2a inset) at λ = 304 (average of 285 and 323 nm bands) and λ = 432 nm for TTF-py, and at λ = 299 and 427 nm for TTF-Ph-py.
Figure 4.1.2. (a) UV-visible absorption spectra in dichloromethane. AlPor-Ph-C_{60} (purple), AlPor-Ph_{2}-C_{60} (maroon), AlPor-Ph_{3}-C_{60} (green), AlPor-Ph (red) and C_{60}-Ph-COOMe (blue); inset: TTF-py (orange) and TTF-Ph-py (cyan). The porphyrin Q bands and TTF bands were multiplied by factor of 10. (b) Absorption titrations of AlPor-Ph_{2}-C_{60} with TTF-py in o-DCB. The inset shows the Benesi-Hildebrand plot of the absorbance change at 604 nm. Calculated binding constant $K = 1.2 \times 10^3$ M$^{-1}$. (c) Fluorescence spectra of AlPor-Ph (red), AlPor-Ph-C_{60} (purple), AlPor-Ph_{2}-C_{60} (maroon) and AlPor-Ph_{3}-C_{60} (green) in o-DCB. Excitation light wavelength 550 nm. (d) Fluorescence titrations of AlPor-Ph_{2}-C_{60} with TTF-py in o-DCB. The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations. In titrations TTF-py was added up to $1.9 \times 10^{-3}$ M in 10 µl (1.12 $\times$ 10$^{-4}$ M) increments to a 1 ml (6 $\times$ 10$^{-5}$ M) solution of AlPor-Ph_{2}-C_{60}.

Addition of TTF-Ph$_n$-py (n = 0, 1) to a solution of AlPor-Ph$_m$-C$_{60}$ (m = 1-3) results in significant changes in the wavelengths of the porphyrin Q-bands as a result of complex formation. Because the 432 nm band of TTF-Ph$_n$-py and AlPor Soret band at 416 nm overlap,
the Q-bands were used to monitor the titrations, see Figure 4.1.2b and Figures S7, S8, S10, S12, S13. The observed shifts in the porphyrin bands are typical of axial coordination of nitrogen ligands to AlPors and confirm the formation of supramolecular triads in the solutions. Similar absorption changes were observed from controlled titration experiments, i.e. py vs AlPor-Phm-C60 (m= 1-3), py vs AlPor-Ph and TTF-Phn-py (n= 0, 1) vs AlPor-Ph, see supporting information Figures S9, S11, S14-S17. Figure 4.1.2b shows an absorbance titration of TTF-py against AlPor-Ph2-C60 from which a Benesi-Hildebrand plot (Figure 4.1.2b inset) can be constructed to obtain the binding constant. A value of $\sim(1.0-1.5) \times 10^3 \text{ M}^{-1}$ is obtained for all of the complexes (Table S1).

Figure 4.1.3. (a-f) Optimized structures of TTF-Phn-py→AlPor-Phm-C60 (n = 0, 1 and m = 1, 2, 3). (g – k) Show the molecular electrostatic potential map (MEP), LUMO+3, HOMO-1, HOMO and LUMO of TTF-Ph-py→AlPor-Ph-C60.
4.1.2.3 DFT Calculations

Further, the geometry and electronic structures of the supramolecular assemblies were predicted by performing Density Functional Theory (DFT) calculations using the B3LYP functional and the 6-311G(d, p) (for H, N, C and O) and 6-311G(df) (Al and S) basis sets using Gaussian 09. Figure 4.1.3a-f shows optimized structures on a Born- Oppenheimer potential energy surface of the triads, TTF-Phn-py→AlPor-Phm-C_{60} and the molecular electrostatic potential map revealing electron rich and deficient sites of the triad and the LUMO+3, HOMO-1, HOMO and LUMO are shown in Figure 4.1.3h-k (see Figures S19 - S21). These orbitals are localized on the AlPor, TTF and C_{60} entities, respectively as expected. The calculated distances between the components of the triads (Table 4.1.1) show that the center-to-center distance between TTF and C_{60} increases from 20.36 Å, with n = 0 and m = 1 to 33.34 Å, with n = 1 and m = 3. The optimized structures also provide the radii of AlPor, TTF and C_{60} units, which are found to be 7.77 Å, 5.47 Å and 4.52 Å respectively.

Table 4.1.1. B3LYP/6-311G(d, p) (for H, N, C and O) and 6-311G(df) (Al and S) optimized edge-to-edge and center-to-center distances for the investigated series of dyads and triads.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Edge-to-edge distance, Å</th>
<th>Center-to-center distance, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlPor-Ph-C_{60}^{a}</td>
<td>9.65</td>
<td>11.73</td>
</tr>
<tr>
<td>TTF-py→AlPor-Ph-C_{60}^{b}</td>
<td>14.18</td>
<td>20.36</td>
</tr>
<tr>
<td>TTF-Ph-py→AlPor-Ph-C_{60}^{b}</td>
<td>18.02</td>
<td>24.22</td>
</tr>
<tr>
<td>AlPor-Ph_{2}-C_{60}^{a}</td>
<td>11.96</td>
<td>15.38</td>
</tr>
<tr>
<td>TTF-py→AlPor-Ph_{2}-C_{60}^{b}</td>
<td>17.90</td>
<td>24.13</td>
</tr>
<tr>
<td>TTF-Ph-py→AlPor-Ph_{2}-C_{60}^{b}</td>
<td>21.22</td>
<td>27.96</td>
</tr>
<tr>
<td>AlPor-Ph_{3}-C_{60}^{a}</td>
<td>16.42</td>
<td>19.87</td>
</tr>
<tr>
<td>TTF-py→AlPor-Ph_{3}-C_{60}^{b}</td>
<td>22.64</td>
<td>29.17</td>
</tr>
<tr>
<td>TTF-Ph-py→AlPor-Ph_{3}-C_{60}^{b}</td>
<td>26.66</td>
<td>33.34</td>
</tr>
</tbody>
</table>

^{a}Distance between AlPor and C_{60}. Edge-to-edge distance for dyad is measured from the nearest C_{60} carbon to Al center. ^{b}Distance between TTF and C_{60}. TTF center is measured from the middle of C=C double bond. Edge-to-edge distance for triad is measured from the nearest C_{60} carbon to the nearest TTF carbon.
4.1.2.4 Energy Level Diagram

The driving force for possible intramolecular electron transfer processes can be estimated using the optical data and redox potentials of the components of the triads. The redox potentials were determined from differential pulse voltammetry measurements in o-DCB with 0.1 M TBAP as the supporting electrolyte. Figure 4.1.S22 shows the differential pulse voltammograms and the corresponding potentials are summarized in Table S1. The values given in Table S1 are relative to ferrocene, which has an oxidation potential of 0.74 V versus Ag wire in o-DCB with 0.1 M TBAP as the electrolyte in our experimental conditions. As seen in Table S1, the potentials of the first oxidation of TTF (~0.7 V), the first oxidation of AlPor (~1.1 V) and the first reduction of C_{60} (~−0.44 V) do not vary significantly in any of the dyads, triads or reference compounds. Hence, as expected no significant perturbation of the molecular orbitals involved in the redox reactions occurs when the dyads and triads are formed. The energy level diagram derived from these data is shown in Figure 4.1.4. The energies of the lowest excited singlet state (E_s) and triplet state (E_t) of C_{60} have been taken from the literature. The singlet and triplet state energies of AlPor have been calculated from its optical absorption and emission spectra, see Figure 4.1.S23. The energies of the radical ion pair states are estimated using the Weller equation:

\[ E_{CS} = e\left[E_{1/2}(D^*/D) - E_{1/2}(A/A^-)\right] + G_s \]

where \( E_{1/2}(D^*/D) \) is the first oxidation potential of the donor, \( E_{1/2}(A/A^-) \) is the first reduction potential of the acceptor. \( G_s \) is ion-pair stabilization and incorporates both the solvent-dependent Coulomb energy change upon ion-pair formation or recombination and the free energy of solvation of the ions,
\[ G_S = \frac{e^2}{(4\pi\varepsilon_0)} \left[ \frac{1}{(R_+)} + \frac{1}{(R_-)} - \frac{1}{R_{D-A}} \right] \frac{1}{\varepsilon_S} - \left( \frac{1}{(2R_+)} + \frac{1}{(2R_-)} \right) \frac{1}{\varepsilon_R} \]

where \( R_+ \), \( R_- \) and \( R_{D-A} \) are donor radius, acceptor radius and center-to-center distance between donor and acceptor, respectively. \( \varepsilon_S \) is the dielectric constant of solvent used for photophysical studies (2.38 and 9.93 for toluene and \( \sigma \)-DCB, respectively). \( \varepsilon_R \) is the dielectric constant of solvent used for measuring the redox potentials, in this case \( \sigma \)-DCB. Note that the assumption of spherical charge distributions on the donor and acceptor and other limitations restrict the accuracy of the estimated energies to at best \( \pm 0.1 \) eV.

Figure 4.1.4. Energy level diagram illustrating the major photophysical processes in newly constructed dyads and triads in \( \sigma \)-DCB.

In the case of TTF-py→AlPor-Ph and TTF-Ph-py→AlPor-Ph, electron transfer from TTF to the excited singlet state of AlPor is exothermic with an estimated free energy change of approximately \(-0.43\) eV (see Figure 4.1.4). However, whether this process can compete with intersystem crossing in the porphyrin depends on the activation barrier to electron transfer. Because the energy of the lowest excited triplet state of AlPor is lower than our estimate of the
charge-separated state energy, triplet electron transfer is probably not feasible in TTF-py→AlPor-Ph and TTF-Ph-py→AlPor-Ph. In the TTF-Phₙ-py→AlPor-Phₘ-C₆₀ (n = 0, 1 and m = 1-3) triads, the sequential electron transfer reactions TTF⁻¹AlPor*-C₆₀→TTF-AlPor*-C₆₀−→TTF*-AlPor-C₆₀− and TTF⁻¹AlPor*-C₆₀→TTF*-AlPor*-C₆₀−→TTF*-AlPor-C₆₀− are both energetically possible. Triplet electron transfer from ³AlPor* to C₆₀ is also energetically favourable but donation from TTF to ³AlPor* is not. Downhill triplet recombination is only feasible from TTF*-AlPor*. With toluene as the solvent, the radical ion-pairs are found to be higher in energy than in o-DCB (Figure 4.1.S24) and the sequential electron transfer reactions remain exergonic. However, all of the calculated charge-separated states are higher in energy than the lowest excited triplet state of AlPor and C₆₀ entities, which increases the possibility of triplet recombination.

4.1.2.5 Fluorescence Spectroscopy

Figure 4.1.2c shows the fluorescence spectra of the dyads, AlPor-Ph-C₆₀, AlPor-Ph₂-C₆₀ and AlPor-Ph₃-C₆₀, and their reference monomer, AlPor-Ph in o-DCB. As discussed previously,⁴⁵,⁴⁶ the fluorescence of AlPor is quenched (80%) in AlPor-Ph-C₆₀ as a result of electron transfer from the excited singlet state (¹AlPor*) to C₆₀. In the case of AlPor-Ph₂-C₆₀ and AlPor-Ph₃-C₆₀, the AlPor fluorescence is also quenched but the quenching (66% and 50%, respectively) is lower than observed with AlPor-Ph-C₆₀. This suggests that the extra phenyl rings between the AlPor and C₆₀ units decrease the electron transfer rate. As shown in the inset in Figure 4.1.2c, the 720 nm band due to fullerene fluorescence is very weak, hence little if any, energy transfer from ¹AlPor* to C₆₀ occurs.
Titration of AlPor-Ph with TTF-py in o-DCB, to form the dyad: TTF-py→AlPor-Ph also results in quenching of the AlPor fluorescence (Figure 4.1.S15). To distinguish intramolecular and intermolecular quenching processes and to investigate possible quenching mechanisms several control experiments were carried out. When AlPor-Ph is titrated with TTF lacking the pyridine group so that it cannot coordinate to AlPor, no change in the fluorescence spectrum is observed (see Figure 4.1.S18). Similarly, titration of AlPor-Ph (Figure 4.1.S17) with pyridine leads primarily to a red shift of the fluorescence bands with little change in intensity. Therefore, both the pyridine and TTF parts of the ligands are required to induce quenching of the fluorescence. From this, we conclude that an intramolecular process that causes radiationless decay of the porphyrin excited state occurs when the pyridine appended TTF unit binds to AlPor. Since the spectral overlap between AlPor emission and TTF absorption is weak, energy transfer from AlPor to TTF can be ruled out as an effective quenching mechanism. Hence, electron transfer (hole transfer) from TTF to $^1$AlPor* is proposed to be responsible for the quenching of AlPor fluorescence. The corresponding titration of AlPor-Ph with TTF-Ph-py to form TTF-Ph-py→AlPor-Ph (Figure 4.1.S16) shows behavior that is intermediate between that in the titrations with pyridine and TTF-py. A clear red shift of the emission is observed, which is accompanied by some quenching. This implies that the phenyl group in the TTF unit slows the electron transfer as would be expected.

Upon addition of TTF-Ph$_n$-py ($n = 0, 1$) to the dyad (AlPor-Ph$_m$-C$_{60}$, $m = 1$-3), the fluorescence changes as a result of the formation of the supramolecular triads. Figure 4.1.2d shows the decrease in AlPor fluorescence with addition of TTF-py to AlPor-Ph$_2$-C$_{60}$ and formation of triad TTF-py→AlPor-Ph$_2$-C$_{60}$. The decrease in fluorescence suggests that the rate
of the proposed hole transfer from TTF to $^1$AlPor* is similar to or greater than the electron transfer rate to the $C_{60}$ unit. Corresponding titrations for the other triads are shown in the supplementary information: TTF-py $\rightarrow$ AlPor-Ph-C$_{60}$ (Figure 4.1.S7), TTF-Ph-py $\rightarrow$ AlPor-Ph-C$_{60}$ (Figure 4.1.S8), TTF-Ph-py $\rightarrow$ AlPor-Ph$_2$-C$_{60}$ (Figure 4.1.S10), TTF-py $\rightarrow$ AlPor-Ph$_3$-C$_{60}$ (Figure 4.1.S12) and TTF-Ph-py $\rightarrow$ AlPor-Ph$_3$-C$_{60}$ (Figure 4.1.S13). The observed fluorescence changes in these triads can be explained by two factors: (1) hole transfer from TTF to AlPor and (2) changes in the intrinsic fluorescence rates as a result of structural changes when py coordinates to Al. It is not possible to distinguish these two effects with certainty. However, a band shift and increase of the fluorescence is indicative of changes in the intrinsic fluorescence properties, whereas the proposed hole transfer from TTF is expected to quench the fluorescence. In all cases, the titrations with TTF-Ph-py (Figures S8, S10 and S13) show primarily a red shift of the fluorescence, while those with TTF-py (Figures 2d, S7 and S12) show quenching.

4.1.2.6 Femtosecond Transient Absorption Studies (fs-TA)

Femtosecond (400 nm of 100 fs pulse width) pump-probe spectral studies were performed to confirm that photoinduced electron transfer occurs in the covalently linked dyads, AlPor-Ph$_{m}$-C$_{60}$, $m = 1$ - 3), and subsequent supramolecular triads, TTF-Ph$_{n}$-py $\rightarrow$ AlPor-Ph$_{m}$-C$_{60}$ ($n = 0, 1$ and $m = 1$ - 3) and to investigate the kinetics of the light-induced processes. The studies were performed in both toluene and $o$-DCB. Although charge separation between TTF and $C_{60}$ was clearly observed in both solvents, only the femtosecond pump-probe data obtained in toluene are discussed here. Formation of TTF$^{**}$ and $C_{60}^{**}$ is known to give absorbance increases in the range of 440-600 nm and 1000-1200 nm and weaker absorbance changes at 550-600 nm while formation $^3C_{60}^*$ results in a strong peak at 700-720 nm. The
triplet state of AlPor has a strong maximum at 500 nm and a weaker peak at 820 nm, while the small absorption changes due to AlPor** are anticipated in the 600 - 650 nm region. First, the features of fs transient absorption data of the reference compound AlPor-Ph were investigated. As shown in Figure 4.1.S25, upon excitation, a broad absorption increase with a maximum at ~450 nm and a long tail stretching into the near IR is observed. Superimposed on the absorption increase are negative bands at 550 nm due to loss of the Q-band absorbance and at 590 and 650 nm due to emission from the S1 state. The absorbance increase and Q-band bleach are formed instantaneously as a result of the S0 → Sn transition. A kinetic phase with a lifetime of about 25 ps is then observed in the decay of the absorbance increase and the rise of the S1 emission bands as the Sn state relaxes to the S1 state. The decay of these bands is beyond the 3 ns time window of our instrument in accordance with the 7.88 ns lifetime of the S1 state determined by time correlated single photon counting (TCSPC) fluorescence measurements in toluene (Figure 4.1.S26). There is a shoulder at 487 at late times, which we tentatively assign to 3AlPor*-Ph. Importantly, in the near-IR region, a peak at 1240 nm with the same decay profile as the singlet excited state is observed, suggesting that this peak corresponds to excited singlet state absorption (See Figure 4.1.S25b for time profiles). Such near-IR peaks corresponding to singlet-singlet transition have also been reported for other porphyrin derivatives. Next, the transient spectral features of AlPor-Phm-C60, m = 1 - 3, were investigated (Figure 4.1.5a and b). Several features of the data provide evidence for the occurrence of photoinduced electron transfer from the 1AlPor* to C60. First, the absorption peak at ~450 nm and the near-IR peak at 1240 nm, and the negative peaks due to S1 emission at 590 and 650 nm decay more rapidly than in AlPor-Ph (see Figure 4.1.5d). The 1AlPor* decay is accompanied by a new band in the
1020 nm region corresponding to the formation of C$_{60}^\cdot$. In addition, broad absorbance in the
875-950 nm region was also observed indicating formation of $^1$C$_{60}^*$ either by direct excitation or
energy transfer from $^1$AlPor$^\ast$. The formation of AlPor$^\ast$, expected to result in an absorption
increase in the 600-650 nm region, was also observed, although overlapped with other peaks in
this wavelength region. The fact that the 1020 nm peak of C$_{60}^\cdot$ and 1240 nm peak of $^1$AlPor$^\ast$
are far from other transient bands allows them to be used to estimate the lifetimes of charge
separation $\tau_{CS}$ and charge recombination, $\tau_{CR}$. The time traces obtained at these wavelengths
are shown in Figure 4.1.5c and d, respectively. As can be seen in Figure 4.1.5c, the rise time of
the absorbance increase is clearly resolved allowing $\tau_{CS}$ to be determined, from which the rate
of charge separation, $k_{CS}$ can be calculated. The lifetime of the decay of the absorbance
increase due to $^1$AlPor$^\ast$ at 1240 nm can also be used to calculate $k_{CS}$ ($k_{CS} = 1/\tau_{dyad} - 1/\tau_{ref}$; where
$\tau_{ref}$ is the lifetime of $^1$AlPor$^\ast$-Ph being 7.88 ns in toluene), (see Figure 4.1.6d). The $k_{CS}$ measured
using these two approaches agree well, within the experimental error. However, the decay of
C$_{60}^\cdot$ is multiexponential with components that are longer than the 3 ns limit of the instrument
(Figure 4.1.5c) which hampers the determination of $\tau_{CR}$. The decay of the C$_{60}^\cdot$ peak correlates
with the decay of the Q-band bleaching at 550 nm showing that it corresponds to charge
recombination to the ground state. In addition, a new absorption increase band is observed at
700 nm corresponding to the formation of $^3$C$_{60}^\ast$. This band could be formed by charge
recombination and/or by direct excitation and relaxation of C$_{60}$. The rise of the 700 nm band
does not correlate directly with the decay of the 1000 nm band thus the $^3$C$_{60}^\ast$ state is probably
populated by intersystem crossing. The values of $\tau_{CS}$ measured in toluene are presented in
Table 4.1.2. As can be seen, the electron transfer to C$_{60}$ occurs with a lifetime >100 ps and
becomes slower as the length of the bridge to the porphyrin become longer, i.e. AlPor-Ph$_3$-C$_{60}$ > AlPor-Ph$_2$-C$_{60}$ > AlPor-Ph-C$_{60}$. The rate constants, $k_{CS}$, for the formation of AlPor$^{+}\cdot$C$_{60}$$^{-}\cdot$ in toluene are also given in Table 4.1.2. These data show that, as expected, the rate of electron transfer in the dyads become slower as the distance between the donor and acceptor increase.

Figure 4.1.5. Femtosecond transient absorption spectra of (a) AlPor-Ph-C$_{60}$ and (b) AlPor-Ph$_2$-C$_{60}$ in toluene at the indicated time intervals. (c) The time profile of the 1000 nm radical anion peak of C$_{60}$ for (i) AlPor-Ph-C$_{60}$, and (ii) AlPor-Ph$_2$-C$_{60}$. (d) Normalized to the peak maxima decay of the 1240 nm peak of (i) AlPor-Ph, (ii) AlPor-Ph$_3$-C$_{60}$, (iii) AlPor-Ph$_2$-C$_{60}$, and (iv) AlPor-Ph-C$_{60}$.

The supramolecular triads, TTF-Ph$_n$-py$\rightarrow$AlPor-Ph$_m$-C$_{60}$, formed by coordinating TTF-Ph$_n$-py to AlPor-Ph$_m$-C$_{60}$ show evidence of sequential electron transfer (Figure 4.1.6, Table 4.1.2). First, as seen from the decay profiles of C$_{60}$$^{+}\cdot$ at 1020 nm, the radical ion-pairs persisted beyond the 3 ns time limit of the spectrometer. The absorption increase band between 450 and 500 nm becomes broader, suggesting the presence of the TTF$^{+}\cdot$ radical cation, which shows a peak at 480 nm when formed by electrochemical oxidation of TTF.$^{55}$ Additionally, the broad peak of
AlPor** in the 600 nm range vanishes upon addition of TTF-py suggesting occurrence of a hole shift process (See Figure 4.1.S27). Interestingly, the $k_{CS}$ measured by monitoring the time profile of the near-IR peaks revealed faster charge separation than observed in the corresponding AlPor-Phm-C$_{60}$ dyads (see Figure 4.1.6c-e for time profiles and Table 4.1.2). For each series of triads with the same AlPor-C$_{60}$ bridge, the TTF-py adduct had the highest rate of charge separation, i.e. the following trend was observed: AlPor-Ph$_{m}$-C$_{60}$ < TTF-py→AlPor-Ph$_{m}$-C$_{60}$ > TTF-Ph-py→AlPor-Ph$_{m}$-C$_{60}$ (Table 4.1.2). Additionally, in the case of AlPor-Ph$_{m}$-C$_{60}$ dyads, charge recombination results in population of $^3$C$_{60}$* in toluene likely due to contributions from $^1$C$_{60}$* generated either by direct excitation or energy transfer from $^1$AlPor*.

Figure 4.1.6. Femtosecond transient absorption spectra of (a) TTF-py→AlPor-Ph$_2$-C$_{60}$ and (b) TTF-Ph-py→AlPor-Ph$_2$-C$_{60}$ in toluene. The normalized to the peak maxima time profiles of the 1240 nm peak of $^1$AlPor* for the investigated AlPor-Ph-C$_{60}$, AlPor-Ph$_2$-C$_{60}$, and AlPor-Ph$_3$-C$_{60}$ dyads (black) in the presence of TTF-py (red) and TTF-Ph-py (blue) to form triads are shown in Figures c, d, and e, respectively. Note that the 1240 nm peak is too noisy due to rapid decay, for that reason only decay fit curves are shown.
Table 4.1.2. Charge separation and recombination lifetimes from *fs*- and *ns*-transient absorption and TREPR data. Parameters used to simulate the TREPR data.

<table>
<thead>
<tr>
<th>Sample</th>
<th><em>fs-TA</em>&lt;sup&gt;a&lt;/sup&gt;</th>
<th><em>ns-TA</em>&lt;sup&gt;c&lt;/sup&gt;</th>
<th>TREPR&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>τ&lt;sub&gt;CS&lt;/sub&gt; (ps)</td>
<td>k&lt;sub&gt;CS&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt; (×10&lt;sup&gt;9&lt;/sup&gt; s&lt;sup&gt;−1&lt;/sup&gt;)</td>
<td>τ&lt;sub&gt;CR&lt;/sub&gt; (ns)</td>
</tr>
<tr>
<td>AlPor-Ph-C&lt;sub&gt;60&lt;/sub&gt;</td>
<td>152</td>
<td>6.45</td>
<td>38</td>
</tr>
<tr>
<td>TTF-py→AlPor-Ph-C&lt;sub&gt;60&lt;/sub&gt;</td>
<td>100</td>
<td>9.87</td>
<td>64</td>
</tr>
<tr>
<td>TTF-Ph-py→AlPor-Ph-C&lt;sub&gt;60&lt;/sub&gt;</td>
<td>144</td>
<td>6.80</td>
<td>96</td>
</tr>
<tr>
<td>AlPor-Ph&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;60&lt;/sub&gt;</td>
<td>664</td>
<td>1.38</td>
<td>-</td>
</tr>
<tr>
<td>TTF-py→AlPor-Ph&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;60&lt;/sub&gt;</td>
<td>220</td>
<td>4.42</td>
<td>-</td>
</tr>
<tr>
<td>TTF-Ph-py→AlPor-Ph&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;60&lt;/sub&gt;</td>
<td>315</td>
<td>3.05</td>
<td>-</td>
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<tr>
<td>AlPor-Ph&lt;sub&gt;3&lt;/sub&gt;-C&lt;sub&gt;60&lt;/sub&gt;</td>
<td>1620</td>
<td>0.49</td>
<td>-</td>
</tr>
<tr>
<td>TTF-py→AlPor-Ph&lt;sub&gt;3&lt;/sub&gt;-C&lt;sub&gt;60&lt;/sub&gt;</td>
<td>196</td>
<td>4.97</td>
<td>-</td>
</tr>
<tr>
<td>TTF-Ph-py→AlPor-Ph&lt;sub&gt;3&lt;/sub&gt;-C&lt;sub&gt;60&lt;/sub&gt;</td>
<td>330</td>
<td>2.91</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup>In Ar-saturated toluene. <sup>b</sup>k<sub>CS</sub> = 1/τ<sub>dyad</sub> − 1/τ<sub>ref</sub>, where τ<sub>ref</sub> is the lifetime of 1<sup>1</sup>AlPor* being 7.88 ns in toluene, here the τ values are decay constants of the 1240 nm peak corresponding to singlet-singlet transition of AlPor. <sup>c</sup>In Ar-saturated o-DCB. τ<sub>S</sub> and τ<sub>T</sub> are the singlet and triplet recombination lifetimes, respectively.

As can be seen in Figures 5 and 6, the decay of the absorbance change at 1000 nm extends beyond the 3 ns limit of the *fs* transient absorption setup. Thus, we have also carried out nanosecond transient absorption measurements to study the long-lived charge separation.

4.1.2.7 Nanosecond Transient Absorption Spectroscopy (ns-TA)

Figure 4.1.7 shows the nanosecond transient absorption difference spectra of the triad, TTF-py→AlPor-Ph-C<sub>60</sub> measured in Ar-saturated o-DCB solution at room temperature using 532-nm laser light to excite mainly the porphyrin unit. The characteristic peak due to C<sub>60</sub>•− is clearly

164
visible at 1020 nm. The time profile at 1020 nm for TTF-py→AlPor-Ph-C₆₀, shown as an inset in Figure 4.1.8, decays to zero within about 400 ns and a fit of the transient yields a first-order rate constant of $1.57 \times 10^7$ s$^{-1}$ for the decay of C₆₀•−. The same decay constant is also observed in the decay trace at 470 nm, where the absorbance increase due to TTF•+ is expected. A slightly lower rate of $1.0 \times 10^7$ s$^{-1}$ is obtained from the corresponding traces for TTF-Ph-py→ AlPor-Ph-C₆₀, Figure 4.1.828. These rate constants are smaller by a factor of about three than the corresponding rate constant of $3 \times 10^7$ s$^{-1}$ obtained for py→ AlPor-Ph-C₆₀ and AlPor-Ph-C₆₀$^{45, 46}$ and suggest that the initial charge separation (AlPor•+•-C₆₀•−) is followed by a hole-shift from AlPor•+ to TTF to give the final charge-separated states, TTF•+-py→ AlPor-Ph-C₆₀•− and TTF•+-Ph-py→ AlPor-Ph-C₆₀•− in the two triads. These states are sufficiently long lived that they are detectable by transient EPR, which allows the spin selectivity of the electron transfer to be studied.

Figure 4.1.7. (a) Nanosecond transient absorption spectra of 0.1 mM TTF-py→AlPor-Ph-C₆₀ observed by 532 nm (ca. 3 mJ/pulse) laser irradiation in o-DCB. Inset: Absorption time profile at 1020 nm. (b) Absorption time profile at 470 nm.
4.1.2.8 Time-Resolved EPR Spectroscopy (TREPR)

Figure 4.1.8 shows the room temperature spin-polarized EPR spectra of four of the triads in o-DCB at two different times after the laser flash. The spectra on the left of the figure were extracted from the full dataset in a time window centered at 75 ns after the laser flash and those on the right are at 550 ns. Positive peaks represent absorption (A) and negative peaks are in emission (E). The spectrum of TTF-py→AlPor-Ph-C₆₀ at early time (Figure 4.1.8, top left) is the narrow A/E pattern typical of a moderately strongly coupled radical pair with predominant population of the T₀ level. The absorptive shoulder on the right hand end of the spectrum is due to a molecular triplet state, probably 3C₆₀*. The other three triads all show the E/A/E/A pattern of a weakly coupled radical pair. The low-field E/A doublet has a g-value of 2.0084 can be assigned to transitions associated with the TTF⁺⁺ radical cation, while the high-field doublet has a g-value of 2.0006 and is from the C₆₀* radical anion. As expected the splitting of the doublets decreases as the distance between the two radicals increases. The linewidths of the peaks associated with C₆₀* are expected to be narrower than those of TTF⁺⁺ because of the lack of unresolved hyperfine couplings in the fullerene. This effect is clearly seen in the spectrum of TTF-Ph-py→AlPor-Ph₂-C₆₀ (Figure 4.1.8, bottom left). For the other triads, mixing of the spin states and/or a distribution of values for the spin-spin coupling results in broader lines and roughly the same width for all four peaks. At later times the polarization patterns all become weaker and invert as a result of spin-selective recombination from the states with singlet character. This leaves population only in the two states (T⁺ and T⁻) with pure triplet character. This evolution of the population distribution is illustrated in the top of Figure 4.1.9. In the bottom part of Figure 4.1.9, transients from the four triads taken at the field
position of the maximum absorptive TTF** signal are shown. The singlet recombination of the radical pair leads to inversion of the signal from absorptive at early time to emissive at late time. The decay of the emissive polarization is due to a combination of spin relaxation and triplet recombination. The four transients in Figure 4.1.9 have been fitted with a kinetic model, which yields the singlet recombination lifetimes shown in Table 4.1.2 and as can be seen in the table these lifetimes agrees well with those obtained from the ns transient absorbance measurements. The fact that the decay of the late signal is roughly the same in all of the samples suggests that it is primarily due to spin relaxation.

Figure 4.1.8. Room temperature spin-polarized transient EPR spectra of the TTF-Phn-py→AlPor-Phm-C60 triads. The spectra on the right and left have been extracted from the time/field data sets in time windows centered at 75 and 550 ns, respectively. The black traces are experimental spectra, and the red traces are simulations. The details of the simulations are given in the text.
The spin polarization patterns of light-induced radical pairs such as those in Figure 4.1.8 are determined by the population distribution of the spin states and they depend on the nature of the precursor to the radical pair. For a precursor in a pure singlet state, each radical has two peaks of equal intensity and opposite polarization. The sign of the polarization $E/A$ or $A/E$ depends on the sign of the spin-spin coupling. If the precursor has triplet character one of the two lines for each radical will be stronger, i.e. the radical will acquire net polarization. Such triplet character can arise either from mixing of the $S$ and $T_0$ during the lifetime of a radical pair precursor, or if the electron transfer is initiated from an excited triplet state. The red lines in the Figure 4.1.9 are simulations in which it has been assumed that the spin states are populated according to a mixture of their singlet and triplet characters. For the early spectra the amount of these two contributions varies and sign of the triplet-character contribution indicates predominant population of $T_0$. For the late spectra the singlet contribution is zero and the sign of the triplet character correspond to population of only $T_+ \text{ and } T_-$. A contribution from the spectrum of the C$_{60}$ triplet state is also included as an absorptive Gaussian lineshape. The exchange coupling and weighting factors of the singlet and triplet contributions used in the simulations are given in Table 4.1.2. As can be seen, the exchange coupling between the radicals decreases as the distance between the two electrons increases. The coupling is expected to follow the relationship $J = J_0 \exp(-\beta(r-r_0))$. From a plot of $\ln(J)$ versus $r$ (Figure 4.1.10a) we obtain a value of $\beta = 0.36 \pm 0.07\text{Å}^{-1}$. This value is within error the same as that obtained for $p$-phenylene bridged biradicals$^{83}$ and porphyrins.$^{84}$ In contrast, $p$-phenyleneethynylene-bridged C$_{60}$−TTF dyads$^{85}$ and thiophene-bridged radicals$^{83}$ have values of $\beta$ that are about a factor of two smaller. If the back reaction occurs by a superexchange
mechanism then the rate should follow the same distance dependence as the exchange coupling, i.e. \( k = k_0 \exp(-\beta(r-r_0)) \). As shown in Figure 4.1.10b, a plot of \( \ln k \) vs \( r \) is linear but the distance dependence of the recombination is much weaker. Weak distance dependence of electron transfer rates is often given as evidence for an incoherent hopping mechanism.\textsuperscript{25} However, for the back reaction observed here, such a mechanism is unlikely because it would involve uphill electron transfer. Thus, the distance dependence of the back reaction does not appear to be governed by the superexchange mechanism but is difficult to rationalize in terms of a hopping mechanism.

For the two triads TTF-py\( \rightarrow \)AlPor-Ph\(_3\)-C\(_{60}\) and TTF-Ph-py\( \rightarrow \)AlPor-Ph\(_3\)-C\(_{60}\) transient EPR signals were not detectable at room temperature in o-DCB, while the shorter triads gave the spectra shown in Figure 4.1.8. The distance dependence of the exchange coupling provides a possible explanation of why this is so. From the plot in Figure 4.1.10a we estimate values of 0.05 and 0.01 mT for the exchange coupling in TTF-py\( \rightarrow \)AlPor-Ph\(_3\)-C\(_{60}\) and TTF-Ph-py\( \rightarrow \)AlPor-Ph\(_3\)-C\(_{60}\), respectively, based on the predicted distances between the radicals. The antiphase doublets of a weakly coupled radical pair arise from the overlap of two oppositely polarized, inhomogeneously broadened lines. The intensity of the spectrum is determined by the overlap of the two lines. If the inhomogeneous linewidth is larger than the spin-spin coupling the degree of overlap and the intensity are proportional to the spin-spin coupling.\textsuperscript{86} Thus, the intensity of the spectra for the two longest triads should be roughly one half and one tenth as intense as that of TTF-Ph-py\( \rightarrow \)AlPor-Ph\(_2\)-C\(_{60}\). Such a reduction in intensity would render the signals very weak but nonetheless detectable. Hence we can surmise that there is probably also some reduction in the quantum yield of TTF\(^{**-}\)-C\(_{60}\)^{•}.
The initial singlet character of the TTF$^{**} \text{C}_{60}^{**}$ radical pair shown in Table 4.1.2 also provides insight into the spin selectivity of the electron transfer. As can be seen the singlet character increases as the distance between the two radicals increases. This is not expected since the lifetime of the primary radical pair should increase and hence greater singlet-triplet mixing should occur as the bridge length increases. However, the fs-transient absorbance data show that a significant amount of singlet charge recombination to the ground state occurs on the timescale of $\sim 1$ ns. The singlet character of the transient EPR can be rationalized as the
result of a decrease in the relative amount of this recombination as the bridge length is increased. Finally, the relative intensity of the late signal is a measure of the fraction of electron transfer originating from either $^3\text{AlPor}$ or $^3\text{C}_{60}$. As can be seen in Table 4.1.2, this fraction is small and does not depend strongly on the structure of the triad.

![Graphs](image)

Figure 4.1.10. Distance dependence of the exchange coupling and back reaction rate. (a) exchange coupling from the simulations of the TREPR spectra. (b) back reaction rate from nanosecond transient absorbance and singlet recombination rate from TREPR data.

4.1.3 Conclusions

The data presented here show that the use of the main group element Al in the porphyrin provides a convenient way of constructing donor acceptor triads. The small reorganization energy of $\text{C}_{60}$ leads to a significant increase in the stability of the final radical pair state compared to similar triads with naphthalenediimide as the acceptor. The data also illustrate the complementary nature of optical and TREPR measurements and the importance of the spin selectively of the electron transfer. The weak distance dependence of the back reaction of the
final radical pair and the significant levels of singlet recombination in the primary radical pair both suggest that further improvement of the yield and stability of the charge separation may be attainable by optimization of the bridge.

4.1.4 Supporting Information

Synthesis

General. All chemicals, solvents and chromatographic materials were obtained from Aldrich Chemicals and were used as received. Anhydrous o-dichlorobenzene (o-DCB) from Aldrich was used for all spectroscopic studies. The supporting electrolyte, tetra-n-butylammoniumperchlorate (TBAP), for the electrochemistry studies was obtained from Fluka Chemicals. The preparation of the AlPor-Ph-C₆₀ dyad and its reference compounds AlPor-Ph and C₆₀-Ph-COOMe have been previously reported.¹,² Note that the AlPor-Ph-C₆₀ dyad was labeled as AlPor-C₆₀ in our previous paper. The ¹H NMR data for AlPor-Ph-C₆₀ (300 MHz, CDCl₃): δ, ppm 9.05 (s, 8H), 8.14 (d, 8H, J = 6.9 Hz), 7.74 (m, 12H), 6.88 (bs, 2H), 5.21 (d, 2H, J = 8.1 Hz), 4.74 (d, 1H, J = 9.6 Hz), 4.45 (s, chiral center, 1H), 4.00 (d, 1H, J = 9.6 Hz), 2.39 (s, 3H). Synthesis of pyridine appended tetrathiafulvalene derivatives (TTF-py and TTF-Ph-py) were reported elsewhere.³

Scheme 4.1.S1. Synthesis of C₆₀-Ph₂-COOH. Reaction conditions: (i) 2M Na₂CO₃, Pd(PPh₃)₄, DMF, stir at 110°C for 12 h under N₂ (ii) 1M HCl and (iii) Toluene, reflux for 5 h under N₂.
Preparation of OHC-Ph2-COOH. A mixture of 4-bromobenzoic acid (1.12 g, 5.60 mmol), 4-formylbenzeneboronic acid (1.00 g, 6.70 mmol) and Pd(PPh3)4 (320 mg, 5 mol%) in DMF (40 mL) was added 2M Na2CO3 (8.2 mL, 16.4 mmol). The mixture was heated at 110°C under nitrogen atmosphere. After 12 h the reaction mixture was cooled and the obtained solid was filtered and washed with MeOH (10 mL). Collected filtrate was evaporated to dryness. The residue was added MeOH:H2O (= 50:10 mL) and acidified with 1M HCl (6 mL). The resulting precipitate was collected, water washed and air-dried. The white solid was washed with chloroform to get the OHC-Ph2-COOH in a pure form. Yield: 1.20 g (94%). 1H NMR (300 MHz, (CD3)2SO): δ ppm 13.08 (bs, 1H), 10.10 (s, 1H), 8.07 (d, 2H, J = 8.3 Hz), 8.04 (d, 2H, J = 8.5 Hz), 7.98 (d, 2H, J = 8.3 Hz), 7.91 (d, 2H, J = 8.5 Hz). ESI MS: m/z 225 [M−1]+ for C14H10O3.

Preparation of C60-Ph2-COOH. A mixture of C60 (100 mg, 0.14 mmol), sarcosine (26 mg, 0.28 mmol) and OHC-Ph2-COOH (64 mg, 0.28 mmol) in dry toluene (100 mL) was refluxed under nitrogen for 5 h. After reaction time toluene was evaporated and obtained crude product was purified by silica gel column chromatography. The column was eluted with toluene:ethylacetate (= 80:20) and collected the unreacted C60 as a first band then desired compound as a second band. The solvent was evaporated to get the pure compound as a brown solid. Yield: 40 mg (30%). 1H NMR (300 MHz, CDCl3): δ ppm 8.15 (d, 2H, J = 7.7 Hz), 7.94 (d, 2H, J = 7.7 Hz), 7.75 (d, 4H, J = 8.2 Hz), 5.06 (d, 1H, J = 10.0 Hz), 5.02 (s, 1H), 4.34 (d, 1H, J = 10.0 Hz), 2.87 (s, 3H). FAB MS: m/z 974 [M]+ for C76H15NO2.

Preparation of Br-Ph2-CHO. To a solution of p-iodobromobenzene (1.20 g, 4.2 mmol) in toluene (10 mL) was added a catalytic amount of Pd(PPh3)4 (320 mg, 5 mol%) and aqueous 2M Na2CO3 (3 mL, 6 mmol). To this a solution of 4-formylbenzeneboronic acid (1.0 g, 6.6 mmol) in ethanol
(10 mL) was added, and the mixture was refluxed for 4 h under nitrogen atmosphere. After cooling, the mixture is extracted three times with dichloromethane and the combined organic phases were washed with water, brine and dried over Na₂SO₄ and the solvent was removed. The residue is purified by silica gel chromatography using dichloromethane:hexane (= 90:10) as eluent, giving the pure compound. Yield: 0.70 g (64%). ¹H NMR (300 MHz, CDCl₃): δ ppm 10.09 (s, 1H), 7.98 (d, 2H, J = 8.7 Hz), 7.74 (d, 2H, J = 8.7 Hz), 7.64 (d, 2H, J = 8.4 Hz), 7.52 (d, 2H, J = 8.4 Hz). FAB MS: m/z 261 [M]⁺ for C₁₃H₉BrO.

Scheme 4.1.S2. Synthesis of C₆₀-Ph₃-COOH. Reaction conditions: (i) 2M Na₂CO₃, Pd(PPh₃)₄, toluene/ethanol, reflux for 4 h under N₂ (ii) KMnO₄, aq. Na₂CO₃, acetone, reflux for 3 h, (iii) Con. HCl, (iv) 2M Na₂CO₃, Pd(PPh₃)₄, DMF, stir at 110°C for 5 h under N₂ (v) 1M HCl and (vi) Toluene, reflux for 9 h under N₂.

Preparation of Br-Ph₂-COOH. To a solution of Br-Ph₂-CHO (350 mg, 1.34 mmol) in 2M Na₂CO₃ (2 mL) and acetone (15 mL) was added aqueous KMnO₄ (245 mg in 4 mL of water). The resulting solution was refluxed for 3 h. After cooling, solution was filtered and washed with acetone and
water mixture. Collected filtrate was acidified (pH = 4-5) with concentrated hydrochloric acid and obtained precipitate was collected, washed with water and air-dried. The solid was washed with hexane to get the desired compound in a pure form. Yield: 300 mg (80%). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) ppm 8.18 (d, 2H, \(J = 8.3\)), 7.68 (d, 2H, \(J = 8.3\ Hz\)), 7.63 (d, 2H, \(J = 8.6\ Hz\)), 7.52 (d, 2H, \(J = 8.6\ Hz\)). FAB MS: \(m/z\) 277 [M]+ for C\(_{13}\)H\(_9\)BrO\(_2\).

Preparation of OHC-Ph\(_3\)-COOH. To a suspension of Br-Ph\(_2\)-COOH (372 mg, 1.34 mmol), OHC-Ph-B(OH)\(_2\) (241 mg, 1.60 mmol) and Pd(PPh\(_3\))\(_4\) (77 mg, 5 mol%) in DMF (15 mL) was added 2M Na\(_2\)CO\(_3\) (2 mL, 4.2 mmol). The mixture was heated at 110 °C for 5 h. After cooling, the solid material was filtered and washed with MeOH (10 mL), and the filtrate was evaporated to dryness. To the residue was added MeOH:H\(_2\)O (= 50:10 mL), and the solution was acidified (pH = 4-5) with 1M HCl. The resulting precipitate was collected, washed with water and methanol and air-dried to get the desired compound. Yield: 202 mg (50%). \(^1\)H NMR (300 MHz, CDCl\(_3\)+drops of CD\(_3\)OD): \(\delta\) ppm 10.03 (s, 1H), 8.13 (d, 2H, \(J = 7.4\ Hz\)), 7.97 (d, 2H, \(J = 8.2\ Hz\)), 7.80 (d, 2H, \(J = 7.4\ Hz\)), 7.74 (s, 4H), 7.71 (d, 2H, \(J = 8.2\ Hz\)). EI MS: \(m/z\) 302 [M]+ for C\(_{20}\)H\(_{14}\)O\(_3\).

Preparation of C\(_{60}\)-Ph\(_3\)-COOH. A mixture of C\(_{60}\) (78 mg, 0.11 mmol), sarcosine (20 mg, 0.22 mmol) and OHC-Ph\(_3\)-COOH (66 mg, 0.22 mmol) in dry toluene (100 mL) was refluxed under nitrogen for 9 h. After reaction time toluene was evaporated and obtained crude product was purified by silica gel column chromatography. The column was eluted with toluene:ethylacetate (= 80:20) and collected the unreacted C\(_{60}\) as a first band then desired compound as a second band. The solvent was evaporated to get the pure compound as a brown solid. Yield: 20 mg (17%). \(^1\)H NMR (300 MHz, CDCl\(_3\)+drops of CD\(_3\)OD): \(\delta\) ppm 8.10 (d, 2H, \(J = 7.8\ Hz\)), 7.88 (bs, 2H),
7.69 (m, 8H), 5.01 (d, 1H, J = 9.6 Hz), 5.00 (s, 1H), 4.28 (d, 1H, J = 9.6 Hz), 2.84 (s, 3H). FAB MS: m/z 1050 [M]+ for C$_{82}$H$_{19}$NO$_2$.

Preparation of AlPor-Ph$_2$-C$_{60}$. Solution of AlPor-OH (30 mg, 0.046 mmol) and C$_{60}$-Ph$_2$-COOH (46 mg, 0.047 mmol) were dissolved in 10 ml of dry toluene, the resulting solution was stirred at 80°C for 17 h. Solvent was evaporated and washed with hexane yields the desired product in a pure form. The obtained pure compound was stored in a CaCl$_2$ desiccator. Yield: 70 mg (95%).$^1$H NMR (300 MHz, CDCl$_3$): $\delta$, ppm 9.07 (s, 8H), 8.14 (d, 8H, J = 6.6 Hz), 7.73 (m, 16H), 6.69 (d, 2H$_b$, J = 8.1 Hz), 5.14 (d, 2H$_a$, J = 8.1 Hz), 4.93 (d, 1H, J = 9.3 Hz), 4.85 (s, 1H), 4.20 (d, 1H, J = 9.9 Hz), 2.73 (s, 3H). FAB MS: m/z 1611.30 [M]+, Calcd. 1611.3154 for C$_{120}$H$_{42}$AlN$_5$O$_2$.

Scheme 4.1.53. Synthesis of axial aluminum(III)porphyrin-fullerene dyads. Reaction conditions: (i) Toluene, stirring at 60-80°C for 12 h under nitrogen.

Preparation of AlPor-Ph$_3$-C$_{60}$. Solution of AlPor-OH (30 mg, 0.046 mmol) and C$_{60}$-Ph$_3$-COOH (49 mg, 0.047 mmol) were dissolved in 10 ml of dry toluene, the resulting solution was stirred at 80°C for 17 h. Solvent was evaporated and wash with hexane yields the desired product in pure form. The obtained pure compound was stored in a CaCl$_2$ desiccator. Yield: 74 mg (96%).$^1$H NMR (300 MHz, CDCl$_3$): $\delta$, ppm 9.10 (s, 8H), 8.18 (d, 8H, J = 6.0 Hz), 7.77 (m, 16H), 7.63 (d, 2H, J
= 9.0 Hz), 7.54 (d, 2H, J = 9.0 Hz), 6.72 (d, 2H, J = 9.0 Hz), 5.21 (d, 2H, J = 9.0 Hz), 4.99 (d, 1H, J = 9.0 Hz), 4.95 (s, 1H), 4.27 (d, 1H, J = 9.0 Hz), 2.83 (s, 3H). FAB MS: m/z 1687 [M]+ for C_{126}H_{46}AlN_{5}O_{2}.

Figure 4.1.S1. $^1$H (top) and $^1$H-$^1$H COSY (bottom) NMR spectra (300 MHz) of AlPor-Ph$_2$-C$_{60}$ in CDCl$_3$. 

177
Figure 4.1.S2. $^1$H (top) and $^1$H-$^1$H COSY (bottom) NMR spectra (300 MHz) of AlPor-Ph$_3$-C$_{60}$ in CDCl$_3$. 

178
Figure 4.1.S3. UV-visible absorption spectra of 0.1 mM solutions of AlPor-Ph-C₆₀ (purple), AlPor-Ph₂-C₆₀ (maroon), AlPor-Ph₃-C₆₀ (green), AlPor-Ph (red), C₆₀COOMe (blue) and 1:1 mixture (magenta) of AlPor-Ph and C₆₀COOMe in dichloromethane. Inset: Magnified spectra between 650-850 nm.

Formation of supramolecular triads (TTF-Phₙ-py→AlPor-Phₘ-C₆₀). The triads shown in Scheme 4.1.S4 were assembled from the components, AlPor-Phₘ-C₆₀ and TTF-Phₙ-py, shown in Figure 4.1.S4.

Figure 4.1.S4. Structural information of investigated reference compound (AlPor-Ph), dyads and pyridine appended TTF derivatives (TTF-py and TTF-Ph-py).
Scheme 4.1. Self-assembly of supramolecular TTF-Phₙ-py→AlPor-Phₘ-C₆₀ triads.

NMR Spectroscopy. Figure 4.1.5, shows the ¹H NMR spectrum of a 1:1 mixture of AlPor-Ph-C₆₀ and TTF-Ph-py (top) along with the individual spectra of AlPor-Ph-C₆₀ (middle) and TTF-Ph-py (bottom). In the coordination complex, shielding due to the porphyrin ring causes an upfield shift of the TTF-Ph-py protons on the pyridine unit (c and d) as well as bridging phenyl moiety (e and f). The magnitude of the shift depends on the distance of the protons from the porphyrin ring and the pyridinyl protons (c and d) display the greatest shift indicating that coordination occurs via the pyridinyl group. Small shift was observed for TTF protons g and h suggests TTF unit is away from porphyrin ring. On the benzoate bridging group to the fullerene, the protons (a) closest to the porphyrin ring show an increased upfield shift upon coordination, suggesting
that the Al center lies out of the porphyrin plane in AlPor-Ph-C$_{60}$ and is pulled into the plane when TTF-Ph-py coordinates. Similar $^1$H NMR titrations were carried out for triad TTF-py→AlPor-Ph-C$_{60}$ and results shown shielding effects for py and TTF protons, Figure 4.1.S6. Overall, the NMR titrations confirm the formation of triads TTF-py→AlPor-Ph-C$_{60}$ and TTF-Ph-py→AlPor-Ph-C$_{60}$.

Figure 4.1.S5. $^1$H NMR (300 MHz) spectra of 2.3 mM solutions of TTF-Ph-py (bottom), AlPor-Ph-C$_{60}$ (middle) and TTF-Ph-py→AlPor-Ph-C$_{60}$ (top) in CDCl$_3$.

Figure 4.1.S6. $^1$H NMR spectrum (300 MHz) of 2.9 mM TTF-py→AlPor-Ph-C$_{60}$ in CDCl$_3$. 
Table 4.1.5.1. Optical and electrochemistry data of investigated triads, dyads and their reference compounds.

<table>
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<tr>
<th>Sample</th>
<th>Binding Constant (M$^{-1}$)</th>
<th>Absorption$^a$$^b$ $\lambda_{max}$ nm (log $\varepsilon$)</th>
<th>Potential (V) vs Fc$^b$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>AlPor-Ph-C$_60$</td>
<td>-</td>
<td>256 (5.06), 307 (4.68), 416 (5.72)</td>
<td>1.10</td>
<td>-0.44, -0.83, -1.00, -1.39</td>
</tr>
<tr>
<td>TTF-py$\rightarrow$AlPor-Ph-C$_60$</td>
<td>1248</td>
<td>-</td>
<td>0.68, 1.02, 1.11</td>
<td>-0.44, -0.82, -1.00, -1.39</td>
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<tr>
<td>TTF-Ph-py$\rightarrow$AlPor-Ph-C$_60$</td>
<td>1217</td>
<td>-</td>
<td>0.71, 1.07</td>
<td>-0.42, -0.82, -1.00, -1.37</td>
</tr>
<tr>
<td>py$\rightarrow$AlPor-Ph-C$_60$</td>
<td>1307</td>
<td>-</td>
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<tr>
<td>AlPor-Ph$_2$-C$_60$</td>
<td>-</td>
<td>256 (5.07), 307 (4.76), 415 (5.74)</td>
<td>1.10</td>
<td>-0.42, -0.77, -1.04, -1.37</td>
</tr>
<tr>
<td>TTF-py$\rightarrow$AlPor-Ph$_2$-C$_60$</td>
<td>1325</td>
<td>-</td>
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<tr>
<td>TTF-Ph-py$\rightarrow$AlPor-Ph$_2$-C$_60$</td>
<td>1544</td>
<td>-</td>
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<tr>
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<td>1352</td>
<td>-</td>
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<tr>
<td>AlPor-Ph$_3$-C$_60$</td>
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<td>257 (5.09), 307 (4.93), 415 (5.74)</td>
<td>1.14</td>
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<td>1352</td>
<td>-</td>
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<tr>
<td>py$\rightarrow$AlPor-Ph$_3$-C$_60$</td>
<td>1450</td>
<td>-</td>
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<tr>
<td>AlPor-Ph</td>
<td>-</td>
<td>415 (5.75)</td>
<td>1.12</td>
<td>-0.97, -1.35</td>
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<td>-</td>
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<td>-1.00, -1.35</td>
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<tr>
<td>C$_{60}$-Ph-COOMe</td>
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<td>TTF-Ph-py</td>
<td>-</td>
<td>298 (4.48), 428 (3.64)</td>
<td>0.73, 1.10</td>
<td></td>
</tr>
</tbody>
</table>

$^a$In dichloromethane. $^b$Redox potentials were reported against ferrocene, where $E_{1/2}$(Fc/Fc$^+$) = 0.74 V with 0.1 M TBAP in o-DCB in our experimental conditions.
Figure 4.1.S7. Spectral titrations of AlPor-Ph-C₆₀ with TTF-py in o-DCB. TTF-py was added up to $1.9 \times 10^{-3}$ M in $1.12 \times 10^{-4}$ M increments to a $6 \times 10^{-5}$ M solution of AlPor-Ph-C₆₀. Left: Absorption titrations, inset shows the Benesi-Hildebrand plot of the change of absorbance at 604 nm. Right: Fluorescence titrations, the excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.

Figure 4.1.S8. Spectral titration of AlPor-Ph-C₆₀ with TTF-Ph-py in o-DCB. TTF-Ph-py was added up to $1.9 \times 10^{-3}$ M in $1.12 \times 10^{-4}$ M increments to a $6 \times 10^{-5}$ M solution of AlPor-Ph-C₆₀. Left: Absorption titrations, inset shows the Benesi-Hildebrand plot of the change of absorbance at 604 nm. Right: Fluorescence titrations, the excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.
Figure 4.1.S9. Spectral titrations of AlPor-Ph-C$_{60}$ with py in o-DCB. Pyridine was added up to $4.51 \times 10^{-3}$ M in $3.48 \times 10^{-4}$ M increments to a $6 \times 10^{-5}$ M solution of AlPor-Ph-C$_{60}$. Left: Absorption titrations, inset shows the Benesi-Hildebrand plot of the change of absorbance at 604 nm. Right: Fluorescence titrations, the excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.

Figure 4.1.S10. Spectral titrations of AlPor-Ph$_2$-C$_{60}$ with TTF-Ph-py in o-DCB. TTF-Ph-py was added up to $1.9 \times 10^{-3}$ M in $1.12 \times 10^{-4}$ M increments to a $6 \times 10^{-5}$ M solution of AlPor-Ph$_2$-C$_{60}$. Left: Absorption titrations, inset shows the Benesi-Hildebrand plot of the change of absorbance at 604 nm. Right: Fluorescence titrations, the excitation wavelength was chosen at the isosbestic point, 554 nm, obtained from UV-visible titrations.
Figure 4.1.S11. Spectral titrations of AlPor-Ph$_2$-C$_{60}$ with py in $\sigma$-DCB. Pyridine was added up to $1.9 \times 10^{-3}$ M in $1.12 \times 10^{-4}$ M increments to a $6 \times 10^{-5}$ M solution of AlPor-Ph$_2$-C$_{60}$. Left: Absorption titrations, inset shows the Benesi-Hildebrand plot of the change of absorbance at 604 nm. Right: Fluorescence titrations, the excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.

Figure 4.1.S12. Spectral titrations of AlPor-Ph$_3$-C$_{60}$ with TTF-py in $\sigma$-DCB. TTF-py was added up to $1.9 \times 10^{-3}$ M in $1.12 \times 10^{-4}$ M increments to a $6 \times 10^{-5}$ M solution of AlPor-Ph$_3$-C$_{60}$. Left: Absorption titrations, inset shows the Benesi-Hildebrand plot of the change of absorbance at 604 nm. Right: Fluorescence titrations, the excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.
Figure 4.1.S13. Spectral titrations of AlPor-Ph3-C60 with TTF-Ph-py in o-DCB. TTF-Ph-py was added up to $1.9 \times 10^{-3}$ M in $1.12 \times 10^{-4}$ M increments to a $6 \times 10^{-5}$ M solution of AlPor-Ph3-C60. Left: Absorption titrations, inset shows the Benesi-Hildebrand plot of the change of absorbance at 605 nm. Right: Fluorescence titrations, the excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.

Figure 4.1.S14. Spectral titrations of AlPor-Ph3-C60 with py in o-DCB. Pyridine was added up to $1.9 \times 10^{-3}$ M in $1.12 \times 10^{-4}$ M increments to a $6 \times 10^{-5}$ M solution of AlPor-Ph3-C60. Left: Absorption titrations, inset shows the Benesi-Hildebrand plot of the change of absorbance at 605 nm. Right: Fluorescence titrations, the excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.
Figure 4.1.S15. Spectral titrations of AlPor-Ph with TTF-py in o-DCB. TTF-py was added up to $1.9 \times 10^{-3}$ M in $1.12 \times 10^{-4}$ M increments to a $6 \times 10^{-5}$ M solution of AlPor-Ph. Left: Absorption titrations, inset shows the Benesi-Hildebrand plot of the change of absorbance at 604 nm. Right: Fluorescence titrations, the excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.

Figure 4.1.S16. Spectral titrations of AlPor-Ph with TTF-Ph-py in o-DCB. TTF-Ph-py was added up to $1.9 \times 10^{-3}$ M in $1.12 \times 10^{-4}$ M increments to a $6 \times 10^{-5}$ M solution of AlPor-Ph. Left: Absorption titrations, inset shows the Benesi-Hildebrand plot of the change of absorbance at 604 nm. Right: Fluorescence titrations, the excitation wavelength was chosen at the isosbestic point, 554 nm, obtained from UV-visible titrations.
Figure 4.1.S17. Spectral titrations of AlPor-Ph with py in o-DCB. Pyridine was added up to $4.5 \times 10^{-3}$ M in $2.23 \times 10^{-4}$ M increments to a $6 \times 10^{-5}$ M solution of AlPor-Ph. Left: Absorption titrations, inset shows the Benesi-Hildebrand plot of the change of absorbance at 604 nm. Right: Fluorescence titrations, the excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.

Figure 4.1.S18. Spectral titrations of AlPor-Ph with TTF in o-DCB. TTF was added up to $3.53 \times 10^{-3}$ M in $2.10 \times 10^{-4}$ M increments to solution of $6 \times 10^{-5}$ M solution of AlPor-Ph. Left: Absorption titrations. Right: Fluorescence titrations, the excitation wavelength was chosen to be 555 nm.
Figure 4.1.S19. Molecular electrostatic potential map (MEP), HOMO-1, HOMO and LUMO of TTF-Ph-py→AlPor-Ph-C₆₀.
Figure 4.1.S20. Molecular electrostatic potential map (MEP), HOMO-1, HOMO and LUMO of TTF-py→AlPor-Ph₂-C₆₀ (top) and TTF-Ph-py→AlPor-Ph₂-C₆₀ (bottom).
Figure 4.1.S21. Molecular electrostatic potential map (MEP), HOMO-1, HOMO and LUMO of TTF-py→AlPor-Ph₃-C₆₀ (top) and TTF-Ph-py→AlPor-Ph₃-C₆₀ (bottom).
Figure 4.1.S22. Differential pulse voltammograms of (a) Ferrocene (magenta), TTF-py (maroon) and TTF-Ph-py (blue) (b) 0.52 mM solution of AlPor-Ph (red), TTF-py→AlPor-Ph (maroon) and TTF-Ph-py→AlPor-Ph (blue) (c) 0.43 mM solution of AlPor-Ph-C_{60} (red), TTF-py→AlPor-Ph-C_{60} (maroon) and TTF-Ph-py→AlPor-Ph-C_{60} (blue) in 0.1 M TBAP, o-DCB.

Figure 4.1.S23. Left: Absorption (black) and fluorescence (red) spectra of AlPor-Ph in o-DCB at room temperature. Right: Phosphorescence spectrum of AlPor-Ph in CH_{2}Cl_{2}:C_{2}H_{5}OH (= 1:1) at 77K.
Figure 4.1.524. Diagram illustrating the energies of the possible charge separated states in newly constructed dyads and triads in toluene. Note that the reported energies of TTF$^{**}$AlPor$^*$, AlPor$^{**}$C$_60^*$ and TTF$^{**}$C$_60^*$ are average values of two dyads (TTF-Ph$_n$-py→AlPor-Ph, n = 0, 1), three dyads (AlPor-Ph$_m$-C$_60$, m = 1-3) and six triads (TTF-Ph$_n$-py→AlPor-Ph$_m$-C$_60$, n = 0, 1 and m = 1-3), respectively.
Figure 4.1.S25. Femtosecond transient spectra of AlPor-Ph in toluene at the indicated time intervals. The time profiles of (i) 487, (ii) 448, (iii) 1240 and (iv) 648 nm are shown.

Figure 4.1.S26. Fluorescence decay curve of AlPor-Ph in Ar-saturated toluene. Excitation and emission wavelengths were at 560 and 590 nm, respectively.
Figure 4.1S27. Femtosecond transient absorption spectra of AlPor-Ph-C_{60} and TTF-py→AlPor-Ph-C_{60} Is in toluene at different time intervals.

Figure 4.1S28. (a) Nanosecond transient absorption spectra of 0.1 mM TTF-Ph-py→AlPor-Ph-C_{60} observed by 532 nm (ca. 3 mJ/pulse) laser irradiation in o-DCB. Inset: Absorption-time profile at 1020 nm. (b) Absorption time profile at 470 nm.
4.2 Modulation of Energy Transfer into Sequential Electron Transfer upon Axial Coordination of Tetrathiafulvalene in an Aluminum(III) Porphyrin-Free-Base Porphyrin Dyad*

4.2.1 Introduction

Inspired by natural photosynthesis, many donor-acceptor (D-A) systems have been synthesized to mimic the function of light harvesting antenna\textsuperscript{1-5} and reaction center\textsuperscript{6-9} complexes. These studies aim not only at a better understanding of the photoinduced energy transfer (EnT) and electron transfer (ET) processes, but also at building artificial photosynthetic systems for solar energy conversion and storage applications as well as photo- and electronic devices.\textsuperscript{10-21} In most of these artificial systems, porphyrin (Por) has emerged as a promising building block and an attractive chromophore because they have structural similarities with chlorophyll as they absorb strongly in the visible region, are often highly fluorescent, have rich redox chemistry, and most importantly their optical and redox properties are easily tunable.\textsuperscript{22} In combination with other photo and redox active species, porphyrins have been used to produce a wide array of covalent and non-covalent multicomponent systems to mimic the light harvesting and reaction center complexes of photosynthetic systems.\textsuperscript{6,8,17,23-28} However, most of these model compounds deal with the photoinduced processes along the porphyrin plane. Little is known about these processes in perpendicular (axial) direction to the porphyrin plane.\textsuperscript{26,29-41} One reason for this is the difficulty associated with attaching different ligands to the porphyrin in the axial position. In this respect, aluminum(III) porphyrins (AlPors) are unique as they form: (i) covalent bond with carboxylic acids\textsuperscript{42-49} or alcohols\textsuperscript{50-53} and (ii) coordination bond with Lewis bases\textsuperscript{42,44,54,55} (eg. pyridine or imidazole). Since AlPor can form two different types of axial bonds, it is possible to attach two different molecular components to the

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opposite faces. These advantages of AlPor provide an excellent opportunity to study the
influence of electronic coupling, orientation, reorganization energy on the energy and electron
transfer processes in perpendicular direction to the porphyrin plane.\textsuperscript{42-45,56,57} Moreover, this
particular geometry not only keeps the axial components spatially well separated from each
other but also prevents aggregation between the molecules, which is a most common problem
in porphyrin based D-A systems.

In a photosystem, light harvesting antenna and reaction center complex work together
to perform the conversion of solar energy into chemical energy.\textsuperscript{58-62} One of the similarities
between the light harvesting antenna and reaction center complex is that they both utilize
chlorophyll molecule as a chromophore. However, chlorophyll’s role is entirely different as it
serves as an energy donor in the light harvesting antenna complex whereas in the reaction
center complex ‘chlorophyll special pair’ performs predominantly the role of an electron donor.
This is because the surrounding protein alters the chlorophyll’s spectral and redox properties
for a desired role in each of these complexes.\textsuperscript{63,64} For artificial systems, there is no surrounding
protein, and therefore other ways of tuning the spectral and redox potential of the
photosensitizer must be required. To mimic the role of the chlorophyll in photosynthesis, here
we report a new vertical AlPor based dyad ‘aluminum(III) porphyrin – free-base porphyrin’
(AlPor-Ph-H\textsubscript{2}Por, see Chart 4.2.1) and corresponding two axially arranged self-assembled triads
‘tetrathiafulvalene – aluminum(III) porphyrin – free-base porphyrin’ (TTF-py→AlPor-Ph-H\textsubscript{2}Por
and TTF-Ph-py→AlPor-Ph-H\textsubscript{2}Por, Figure 4.2.1). We have chosen tetrathiafulvalene (TTF) as the
secondary donor because of its strong electron donating ability, which makes it an excellent
candidate as a reductive electron quencher in D-A systems.\textsuperscript{25,65,66} As an acceptor, we have
selected free-base porphyrin (H$_2$Por) with electron withdrawing fluorinated phenyl substituents in its meso positions. Its positive redox potentials and strong spectral overlap with AlPor makes the selected H$_2$Por as an acceptor for both energy and electron transfer processes.$^{67,68}$ Time-resolved studies have shown that these compounds undergo photoinduced energy and/or electron transfer processes. We will also show that the energy and electron donating nature of AlPor can be modulated by changing the solvent polarity or by stimulating a new competing process using TTF molecule. In the AlPor-Ph-H$_2$Por dyad, AlPor serves as an energy donor to the H$_2$Por. In contrast, the same AlPor in the triad acts as an electron acceptor/donor in the presence of secondary electron donor TTF moiety.

Scheme 4.2.1. Structure of investigated compounds in this study.
4.2.2 Results and Discussion

4.2.2.1 Synthesis

Porphyrrin dyad was prepared by previously established methods \(^\text{42,44,45,70}\) in quantitative yields. Complete experimental details are shown in Schemes 4.2.S1 and 4.2.S2 (see supporting information) as well as in the experimental section. The dyad (AlPor-Ph-H\(_2\)Por) was prepared by reacting equal molar ratios of AlPor-OH and H\(_2\)Por-Ph-COOH and the reaction was monitored by NMR spectroscopy. Obtained dyad was stored on freshly prepared CaCl\(_2\) desiccator prior to optical studies. The triads shown in Figure 4.2.1 were assembled by using the dyad (AlPor-Ph-H\(_2\)Por) and TTF-py/TTF-Ph-py derivatives in non-coordinating solvents. Lewis acid-base interactions were utilized to build these vertically arranged supramolecular self-assembled triads. NMR, UV-visible absorption and steady-state fluorescence titrations were employed to...
monitor the formation of triads. However, the formed self-assembled triads could not be isolated.

4.2.2.2 Structural Characterization

Preliminary characterization of the dyad was carried out by ESI mass spectrometry. The mass spectrum of dyad AlPor-Ph-H2Por showed peaks at 1567 and 639, which corresponds to the mass (m/z) of [M + H]⁺ and [M − axial H₂Por]⁺, respectively. The ¹H NMR spectra of dyad AlPor-Ph-H₂Por and one of its monomers from which it was prepared, H₂Por-Ph-COOH, are shown in Figure S4. Shielding effects are apparent for the protons on the axial porphyrin subunit. For example, resonances due to the phenyl protons b and a (Figure 4.2.1), which appear at 8.58 and 8.37 ppm in the isolated H₂Por-Ph-COOH porphyrin are strongly shifted upfield to 7.29 and 5.51 ppm, respectively in dyad AlPor-Ph-H₂Por due to the ring current effect of the porphyrin macrocycle. Similarly, resonances due to the β-protons (c, d and e) as well as inner NH protons are shifted upfield compared to the corresponding resonances in the spectrum of compound H₂Por-Ph-COOH. These chemical shifts (δ) agree well with those of axial bonding type porphyrin systems.⁴²,⁴⁴,⁴⁵,⁷⁰ Hence, the Δδ values (i.e. δ_{monomer} − δ_{dyad}) are a function of their proximity to the porphyrin ring.

Figure 4.2.2 shows the ¹H NMR spectrum of triad (TTF-py→AlPor-Ph-H₂Por (bottom), that is 1:1 mixture of AlPor-Ph-H₂Por and TTF-py) along with the individual spectra of AlPor-Ph-H₂Por (middle) and TTF-py (top). In the triad complex, TTF-py→AlPor-Ph-H₂Por, shielding due to the porphyrin ring causes an upfield shift of the TTF-py protons on the pyridine unit (f and g) and TTF moiety (j and k). The magnitude of the shift depends on the distance of the protons from the porphyrin ring, hence the pyridinyl protons (f and g) display the large shift indicating
that coordination occurs via the pyridinyl group. On the benzoate bridging group to the H$_2$Por, the protons ($\alpha$) closest to the porphyrin ring show an increased upfield shift upon coordination, suggesting that the aluminum(III) center lies out of the porphyrin plane in AlPor-Ph-H$_2$Por and is pulled into the plane when TTF-py coordinates. Analogous results were obtained from the triad, TTF-Ph-py→AlPor-Ph-H$_2$Por (Figures S5).

![Figure 4.2.2. 1H NMR (300 MHz) spectra of TTF-py (top), AlPor-Ph-H$_2$Por (middle) and TTF-py→AlPor-Ph-H$_2$Por (bottom) in CDCl$_3$.](image)

4.2.2.3 UV-Visible Absorption Spectroscopy

The UV-visible spectra of dyad AlPor-Ph-H$_2$Por and its reference compounds (AlPor-Ph and H$_2$Por-Ph) were measured in dichloromethane and the spectra are shown in Figure 4.2.3. The band positions (Q-bands and B- or Soret bands) and their molar extinction coefficients are summarized in Table 4.2.1. As shown in Figure 4.2.3 and Table 4.2.1, the absorption spectrum of the dyad is essentially a linear combination of its reference porphyrins. Furthermore, the band positions and molar extinction coefficients ($\varepsilon$) of the dyad are similar to corresponding monomer porphyrins. Therefore, the majority of absorbance at 510, 547 and 639 nm is attributed to the H$_2$Por (87%), AlPor (90%) and H$_2$Por (60%), respectively. Absorption spectrum
of dyad AlPor-Ph-H$_2$Por, also measured in acetonitrile, is shown in Figure 4.2.S6. Noticeable differences are observed when compared with the spectrum in dichloromethane. The AlPor bands are red shifted (~10 nm) due to coordination of solvent at the Al center of the AlPor. However, the band positions and molar extinction coefficients remain similar to its monomeric compounds. Overall, the absorption studies suggest that there exist no or weak interactions between basal porphyrin (AlPor) and axial porphyrin (H$_2$Por). The absorption bands of AlPor and H$_2$Por are weakly overlapping, therefore by choosing the wavelengths of 550/560 nm and 640 nm it is possible to excite mostly AlPor and the axial H$_2$Por units, respectively for steady-state fluorescence studies. The py-appended TTF derivatives (TTF-py and TTF-Ph-py) have relatively weak and very broad absorption bands (see Figure S7) at $\lambda = 304$ (average of 285 and 324 nm bands) and $\lambda = 435$ nm for TTF-py, and at $\lambda = 298$ and 428 nm for TTF-Ph-py.

Figure 4.2.3. UV-visible absorption spectra of dyad AlPor-Ph-H$_2$Por (green) and reference compounds H$_2$Por-Ph (blue) and AlPor-Ph (red) in dichloromethane.

Figure 4.2.4a shows absorption titrations of TTF-py vs AlPor-Ph-H$_2$Por in dichloromethane. Upon addition of TTF-py, the Q bands of the porphyrin 547 and 586 nm are shifted to 563 and 603 nm. Isosbestic point is observed at 555 nm, indicating the formation of
TTF-py→AlPor-Ph-H₂Por in an equilibrium, and the shifts in the porphyrin bands are typical of axial coordination of nitrogen ligands to AlPors.⁴²,⁴⁴,⁴⁵,⁵⁴,⁵⁵ Benesi-Hildebrand analysis⁶⁹ (Figure 4.2.4a, inset) gives a linear plot indicating that a 1:1 complex is formed, and the slope yields a binding constant $K = 1.8 \times 10^3 \text{ M}^{-1}$. In a similar fashion, the binding constant $K$ was calculated for the titrations of TTF-Ph-py vs AlPor-Ph-H₂Por (Figure S8a), py vs AlPor-Ph-H₂Por (Figure S10a) and the data are summarized in Table S1. Titrations TTF-py vs AlPor-Ph and TTF-Ph-py vs AlPor-Ph and corresponding binding constants have been reported previously.⁴⁵ Titrations of TTF-py/TTF-Ph-py with AlPor-Ph-H₂Por have shown greater binding ($\sim 2.0 \times 10^3 \text{ M}^{-1}$) than that of the AlPor-Ph ($\sim 1.0 \times 10^3 \text{ M}^{-1}$), which suggests that as the electron withdrawing nature (Ph < H₂Por) of the axial ligand increases, the Al center becomes a better Lewis acid, hence it binds stronger with the Lewis base pyridine. Together with NMR and absorption titrations we conclude the formation of the triad (TTF-py→AlPor-Ph-H₂Por or TTF-Ph-py→AlPor-Ph-H₂Por) in the solution.

Table 4.2.1. UV-visible absorption and steady-state fluorescence data of investigated compounds.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorption</th>
<th>Fluorescence</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}, \text{nm} \ (\log \varepsilon)$</td>
<td>Q-Bands/TTF</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AlPor-Ph</td>
<td>585 (3.42), 547 (4.32), 510 (3.44)</td>
<td>416 (5.74)</td>
</tr>
<tr>
<td>H₂Por-Ph</td>
<td>639 (2.96), 585 (3.78), 540 (3.46), 510 (4.27)</td>
<td>415 (5.47)</td>
</tr>
<tr>
<td>AlPor-Ph-H₂Por</td>
<td>639 (3.25), 586 (3.95), 547 (4.37), 510 (4.33)</td>
<td>415 (5.85)</td>
</tr>
<tr>
<td>TTF-py</td>
<td>435 (3.45), 324 (4.17), 285 (4.22)</td>
<td>---</td>
</tr>
<tr>
<td>TTF-Ph-py</td>
<td>428 (3.64), 298 (4.48)</td>
<td>---</td>
</tr>
</tbody>
</table>

⁶ Spectra were measured in dichloromethane.
Figure 4.2.4. (a) Absorption and (b) fluorescence titrations of AlPor-Ph-H₂Por with TTF-py in dichloromethane. The inset shows the Benesi-Hildebrand plot of the change of absorbance at 603 nm. TTF-py was added up to $1.88 \times 10^{-3}$ M in 20 μL ($2.22 \times 10^{-4}$ M) increments to 1 mL ($6 \times 10^{-5}$ M) solution of AlPor-Ph-H₂Por. The excitation wavelength was chosen at the isosbestic point, 555 nm, which was obtained from absorption titrations.

4.2.2.4 Cyclic Voltammetry

Cyclic voltammetry of the newly investigated dyad and reference monomers were measured in 0.1 M TBAClO₄ dichloromethane with ferrocene as an internal standard. Representative voltammograms are shown in Figure S11 and the data are summarized in Table 4.2.2. The redox processes of all the compounds are found to be one-electron reversible based on the peak-to-peak separation values, and the cathodic-to-anodic peak current ratio. The voltammogram of the dyad is essentially a sum of the voltammograms of its reference monomers AlPor-Ph and H₂Por-Ph. During the cathodic scan, dyad showed three reduction processes. On the basis of the respective monomers, the observed first and third processes are assigned to the first and second reduction of axial porphyrin (H₂Por) unit, whereas the second process is assigned to the first reduction of AlPor unit. Conversely, the anodic scan reveals four oxidation processes for the dyad. The first two processes are assigned to the AlPor and later
processes belong to the axial H$_2$Por unit. As anticipated, the dyad showed a combination of processes from their respective monomeric porphyrin units without any perturbation in their redox potentials. Therefore, the observed cyclic voltammograms and redox data suggest that the components of the dyad do not influence one another significantly. The TTF derivatives (TTF-py and TTF-Ph-py) show two processes corresponding to the first and second oxidation of TTF moiety. These results have been published elsewhere.$^{45}$

Table 4.2.2. Redox Potential Data of Investigated Compounds in Dichloromethane with 0.1 M TBAClO$_4$ as a Supporting Electrolyte.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Potential (V vs SCE)</th>
<th>Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlPor-Ph-H$_2$Por</td>
<td>0.91, 1.12, 1.54,</td>
<td>−0.87, −1.20, −1.35</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AlPor-Ph</td>
<td>0.91</td>
<td>−1.21</td>
<td></td>
</tr>
<tr>
<td>H$_2$Por-Ph</td>
<td>1.51, 1.77</td>
<td>−0.87, −1.30</td>
<td></td>
</tr>
<tr>
<td>TTF-py</td>
<td>0.48, 0.83</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>TTF-Ph-py</td>
<td>0.47, 0.87</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

The redox potentials are used in combination with optical data to estimate the energetics of the energy and electron transfer reactions in the investigated compounds. Figure 4.2.5 summarizes the energy levels of the dyad and its corresponding supramolecular triads. The energies of the radical ion pair states ($E_{CS}$) and free energy change for the charge separation ($\Delta G_{CS}$) are estimated using the Weller equation,$^{71,72}$

$$E_{CS} = e \left[ E_{1/2}(D^+/D) - E_{1/2}(A^+ / A) \right] + G_3$$  \hspace{1cm} (1)

$$\Delta G_{CS} = E_{CS} - E_{0,0} \hspace{1cm} (2)$$
where $E_{1/2}(D^{**}/D)$ is the first oxidation potential of the donor, $E_{1/2}(A/A^{**})$ is the first reduction potential of the acceptor. $G_S$ is ion-pair stabilization and incorporates both the solvent-dependent Coulomb energy change upon ion-pair formation and the free energy of solvation of the ions,

$$G_S = \frac{e^4}{4\pi\varepsilon_0} \left[ \frac{1}{2R^+} + \frac{1}{2R^-} - \frac{1}{R_{D-A}} \right] \epsilon_s \left[ \frac{1}{2R^+} + \frac{1}{2R^-} \right]$$

(3)

where $R^+$, $R^-$ and $R_{D-A}$ are the donor radius, acceptor radius and center-to-center distance between the donor and acceptor, respectively. $\varepsilon_S$ is the dielectric constant of the solvent used for the photophysical studies (9.1 and 37.5 for dichloromethane and acetonitrile, respectively). $\varepsilon_R$ is the dielectric constant of the solvent used for measuring the redox potentials, in this case dichloromethane. The lowest excited singlet state energy ($E_{0-0}$) is estimated from the crossing point of absorption and fluorescence spectra and found to be 579 and 620 nm for AlPor and H2Por, respectively (see Figure 4.2.S12). Similarly, the band position of phosphorescence spectrum (see Figure 4.2.S13) at 768 and 770 nm of AlPor-Ph and H2Por-Ph, respectively is taken as the lowest excited triplet state. The calculated energy levels suggest that energy transfer (EnT), electron transfer (ET) and electron shift (ES) processes are energetically feasible in the investigated dyad and its corresponding self-assembled supramolecular triads. With acetonitrile as the solvent, the radical ion-pairs are found to be slightly lower in energy than in dichloromethane (Figure 4.2.S14).
4.2.2.5 Fluorescence Spectroscopy

Steady-state fluorescence measurements were performed in dichloromethane and acetonitrile. Figure 4.2.6a illustrates the fluorescence spectra of the dyad and its corresponding monomers in dichloromethane and the data are summarized in Table 4.2.1. As shown in Figure 4.2.6a, excitation of the dyad at 550 nm (where 90% of light is absorbed by AlPor) results in appearance of fluorescence bands due to H$_2$Por (bands II and III) and AlPor (bands I and II) components. It was found that the fluorescence band maxima of AlPor and H$_2$Por components are quite close to those of AlPor-Ph or H$_2$Por-Ph, respectively. However, the fluorescence intensity of AlPor component is strongly quenched (90%, emission monitored at the band I, see Table 4.2.1) in comparison with the reference compound AlPor-Ph. In contrast, band III intensity increased with respect to H$_2$Por-Ph. These results clearly suggest that the AlPor first excited singlet state ($^{1}$AlPor*) is being strongly quenched by H$_2$Por through singlet-singlet
energy transfer mechanism. The possibility of energy transfer is supported by significant spectral overlap between the fluorescence spectrum of AlPor and absorption spectrum of H₂Por, Figure S15a. This is further investigated by using the fluorescence excitation spectrum. Figure 4.2.6b shows the corrected excitation spectrum of the dyad in dichloromethane collected at 720 nm (emission monochromator) where only the H₂Por emits. Overlap of the corrected and normalized excitation spectra with the corresponding absorption spectra revealed that the singlet-singlet energy transfer (EnT) efficiency is ~70% for the dyad in dichloromethane. Thus, it appears that the major portion (70% out of 90%) of ¹AlPor* state is quenched due to the energy transfer process. The remaining 20% quenching could be attributed to the electron transfer (ET) from ¹AlPor* to H₂Por as the Gibbs free energy change (ΔG_{CS}) for this process was found to be exergonic (−0.49 eV) in dichloromethane. Furthermore, excitation of the dyad at 640 nm (where 60% light is absorbed by H₂Por) showed a band exclusively due to the free-base component in the ~720 nm (band III) region and its intensity was found to be similar to the sum of the calculated spectrum of H₂Por-Ph + AlPor-Ph, Figure S15b. Thus, we conclude that electron transfer from AlPor to the excited singlet state of free-base porphyrin (¹H₂Por*) is weak or negligible, although the corresponding ΔG_{CS} is estimated to be −0.34 eV.
Figure 4.2.7a illustrates the fluorescence spectra of the dyad and corresponding monomers in acetonitrile. Solutions were excited at 560 nm, where AlPor absorbs 95% of light. The band positions of the dyad are quite similar to its reference monomeric porphyrins, Figure 4.2.7a. However, two changes can be seen: (1) fluorescence bands of AlPor are red shifted (~10 nm) in comparison with dichloromethane data, and (2) fluorescence intensity is strongly quenched (~91%). The red shift can be explained by the coordination of acetonitrile to AlPor. To examine the quenching mechanism, spectral overlap between AlPor fluorescence and H2Por absorption was estimated, see Figure S16a. Significant spectral overlap has been found, although it is slightly smaller compared to the overlap in dichloromethane solution. Despite having a strong spectral overlap, the fluorescence excitation spectrum (collected at 720 nm, Figure 4.2.7b) of the dyad did not revealed AlPor excitation.
bands (at 560 and 610 nm) suggesting that the energy transfer is a minor process or negligible from $^1\text{AlPor}^*$ to $\text{H}_2\text{Por}$ unit in polar acetonitrile. Hence, the observed strong quenching can be attributed solely to the electron transfer process from $^1\text{AlPor}^*$ to $\text{H}_2\text{Por}$ unit. The Gibbs free energy change ($\Delta G_{CS}$) for this process found to be $-0.54$ eV. On the other hand, excitation of the dyad at 640 nm (where 60% light is absorbed by $\text{H}_2\text{Por}$) also resulted in quantitative quenching of 720 nm band, which is exclusively coming from $\text{H}_2\text{Por}$, Figure S16b. A careful examination of the energy level diagram suggests that this quenching could be attributed to the electron transfer from AlPor to $^1\text{H}_2\text{Por}^*$ and the corresponding $\Delta G_{CS}$ found to be exergonic by $-0.39$ eV.

Figure 4.2.7. (a) Steady-state fluorescence spectra of AlPor-Ph-$\text{H}_2\text{Por}$ (green), AlPor-Ph (red) and $\text{H}_2\text{Por}$-Ph (blue) with excitation at 560 nm in acetonitrile. (b) Absorption (solid) and corrected fluorescence excitation (dashed) spectra of dyad in acetonitrile and the spectra were normalized between 610-650 nm. The excitation spectrum was collected at 720 nm corresponding to emission of $\text{H}_2\text{Por}$.

Figure 4.2.4b shows the fluorescence spectra of the AlPor-Ph-$\text{H}_2\text{Por}$ dyad with increasing amounts of pyridine-appended tetrathiafulvalene (TTF-py) in dichloromethane. The excitation wavelength was adjusted to the isosbestic point at 555 nm (where 95% of absorption is due to AlPor). In the absence of TTF-py, the AlPor-Ph-$\text{H}_2\text{Por}$ dyad shows AlPor bands (I & II) and $\text{H}_2\text{Por}$
bands (II & III) similar to those of its monomeric compounds AlPor-Ph and H₂Por-Ph. However, their intensities were strongly quenched due to the energy transfer from ¹AlPor* to axial H₂Por. Upon addition of TTF-py, the fluorescence bands of AlPor (I & II) shifted to longer wavelengths and the relative fluorescence intensities of all three bands (I, II & III) are strongly quenched. These notable spectral changes indicate the formation of TTF-py→AlPor-Ph-H₂Por triad in the solution. However, to explain the possible quenching mechanism/s various control titrations were carried out. Upon addition of py (without appended TTF unit, Figure S10b) or TTF (without appended py group, Figure S9b) to the dyad revealed no considerable change in fluorescence intensity. On the other hand, addition of TTF-py to the reference monomer AlPor-Ph revealed electron transfer process from TTF to ¹AlPor* unit; these results have been reported previously.⁴²,⁴⁵ Therefore, the most likely explanation for the quenching of fluorescence bands (I & II) is the electron transfer from TTF to ¹AlPor* upon triad formation. This process is exergonic (−0.59 eV) and has been observed in other systems in which TTF was attached axially to a porphyrin macrocycle.⁴²,⁴⁵,⁷⁰,⁷⁴ Insertion of an additional phenyl spacer between the TTF and py units is expected to decrease the electronic coupling and to slow down the electron transfer rate. Consistent with this expectation, bands I & II are weakly quenched in titrations of TTF-Ph-py vs AlPor-Ph-H₂Por (see Figure S8b), that is formation of TTF-Ph-py→AlPor-Ph-H₂Por triad. Regardless of the fluorescence trends in bands I & II, intriguingly, the band III quenched in both the triads upon addition of py appended TTF derivatives. This could be due to newly introduced electron transfer process between the TTF and ¹AlPor* units. As a consequence of the electron transfer, the ²AlPor* state is being quenched rapidly by TTF unit, hence the energy transfer from ³AlPor* to H₂Por is expected to be blocked. Thus, band III, which is predominantly
the result of energy transfer process in triads (TTF-py→AlPor-Ph-H₂Por and TTF-Ph-py→AlPor-Ph-H₂Por), reduces significantly. To verify this scheme, the fluorescence excitation spectrum was collected for the triads, TTF-py→AlPor-Ph-H₂Por (Figure 4.2.8) and TTF-Ph-py→AlPor-Ph-H₂Por (Figure S17), at 720 nm where the emission is exclusively from H₂Por unit. As shown in Figure 4.2.8, solid curve represents the absorption spectra of the triad consisting of pyridine coordinated hexavalent AlPor bands (560 and 614 nm) and H₂Por bands (590 and 640 nm) as well as a minor uncomplexed pentavalent AlPor (550 nm). Interestingly, the bands at 560 and 614 nm are completely absent in the excitation spectra (dashed line). These results evidently suggest that the energy transfer is not participating in quenching of ¹AlPor* state in the triad molecule. Overall, two changes occur in ¹AlPor* state due to presence of TTF redox center: (1) it initiates the electron transfer from TTF to ¹AlPor* and (2) it inhibits the energy transfer from ¹AlPor* to H₂Por. Moreover, these results suggest that the electron transfer from TTF to ¹AlPor* is presumably faster than that of energy transfer from ¹AlPor* to H₂Por.

4.2.2.6 Femtosecond Transient Absorption Spectroscopy

Femtosecond transient absorption studies were performed in 1,2-dichlorobenzene (o-DCB) (instead of low boiling dichloroethane) and acetonitrile to secure evidence of energy transfer, electron transfer and electron shift processes in the dyad and triads. Samples were excited using 400 nm wavelength light where the absorbance ratio of AlPor and H₂Por is approximately 1:2.
Figure 4.2.8. Absorption (solid) and corrected fluorescence excitation (dashed) spectra of triad TTF-py→AlPor-Ph-H₂Por in dichloromethane and the spectra were normalized between 610-650 nm. The excitation spectrum was collected at 720 nm corresponding to emission band of H₂Por. TTF-py and AlPor-Ph-H₂Por are present in $1.88 \times 10^{-3}$ M and $6 \times 10^{-5}$ M in solution, respectively.

(a) In o-dichlorobenzene. First, transient spectra of the precursor compounds, AlPor-Ph and H₂Por-Ph, were investigated. As shown in Figure S18a, excitation of AlPor-Ph instantly populated the $S_1$ and $S_2$ states with a maximum in the ~450 nm region. At higher wavelength region, a depleted signal in the Q-band region of AlPor (550 nm), opposite mimic of the ground state absorption of the Q-band was observed. In addition, depleted bands at 592 and 648 nm, corresponding to stimulated emission of Al porphyrin were observed. Positive peak maxima at 450, 576, 614, and 681 nm were also observed. Interestingly, in the near-IR region, an additional peak at 1256 nm was observed. The decay rate of this peak lasted over 3 ns (see Figure S18b), the monitoring window of our instrument setup, suggesting that this could be due to the singlet-singlet excited state of AlPor.⁴² Similarly, the instantly formed $S_1$ and $S_2$ states of H₂Por-Ph upon excitation revealed depleted peaks at 509, 533 and 585 nm corresponding to their Q-band absorption, and at 647 and 720 nm corresponding to stimulated emission of free-
base porphyrin (Figure 4.2.S19a). Positive peaks at 440, 530, 558, 616, and 680 nm were observed. In the near-infrared region, a peak at 1067 nm was also observed corresponding to the singlet excited state of free-base porphyrin. The excited singlet state lifetime ($\tau$) of AlPor and H$_2$Por is measured using the time-resolved fluorescence method and found to be 5.80 and 9.00 ns, respectively (see Figure 4.2.S20 for decay curves) in dichloromethane.

To help interpret the transient spectral data of charge separation products, spectroelectrochemical studies were performed on H$_2$Por, AlPor and TTF, see Figure 4.2.S21-S23. The one-electron reduced product of H$_2$Por-Ph (Figure 4.2.S21) revealed radical anion peaks at 443, 557, 588 and 632 nm. The Soret band of H$_2$Por located at 415 nm revealed a red-shift of 28 nm and appeared at 443 nm. The one-electron oxidized product of AlPor-Ph (Figure 4.2.S22 top spectra) showed peaks at 447, 600 and 685 nm along with broad peaks at 791 and 882 nm. The radical anion of AlPor-Ph (Figure 4.2.S22 bottom spectra) exhibited peaks at 432, 570, 610 and 645 nm. The Soret band red-shifted from 418 nm to 432 nm. The radical cation peaks of TTF were located at 450 and 610 nm (Figure 4.2.S23).

As shown in Figure 4.2.9a, femtosecond transient spectra obtained for the AlPor-Ph-H$_2$Por dyad were rather complex revealing peaks corresponding to both AlPor and H$_2$Por entities. That is, negative peaks at 509, 545, 645, and 716, and positive peaks at 448, 528, 565, 618, 671, 1064 and 1240 nm were observed. However, it was possible to secure evidence for singlet-singlet energy transfer from AlPor to H$_2$Por. At the early time scale, the depleted peaks of AlPor located at 545 and 585 nm recovered faster than that observed for pristine AlPor while the negative growth of stimulated emission of H$_2$Por at 646 and 716 nm were much faster than that seen in pristine H$_2$Por. This was also the case for the singlet peaks of H$_2$Por at 1064 nm and
AlPor at 1240 nm; the former grew in intensity at the expense of the latter. By taking the lifetime and decay rate constant of the AlPor peak at 1240 nm (3.31 ns, 3.02 × 10^8 s⁻¹) and using a lifetime and rate constant of ¹AlPor* (5.80 ns, 1.72 × 10^8 s⁻¹), a rate constant for energy transfer process, \( k_{\text{ET}} \) in this dyad was estimated to be 1.78 × 10^8 s⁻¹. As predicted, coordination of py to AlPor-Ph-H₂Por (which forms hexa-valent Al center) had no noticeable changes in its spectral features (Figure S24).

Figure 4.2.9. (a) Femtosecond transient absorption spectra and (b) decay profile at 1240 nm of AlPor-Ph-H₂Por in \( \alpha \)-DCB.

From steady-state experiments it was postulated that quenching of the ¹AlPor* state in the dyads TTF-Ph<sub>n</sub>-py→AlPor-Ph (n = 0, 1) is due to the electron transfer from TTF to ¹AlPor* unit. To verify this claim femtosecond transient absorption studies were performed on these dyads. As shown in Figure 4.2.10a, upon excitation of the dyad (TTF-py→AlPor-Ph), absorbance with maximum in the ~450 nm region characteristic of ¹AlPor* state was observed. Subsequently, the ¹AlPor* state is evolved into the TTF⁺•AlPor⁻• charge-separated state with a rate constant (\( k_{\text{ET}} \)) of 1.25 × 10¹⁰ s⁻¹ (see Figure 4.2.10b). This state can be readily identified by distinctive peaks for TTF⁺ in the ~496 nm region, and at ~570 and ~610 nm for the counterpart
AlPor\(^{-}\). Similarly, the transient absorption spectra of TTF-Ph-py→AlPor-Ph dyad was measured and the spectra are shown in Figure 4.2.S25. As anticipated, the charge-separated state TTF\(^{**}\)AlPor\(^{-}\) formed with a rate constant of 8.33 × 10\(^9\) s\(^{-1}\), which is slightly slower than the rate constant in TTF-py→AlPor-Ph. This is because of the increased distance between TTF and AlPor in TTF-Ph-py→AlPor-Ph due to an extra phenyl spacer unit. Overall, these results conclude the occurrence of electron transfer in TTF-Ph\(_n\)-py→AlPor-Ph (n = 0, 1) dyads that are consistent with steady-state fluorescence results.

Figure 4.2.10. (a) Femtosecond transient absorption spectra, and (b) decay profile at 1240 nm of TTF-py→AlPor-Ph (1:3 ratio) in o-DCB.

For transient absorption studies, triads (TTF-py→AlPor-Ph-H\(_2\)Por and TTF-Ph-py→AlPor-Ph-H\(_2\)Por) were prepared by adding the TTF-py or TTF-Ph-py (0.15 mM) to AlPor-Ph-H\(_2\)Por (0.05 mM) in o-DCB. The resultant solutions were excited at 400 nm where the absorption ratio of AlPor and H\(_2\)Por is 1:2. As shown in Figure 4.2.S26, the transient spectra of the triads appeared to be even more complex and identifying spectral features was a challenging task. This is because of two reasons: (i) due to moderate binding constant between TTF-py (or TTF-Ph-py)
and AlPor-Ph-H$_2$Por, the experimental solutions comprised only ~25% (0.013 mM) of the triad and the remaining ~75% of the sample existed as individual components, and (ii) due to strong spectral presence of AlPor and H$_2$Por in the monitoring visible region, it was difficult to isolate the TTF$^{**}$, AlPor$^{-*}$ and H$_2$Por$^{-*}$ radical ion peaks. However, the early spectral features (<1 ps after excitation) to some extent suggest the occurrence of electron transfer and electron shift processes in presence of TTF unit. Figure 4.2.11 shows the absorption changes at 500 fs after excitation of the sample. There are significant differences in spectral features of the dyad and its corresponding triads. The absorbance change ($\Delta$A) diminished to half for TTF-py$\rightarrow$AlPor-Ph-H$_2$Por triad compared to its reference dyad (AlPor-Ph-H$_2$Por) suggesting a rapid quenching of $^1$AlPor$^*$ state by the electron transfer from TTF unit. In the case of TTF-Ph-py$\rightarrow$AlPor-Ph-H$_2$Por triad, the absorbance change was found to be higher than the TTF-py$\rightarrow$AlPor-Ph-H$_2$Por triad, which indicates the electron transfer is slightly slower because of the extra phenyl ring between the TTF and AlPor units. The formation of TTF$^{**}$ and AlPor$^-*$, expected to result in absorption changes in the 450-500 nm and 600-650 nm region, respectively, were also observed, although overlapped with other peaks in this wavelength region. After 1 ps, the visible region is obscured by intense spectral features from the dyad (unbound 75%). Hence, it was challenging to track the time course of electron shift and charge recombination processes. However, further evidence for electron transfer came from the near-IR peak of AlPor as it undergoes an additional quenching (see Figure 4.2.11b & c and Figure 4.2.9b). On the other hand, evidence for the electron shift from AlPor$^{-*}$ to H$_2$Por is inferred from the observed low efficiency of energy transfer from $^1$AlPor$^*$ to H$_2$Por. As shown in Figure S27, depleted emission of the free-base porphyrin at ~647 nm decreases which suggest the $^1$AlPor$^*$ state is being involved in the
electron transfer process rather than energy transfer in the triad (TTF-py→AlPor-Ph-H2Por or TTF-Ph-py→AlPor-Ph-H2Por) molecule.

Figure 4.2.11. Femtosecond transient absorption spectra of (a) AlPor-Ph-H2Por (black), TTF-py→AlPor-Ph-H2Por (red) and TTF-Ph-py→AlPor-Ph-H2Por at a delay time of 500 ps, (b) decay profile at 1244 nm of TTF-py→AlPor-Ph-H2Por and (c) decay profile at 1244 nm of TTF-Ph-py→AlPor-Ph-H2Por in o-DCB.

(b) In acetonitrile: To establish the evidence for a charge-separation in polar solvents, femtosecond transient absorption studies were performed on the dyad (AlPor-Ph-H2Por) and its reference monomers (AlPor-Ph and H2Por-Ph) in acetonitrile. As shown in Figure 4.2.S28a, for AlPor-Ph there were instantly populated S1 and S2 states, bleaching due to both absorption (558 nm) and emission (598 and 660 nm) peaks, positive peak maxima (450, 580, 627, and 704 nm) and a near-infrared (1205 nm) peak was observed. The other reference compound, H2Por-Ph (Figure 4.2.S29a) showed instantaneous formation of the S1 and S2 states, bleaching due to the absorption (505, 539 and 581 nm) and stimulated emission (635 and 707 nm) peaks, positive peaks (440, 530, 558, 616, and 680 nm) and also the near-infrared (1023 nm) peak. The
observed near-infrared peaks for AlPor-Ph and H2Por-Ph correspond to singlet-singlet transition and they decayed slower than the 3 ns monitoring window of our instrument setup (Figures 4.2.S28b & S29b). Figure 4.2.12 shows the femtosecond transient absorption spectra of AlPor-Ph-H2Por in acetonitrile at 200 ps (see Figure 4.2.S30 for spectra at other delay times). The spectra revealed peaks from both the AlPor and H2Por units. However, the observed peaks decayed rapidly while the bleaching at 505 and 558 nm was recovered faster than their pristine compounds. The formation of AlPor** and H2Por**, anticipated to result in absorption changes in the 540 - 590 nm and 600 - 650 nm region, respectively, were also observed, see Figure 4.2.12a inset. By monitoring the near-infrared peak of AlPor, the rate of charge separation was estimated to be 1.79 × 10^8 s⁻¹, see Figures 4.2.12b. Transient absorption studies on triad solutions were not carried out because the experimental solutions contain a very small amount of triad molecule. These lower concentrations are caused by the competition between TTF-Phₙ-py and CH₃CN binding to the Al center.

Figure 4.2.12. (a) Femtosecond transient absorption spectra of AlPor-Ph (red), H2Por-Ph (blue) and AlPor-Ph-H2Por (green) at 200 ps, and (b) time profile at ~1205 nm of AlPor-Ph-H2Por in acetonitrile.
Modulation of energy transfer into electron transfer. Figure 4.2.13 summarizes the photoinduced processes that are involved in the dyad and its corresponding triads. Upon photoexcitation of AlPor in the dyad in non-coordinating solvents (dichloromethane or o-DCB), AlPor moiety serves as an antenna by transferring its singlet excitation to the H$_2$Por with a rate constant ($k_{\text{EnT}}$) of $1.78 \times 10^8$ s$^{-1}$. In contrast, the same AlPor in dyad acts as an electron acceptor in the presence of TTF (i.e. formation of triad) and it initiates a sequential electron transfer between TTF, AlPor and H$_2$Por components. In triads, photoexcitation of the AlPor results in rapid electron transfer from TTF to $^1$AlPor$^*$ with a rate constant ($k_{\text{ET}}$) of $8.33 \times 10^9$ – $1.25 \times 10^{10}$ s$^{-1}$ to yield a primary radical pair TTF$^{**}$-AlPor$^{*-}$-H$_2$Por. This is followed by electron shift to produce the final charge separated state TTF$^{**}$-AlPor-H$_2$Por$^{*-}$. The electron transfer between TTF and $^1$AlPor$^*$ redox centers was found to be nearly two orders of magnitude faster than the energy transfer between $^1$AlPor$^*$ and H$_2$Por entities. Consequently, the electron transfer outperforms the energy transfer process and generates the primary radical ion-pair, which ultimately undergoes an electron shift to yield the final radical ion-pair. Therefore, these results represent the modulation of energy transfer into sequential electron transfer via axial coordination TTF moiety.
As revealed by transient spectral studies, energy transfer is the main quenching mechanism for $^{1}\text{AlPor}^*$ in the dyad, AlPor-Ph-H$_2$Por in nonpolar solvents. However, this is no longer the case in the triads (TTF-Ph$_n$-py→AlPor-Ph-H$_2$Por, n = 0,1) where a new decay pathway for $^{1}\text{AlPor}^*$ state opens up in the presence of electron rich TTF moiety. The optical studies identified electron transfer as the new process from TTF to $^{1}\text{AlPor}^*$, and moreover, it was found to be much faster than the energy transfer from $^{1}\text{AlPor}^*$ to H$_2$Por. These results can be explained by using the electronic coupling between TTF and AlPor units as well as the Gibbs free energy change. Our recent DFT studies on TTF-Ph$_n$-py→AlPor-Ph (n = 0,1), where the py appended TTF derivatives were bound to pristine AlPor-Ph through a coordination bond in axial direction, revealed a significant delocalization of their molecular orbitals (HOMO and LUMO) onto the bridging unit.\textsuperscript{42,45} As anticipated, the HOMO and LUMO are localized primarily on the TTF and AlPor units, respectively. However, in both cases some delocalization onto the Ph and/or Py bridge occurs. This results in a substantial electronic coupling between donor (TTF)
and acceptor (AlPor) units, which could potentially favors the electron transfer process. On the other hand, Figure 4.2.5 reveals that the electron transfer process is more exergonic (−0.59 eV) than the energy transfer (−0.15 eV) process. Together with strong electronic coupling and large driving force, it is reasonable to expect that the $^1$AlPor$^*$ state in the triad would quench strongly by rapid electron transfer rather than energy transfer.

4.2.3 Conclusions

The above presented results show that it is possible to construct multicomponent ‘Donor-AlPor-Acceptor’ systems in axial direction by exploiting the unique properties of the AlPor. Excited state properties revealed that energy transfer (major) and electron transfer (minor) from $^1$AlPor$^*$ to H$_2$Por coexist in the dyad (AlPor-Ph-H$_2$Por) molecule. However, the relative ratio can be modulated: (i) by changing the solvent polarity or (ii) by converting the dyad (AlPor-Ph-H$_2$Por) into triad (TTF-Ph$_n$-py→AlPor-Ph-H$_2$Por, n = 0,1) using the secondary electron donor (TTF) through axial linkage. These results represent the first such example where energy donor is converted into electron acceptor/donor through axial coordination of TTF moiety. However, the pyridine unit was found to be less optimal for linking the TTF to the dyad molecules. Because of its moderate binding constant, the equilibrium in triad solutions always pushed more towards the dyad in our experimental solutions, see Figure 1. This hampered the tracking of electron shift and charge recombination processes in the triad molecule. Recent studies suggest that imidazole binds two orders of magnitude stronger than pyridine. Currently, we are exploring these ideas in construction of new triads with a better association constant.
4.2.4 Supporting Information

Scheme 4.2.S1. Synthesis of free-base porphyrin derivatives. Reaction conditions: (i) BF₃(OEt)₂, dichloromethane, 3 h, room temperature, N₂ (ii) p-chloranil, 12 h (iii) TFA, HCl, reflux, 48 h.

Scheme 4.2.S2. Synthesis of investigated dimers AlPor-Ph-H₂Por. Reaction conditions: dichloromethane, 12 h, room temperature, N₂.

Preparation of H₂Por-Ph-COOCH₃. 4-Methylcarboxybenzaldehyde (0.70 g, 4.3 mmol), pentafluorobenzaldehyde (2.50 g, 12.8 mmol) and pyrrole (1.15 g, 17.2 mmol) were dissolved in 2.5 L of dry dichloromethane. The resultant solution was purged with N₂ for 30 min followed by the addition of BF₃·Et₂O (0.43 mL, 3.44 mmol) and the solution was stirred at room
temperature. To protect the reaction from light the flask was covered by aluminum foil. After 3 h the reaction turns brown solution and was added p-Chloranil (8.35 g, 34.4 mmol). The dark solution was stirred for 12 h, and then concentrated under reduced pressure. The residue was first purified by silica chromatography (dichloromethane:hexane = 50:50) to obtain a crude mixture. The mixture was then redissolved in 400 mL dichloromethane and washed with 3 x 200 mL of 0.5 M NaOH to remove most of the p-chloranil. The solution was dried with Na₂SO₄, concentrated and purified by chromatography using dichloromethane:hexane (= 70:30) to afford desired compound as purple solid. Yield = 1.0 g (24%). Mass (ESI): m/z 943.1175 for [M+1]⁺, calculated 943.1190 for C₄₆H₁₈F₁₅N₄O₂. ¹H NMR (300 MHz, CDCl₃): 8.92 (m, 6H), 8.83 (d, 2H, J = 6.0 Hz), 8.48 (d, 2H, J = 6.0 Hz), 8.31 (d, 2H, J = 9.0 Hz), 4.31 (s, 3H), -2.87 (bs, 2H).

Figure 4.2.S1. ¹H NMR (300 MHz) spectrum of H₂Por-Ph-COOCH₃ in CDCl₃.
Preparation of H$_2$Por-Ph-COOH. H$_2$Por-Ph-COOCH$_3$ (100 mg, 0.11 mmol) was dissolved completely in 10 mL of TFA. To this 10 mL of con.HCl was added and resultant solution was heated at 90°C. After 48 h reaction was added to the 50 ml ice water and neutralized with saturated NaHCO$_3$. The resultant suspension was extracted with dichloromethane (3 × 100 ml) and pass through anhydrous Na$_2$SO$_4$. Solvent was evaporated on obtained crude was subjected to column chromatography with SiO$_2$ gel. Column was eluted with dichloromethane:methanol (= 95:5) and collect the last polar band. Solvent was evaporated and crude was washed with hexane to get pure desired product as purple solid. Yield = 93 mg (95%). ESI MS: m/z 929.1012 for [M+1]$^+$, calculated 929.1034 for C$_{45}$H$_{16}$F$_{15}$N$_4$O$_2$. $^1$H NMR (300 MHz, CDCl$_3$): 8.91 (m, 8H), 8.58 (d, 2H, J = 8.0 Hz), 8.37 (d, 2H, J = 8.0 Hz), −2.85 (bs, 2H).

Figure 4.2.S2. $^1$H NMR (300 MHz) spectrum of H$_2$Por-Ph-COOH in CDCl$_3$. 
Figure 4.2.S3. $^1$H NMR (300 MHz) spectrum of AlPor-Ph-H$_2$Por in CDCl$_3$.

Figure 4.2.S4. $^1$H NMR (300 MHz) spectrum of H$_2$Por-Ph-COOH (top) and AlPor-Ph-H$_2$Por (bottom) in CDCl$_3$. 
Figure 4.2.S5. $^1$H NMR (300 MHz) spectrum of TTF-Ph-py→AlPor-Ph-H$_2$Por in CDCl$_3$.

Figure 4.2.S6. UV-visible absorption spectra of dimer AlPor-Ph-H$_2$Por (green) and its reference compounds AlPor-Ph (red) and H$_2$Por-Ph (blue) in acetonitrile.
Figure 4.2.S7. UV-visible absorption spectra of TTF-py (orange) and TTF-Ph-py (maroon) in dichloromethane.

Figure 4.2.S8. (a) Absorption and (b) fluorescence titration of AlPor-Ph-H2Por with TTF-Ph-py in dichloromethane. The insets show the Benesi-Hildebrand plot of the change of absorbance at 603 nm. TTF-Ph-py was added up to $1.88 \times 10^{-3}$ M in 20 μL ($2.22 \times 10^{-4}$ M) increments to 1 mL ($6 \times 10^{-5}$ M) solution of dimer. The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.
Figure 4.2.S9. (a) Absorption (b) fluorescence titration of AlPor-Ph-H₂Por with TTF in dichloromethane. TTF was added up to $1.88 \times 10^{-3}$ M in $20 \mu$L ($2.22 \times 10^{-4}$ M) increments to 1 mL ($6 \times 10^{-5}$ M) solution of dimer. The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.

Figure 4.2.S10. (a) Absorption and (b) fluorescence titration of AlPor-Ph-H₂Por with py in dichloromethane. The insets shows the Benesi-Hildebrand plot of the change of absorbance at 603 nm. Py was added up to $1.88 \times 10^{-3}$ M in $20 \mu$L ($2.22 \times 10^{-4}$ M) increments to 1 mL ($6 \times 10^{-5}$ M) solution of dimer. The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.
Table 4.2.S1. UV-visible absorption titration data and binding constants in dichloromethane.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$K$ ($M^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlPor-Ph-H$_2$Por</td>
<td>-</td>
</tr>
<tr>
<td>TTF-py→AlPor-Ph-H$_2$Por</td>
<td>1882</td>
</tr>
<tr>
<td>TTF-Ph-py→AlPor-Ph-H$_2$Por</td>
<td>2041</td>
</tr>
<tr>
<td>py→AlPor-Ph-H$_2$Por</td>
<td>2415</td>
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<td>796</td>
</tr>
<tr>
<td>py→AlPor-Ph</td>
<td>796</td>
</tr>
</tbody>
</table>

Figure 4.2.S11. Cyclic voltammograms of AlPor-Ph (red), H$_2$Por-Ph (blue) and AlPor-Ph-H$_2$Por (green) in 0.1 M TBAP dichloromethane. Data were measured with ferrocene as an internal standard. Note that the oxidation at 0.48 V in all voltammograms is due to the ferrocene. Scan rate 25 mV/sec.
Figure 4.2.S12. Absorption (black) and fluorescence (red) spectra of (a) AlPor-Ph and (b) H2Por-Ph at room temperature.

Figure 4.2.S13. Phosphorescence spectra of AlPor-Ph (red) and H2Por-Ph (blue) in CH2Cl2:C2H5OH (1:1) at 77K.
Figure 4.2.S14. Energy level diagram for the dyad in acetonitrile. Black dashed lines represent electron transfer.

Figure 4.2.S15. (a) Spectral overlap between investigated porphyrin units: AlPor fluorescence spectrum (red) and H$_2$Por absorption spectrum (blue) in dichloromethane. (b) Steady-state fluorescence spectra of AlPor-Ph-H$_2$Por (green), AlPor-Ph (red), H$_2$Por-Ph (blue) and the calculated spectrum of H$_2$Por-Ph+AlPor-Ph (orange) with excitation at 640 nm in dichloromethane.
Figure 4.2.S16. (a) Spectral overlap between investigated porphyrin units: AlPor fluorescence spectrum (red) and H$_2$Por absorption spectrum (blue) in acetonitrile. (b) Steady-state fluorescence spectra of AlPor-Ph-H$_2$Por (green), AlPor-Ph (red), H$_2$Por-Ph (blue) and the calculated spectrum of H$_2$Por-Ph+AlPor-Ph (orange) with excitation at 640 nm acetonitrile.

Figure 4.2.S17. Absorption (solid) and corrected fluorescence excitation (dashed) spectra of triad TTF-Ph-py→AlPor-Ph-H$_2$Por in dichloromethane and the spectra were normalized between 610-650 nm. TTF-Ph-py and AlPor-Ph-H$_2$Por are present in $1.88 \times 10^{-3}$ M and $6 \times 10^{-5}$ M in solution, respectively.
Figure 4.2.S18. (a) Femtosecond transient absorption spectra and (b) decay profile at 1247 nm of AlPor-Ph in o-DCB.

Figure 4.2.S19. (a) Femtosecond transient absorption spectra and (b) decay profile at 1061 nm of H2Por-Ph in o-DCB.
Figure 4.2.S20. Fluorescence decay curve of (a) AlPor-Ph (collected at 608 nm) and (b) H$_2$Por-Ph (collected at 708 nm) in dichloromethane. Excitation wavelength at 406 nm.

Figure 4.2.S21. Spectral changes during the reduction of H$_2$Por-Ph at -0.87 V in o-DCB.
Figure 4.2.S22. Spectral changes during the oxidation (top) and reduction (bottom) of AlPor-Ph at 1.12V and -0.97V, respectively in o-DCB.

Figure 4.2.S23. Spectral changes during the oxidation of TTF-py at 0.69 V in o-DCB.
Figure 4.2.S24. Femtosecond transient absorption spectra of py→AlPor-Ph-H₂Por in o-DCB.

Figure 4.2.S25. (a) Femtosecond transient absorption spectra and (b) decay profile at 1257 nm of TTF-Ph-py→AlPor-Ph in o-DCB.
Figure 4.2.S26. Femtosecond transient absorption spectra of (a) TTF-py→AlPor-Ph-H₂Por, and (b) TTF-Ph-py→AlPor-Ph-H₂Por in o-DCB.

Figure 4.2.S27. Femtosecond transient absorption spectra of AlPor-Ph-H₂Por (black), TTF-py→AlPor-Ph-H₂Por (red) and TTF-Ph-py→AlPor-Ph-H₂Por (blue) in o-DCB at different times after excitation.
Figure 4.2.S28. (a) Femtosecond transient absorption spectra of AlPor-Ph and (b) decay profile at 1213 nm in acetonitrile.

Figure 4.2.S29. (a) Femtosecond transient absorption spectra of H₂Por-Ph and (b) decay profile at 1020 nm in acetonitrile.
4.3 Ultrafast Charge Separation and Charge Stabilization in Axially Linked ‘Tetrathiafulvalene-Aluminum(III) Porphyrin-Gold(III) Porphyrin’ Reaction Center Mimics*

4.3.1 Introduction

Photosynthesis is nature’s most well-designed process, in which sunlight is converted into chemical energy. In this process, the fundamental reactions such as photoinduced energy transfer (EnT) and electron transfer (ET) between photosynthetic molecular components are well optimized to drive the desired reactions towards conversion of solar energy into chemical energy. Over the last few decades, a significant amount of progress has been achieved in terms of understanding the factors that govern EnT and ET in photosynthesis by using multi-component synthetic models with the objective of tapping the solar energy for future energy needs. Within these synthetic models, porphyrin (Por) molecules have emerged as promising building blocks for construction of multi-component donor-Por-acceptor systems where they mimic the role of chlorophyll pigment of natural photosynthesis. This is because porphyrins are

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easy to functionalize, absorb strongly in the visible region, are often highly fluorescent, have rich redox chemistry, and moreover their optical and redox properties are easily tunable.\textsuperscript{18} However, most of these model compounds are based on the transition metal porphyrins. Moreover, their photoinduced processes are focused along the plane of the porphyrin. Very few examples are known where the photoinduced processes are in axial or perpendicular direction to the porphyrin plane.\textsuperscript{19-25} This is mainly because of the synthetic challenges where two ligands cannot be attached using transition metal porphyrins. This problem can be addressed by using main group element porphyrins, such as aluminum(III) porphyrin,\textsuperscript{26-29} tin(IV) porphyrin\textsuperscript{27, 30-36} or phosphorus(V) porphyrins,\textsuperscript{27, 30, 37-40} which generally have one or two axial bonds and they can be utilized to attach redox active electron donor (D) and/or acceptor (A) units.

Among the main group porphyrins, aluminum(III) porphyrins (AlPor) are unique, because the axial hydroxide of AlPor reacts with carboxylic acids to form covalent ester linkages while Lewis bases such as pyridine and Lewis acid.\textsuperscript{41-46} The combination of these properties makes AlPor a unique candidate for constructing ‘axial-bonding’ type multi-component D-AlPor-A systems. Over the last few years, we have reported a few novel AlPor based D-AlPor-A systems consisting of three-dimensional (3D) fullerene or two-dimensional (2D) naphthalenediimide as an electron acceptor; and ferrocene, tetrathiafulvalene or phenothiazine entities as secondary electron donors.\textsuperscript{47-51} In these systems, the EnT and ET reactions were investigated in the axial direction as a function of electronic coupling, orientation, reorganization energy, and the distance between donor and acceptor units. More recently, we reported AlPor based dyad (AlPor-Ph-H\textsubscript{2}Por) where axially bound fluoro-substituted free-base porphyrin (H\textsubscript{2}Por) was
projected as a two-dimensional (2D) electron acceptor to study the electron transfer in axial direction. However, due to the strong spectral overlap between AlPor emission and H₂Por absorption, it was found that the H₂Por unit acts as an energy acceptor rather than electron acceptor. By altering the optical and redox properties of axial H₂Por unit it is possible to change its role in photoinduced processes. One-way to tune the optical and redox properties of axial H₂Por unit is metalation.

In the present study we have chosen gold(III) as a metal ion because its insertion (that is formation of AuPor⁺) results in: (i) decrease in spectral overlap between AlPor emission and AuPor⁺ absorption, (ii) positive shift in redox potentials, and (iii) increase in the first excited singlet state of acceptor porphyrin (AuPor⁺). Together with these alterations, electron transfer is expected to outcompete the singlet-singlet energy transfer from AlPor to AuPor⁺ in newly synthesized dyad AlPor-Ph-AuPor⁺ (see Chart 4.3.1) and thus guarantee the sequential electron transfer in its corresponding triads (TTF-py→AlPor-Ph-AuPor⁺ and TTF-Ph-py→AlPor-Ph-AuPor⁺, see Figure 4.3.1) where the electron transfer could be studied in axial direction as a function of distance. On the other hand, gold(III) porphyrins are often used as electron acceptors in D-A systems. Due to the heavy atom effect of gold metal, its first excited singlet state undergoes rapid intersystem crossing to form a triplet state. The formed triplet state can undergo electron transfer and it can be involved in triplet–triplet energy transfer processes. Hence, gold(III) porphyrin as an electron acceptor in the present study will enable us to study the participation of its triplet state in photoinduced processes. We have chosen tetrathiafulvalene (TTF) as the secondary donor because of its strong electron donating ability, which makes it an excellent candidate as a reductive electron quencher or hole acceptor in D-A systems.
The general structures of the dyad and its corresponding triads are shown in Chart 4.3.1 and Figure 4.3.1, where the TTF and fluoro-substituted gold(III) porphyrin (AuPor⁺) units are located on opposite faces of the AlPor. We will show that efficient ultrafast electron transfer occurs between AlPor and AuPor⁺ in the dyad as well as triads. Furthermore, formed primary charge separated state is stabilized by charge shift from TTF unit in the case of triads.

Scheme 4.3.1. Structural information of investigated compounds in this study.

Figure 4.3.1. Formation of vertically arranged self-assembled supramolecular triads through Lewis acid-base interactions.
4.3.2 Results and Discussion

4.3.2.1 Synthesis

Gold(III) metalation was performed by using AuCl₃ according to the reported methods. However, low yields (20-25%) were obtained in our experimental conditions. Despite many other decent methods for gold metalation reported in the literature, we used this route due to limitations of our chemical inventory. The counter ion exchange was performed by dissolving the chloride salt in methanol and then precipitating as PF₆ salt by addition of saturated aqueous NH₄PF₆. The dyad, AlPor-Ph-AuPor⁺, was prepared in quantitative yields (Scheme 4.3.S2) by reacting equal molar ratios of AlPor-OH and AuPor-Ph-COOH.PF₆ in dichloromethane. Formation of the dyad was monitored by NMR spectroscopy. Obtained dyad was stored in a freshly prepared CaCl₂ desiccator prior to optical studies. The triads shown in Figure 4.3.1 were assembled by using the dyad (AlPor-Ph-AuPor⁺) and TTF-py/TTF-Ph-py derivatives in non-coordinating solvents. Lewis acid-base interactions were utilized to build these vertically arranged supramolecular self-assembled triads. NMR, UV-visible absorption and steady-state fluorescence titrations were employed to monitor the formation of triads. However, the formed self-assembled triads could not be isolated.

4.3.2.2 Structural Characterization

The mass spectrum of dyad AlPor-Ph-AuPor.PF₆ showed peaks at 1761 and 639 ascribable to the mass (m/z) of [M–PF₆]⁺ and [M–PF₆–axial Por]⁺, respectively. The ¹H NMR spectra of the dyad (AlPor-Ph-AuPor⁺) and its axial unbound component (AuPor⁺-Ph-COOH) were measured in CDCl₃ and are shown in Figure 4.3.S5 (top spectrum) and Figure 4.3.S3, respectively. As expected, shielding effects are observed for the proton of axial AuPor⁺. Protons
$a$ and $b$ that appear at 8.55 and 8.25 ppm in free AuPor$^+$-Ph-COOH compound are shifted to 5.60 and 7.26 ppm, respectively due to the ring current effect of the porphyrin macrocycle. Similarly, resonances due to the $\beta$-protons ($c$, $d$ and $e$) are also shifted upfield compared to the corresponding resonances in the spectrum of compound AuPor$^+$-Ph-COOH. These chemical shifts ($\delta$) agree well with those of axial bonding type porphyrin systems. However, the observed peaks are very broad and were found to be sensitive towards the concentration of the dyad, see Figure 4.3.S5. Interestingly, at higher concentration (Figure S5, bottom spectrum) an additional peak at 5.11 ppm was observed for protons $a$ suggesting that in some portion of the sample, the Al centre of AlPor exists in the hexavalent state. In a typical pentavalent AlPor, the Al centre lies out of the porphyrin plane and is pulled into the plane when it converts to the hexavalent complex due to the axial coordination. If such a phenomenon exists in the dyad solution, the axial AuPor$^+$ could be brought even closer to AlPor ring, which may cause an additional shielding on protons $a$ and therefore lower chemical shift. Since the spectrum is measured in non-coordinating solvent (CDCl$_3$), the possibility of the axial coordination by solvent can be safely ruled out. However, careful examination of the dyad structure reveals that the valency conversion is feasible if the counter ion PF$_6^-$ from the dyad molecule is involved in such coordination, Figure 4.3.2. The strong electron withdrawing nature of AuPor$^+$ (which will be discussed in the electrochemistry section) enhances the Lewis acidity of the Al center that can readily coordinate to a fluorine atom of PF$_6^-$ ion, which typically acts as a strong Lewis base. Such behaviour has been noticed previously in other systems. This type of Lewis acid-base interaction brings the dyad molecules closer to each other in solution and perhaps forms molecular aggregates. Moreover, this probability would be greater at higher concentrations.
Figure 4.3.2 shows the proposed hexavalent complex and it clearly explains the observed broad peaks and additional chemical shift for protons a at higher concentrations in a non-coordinating solvent. In contrast, coordinating solvents (e.g. CD$_3$CN) resulted in a well-resolved spectrum because the solvent is present in large excess and its coordination out competes the PF$_6^-$ coordination with Al centre. Consequently, dyad molecules are expected to lie far from each other in solution. Therefore a well-resolved spectrum is observed, Figure S6. Additionally, the Al centre is continually present in the hexavalent state, hence only one peak is observed for the protons a (at 5.00 ppm). The chemical shift of the $^{31}$P NMR signal due to the counter ion phosphorus atom in the dyad appears at −143.38 ppm. Overall, the upfield shift of axially linked porphyrin confirms the structure of the investigated dyad molecule.

As shown in Figure 4.3.1, the self-assembled supramolecular triads have been assembled from the components AlPor-Ph-AuPor$^+$ and TTF-py (or TTF-Ph-py). The NMR, UV-visible absorption and fluorescence spectroscopic methods were used to monitor the formation of triads. Figure S7 shows the $^1$H NMR spectrum of a 1:1 mixture of AlPor-Ph-AuPor$^+$ and TTF-py. In the coordination complex, shielding due to the porphyrin ring causes an upfield shift of
TTF-py protons. The protons $f$, $g$, $j$ and $k$ appear at 8.61, 7.26, 6.85 and 6.37 ppm in free TTF-py, whereas in the triad they appear at 6.57, 6.63, 6.57 and 6.29 ppm. The magnitude of the shift depends on the distance of the protons from the porphyrin ring, and the pyridinyl protons ($f$ and $g$) display the greatest shift indicating that coordination occurs via the pyridinyl group. On the benzoate bridging group to the AuPor$^+$, the protons $a$ closest to the porphyrin ring show an increased upfield shift upon coordination. Overall, the observed changes in chemical shift suggest the formation of self-assembled triad TTF-py$\rightarrow$AlPor-Ph-AuPor$^+$. Analogous results were obtained from the triad TTF-Ph-py$\rightarrow$AlPor-Ph-AuPor$^+$ (Figure S8, ESI).

4.3.2.3 UV-Visible Absorption Spectroscopy

The UV-visible spectra of dyad AlPor-Ph-AuPor$^+$ and corresponding reference compounds (AlPor-Ph and AuPor$^+$-Ph) were measured in dichloromethane and are shown in Figure 4.3.3a. The band positions (Q-bands and B- or Soret Bands) and their molar extinction coefficients are summarized in Table 4.3.1. The UV-visible absorption spectrum of the dyad reveals the absorption bands, which correspond to its reference porphyrins AlPor-Ph and AuPor$^+$-Ph. The majority of the absorbance at 406, 415, 520 and 550 nm is attributed to the AuPor$^+$ (75%), AlPor (90%), AuPor$^+$ (76%) and AlPor (80%), respectively. The molar extinction coefficients ($\epsilon$) at 415 and 550 nm, which correspond to AlPor unit, are slightly lower than that of the reference AlPor-Ph compound. Moreover, the spectrum exhibited a new absorption band at 603 nm and was found to be sensitive to the concentration of the dyad as it appears only at higher concentrations, Figure 4.3.3b. This behaviour is complementary with NMR results and supports the PF$_6^-$ ion binding to the Al centre of AlPor to form the hexavalent AlPor, Figure 4.3.2. The observed new band at 603 nm for AlPor-Ph-AuPor$^+$ is a characteristic feature of
hexavalent AlPor.\textsuperscript{47,49,50} Additionally, the lower $\varepsilon$ values for bands at 415 and 550 nm are also a typical behaviour of hexavalent AlPor as these bands diminish during the conversion of pentavalent to hexavalent Al center.\textsuperscript{47,49,50} The py-appended TTF derivatives (TTF-py and TTF-Ph-py) have relatively weak and very broad absorption bands at $\lambda = 304$ (average of 285 and 324 nm bands) and $\lambda = 435$ nm for TTF-py, and at $\lambda = 298$ and 428 nm for TTF-Ph-py (Figure 4.3.5S9, ESI).\textsuperscript{52} Overall, the absorption studies suggest that there are no interactions between basal (AlPor) and axial porphyrin (H$_2$Por or AuPor$^+$) units. Furthermore, the absorption bands of AlPor and AuPor are overlapping; therefore by choosing the wavelengths of 550/560 nm and 520 nm it is possible to excite mostly AlPor and the axial AuPor$^+$ units, respectively.

Figure 4.3.3. UV-visible absorption spectra of (a) AlPor-Ph-AuPor$^+$ (green), AuPor$^+$-Ph (blue) and AlPor-Ph (red) in dichloromethane and (b) AlPor-Ph-AuPor.PF$_6$ in dichloromethane at different concentrations.
Table 4.3.1. UV-visible absorption, fluorescence and redox potential data of investigated compounds in dichloromethane.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorption $\lambda_{\text{max}}$, nm (log $\varepsilon$)</th>
<th>Fluorescence $\lambda_{\text{ex}} = 550$ nm $\lambda_{\text{em}}$, %Q</th>
<th>Potential (vs SCE)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B-Bands Q-Bands/TTF</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AlPor-Ph</td>
<td>416 (5.74) 585 (3.42), 547 (4.32), 510 (3.44)</td>
<td>595, 646 0.91 -1.21</td>
<td></td>
</tr>
<tr>
<td>AuPor$^+$-Ph</td>
<td>404 (5.36) 554 (3.77), 520 (4.06)</td>
<td>- 1.82 -0.28, -0.82</td>
<td></td>
</tr>
<tr>
<td>AlPor-Ph-AuPor$^+$</td>
<td>406 (5.46), 415 (5.59) 604 (3.28), 586 (3.41), 549 (4.24), 521 (4.15)</td>
<td>592, 644 (88%) 0.91, 1.16 -0.29, -0.82, -1.20</td>
<td></td>
</tr>
<tr>
<td>TTF-py</td>
<td>- 435 (3.45), 324 (4.17), 285 (4.22)</td>
<td>- 0.48, 0.83 -</td>
<td></td>
</tr>
<tr>
<td>TTF-Ph-py</td>
<td>- 428 (3.64), 298 (4.48)</td>
<td>- 0.47, 0.87 -</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Redox potential were measured in dichloromethane with 0.1 M TBAClO$_4$ as a supporting electrolyte.

Figure 4.3.4a shows the absorption titrations of TTF-py vs AlPor-Ph-AuPor$^+$ in dichloromethane. Upon addition of the TTF-py, the Q band at 549 nm of AlPor is shifted to 560 nm as well as the absorbance at 604 nm increases. Isosbestic point is observed at 555 nm, indicating the formation of triad TTF-py$\rightarrow$AlPor-Ph-AuPor$^+$ in equilibrium, and the changes in the porphyrin bands are typical of axial coordination of nitrogen ligands to AlPor.$^{47, 49, 50, 52}$ Benesi-Hildebrandt analysis (Figure 4.3.4a, inset) gives a linear plot indicating that a 1:1 complex is formed, and the slope yields a binding constant ($K$) $\approx 3.3 \times 10^3$ M$^{-1}$. In a similar fashion, the binding constant $K$ was calculated from the titrations of TTF-Ph-py vs AlPor-Ph-AuPor$^+$ (Figure 4.3.510a) and found to be $3.5 \times 10^3$ M$^{-1}$. Titrations of TTF-py vs AlPor-Ph and TTF-Ph-py vs AlPor-Ph have been reported elsewhere.$^{50}$ Interesting trends were observed in $K$ values. Titrations of TTF-py (or TTF-Ph-py) vs AlPor-Ph-AuPor$^+$ resulted in a higher degree of binding ($\approx 3.3 \times 10^3$ M$^{-1}$) than that of TTF-py (or TTF-Ph-py) vs AlPor-Ph-H$_2$Por$^{52}$ ($\approx 2.0 \times 10^3$ M$^{-1}$).
and TTF-py (or TTF-Ph-py) vs AlPor-Ph\(^5\) (≈1.0 \times 10^3 \text{ M}^{-1}\). These results can be explained by the withdrawing nature of the axial subunit as it increases in order of Ph < H\(_2\)Por < AuPor\(^+\). The Al center becomes a better Lewis acid and hence it binds strongly with Lewis base pyridine. Together with NMR and UV-visible absorption titrations, formation of the triads (TTF-py\(\rightarrow\)AlPor-Ph-AuPor\(^+\) and TTF-Ph-py\(\rightarrow\)AlPor-Ph-AuPor\(^+\)) in dichloromethane solutions can be concluded.

![Absorbance and Fluorescence Spectra](image)

**Figure 4.3.4.** Titrations of AlPor-Ph-AuPor\(^+\) with TTF-py in dichloromethane. TTF-py was added up to 1.88 \times 10^{-3} \text{ M} in 20 \mu\text{L} (2.22 \times 10^{-4} \text{ M}) increments to 1 mL (6 \times 10^{-5} \text{ M}) solution of AlPor-Ph-AuPor\(^+\). (a) Absorption titrations: Inset shows the Benesi-Hildebrand plot of the change of absorbance at 603 nm. (b) Fluorescence titrations: The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations. The inset shows Job’s plot where the total concentration of [AlPor-Ph-AuPor\(^+\)]+[TTF-py] was maintained constant at 4.2 \times 10^{-5} \text{ M}.

### 4.3.2.4 Cyclic Voltammetry and Energetics

Cyclic voltammetry of newly investigated dyad and its reference compounds was measured in dichloromethane with 0.1 M TBAClO\(_4\). Ferrocene was used as an internal standard. Representative voltammograms are shown in Figure 4.3.5 and the data is summarized in Table 4.3.1. The redox processes of all the compounds are found to be one-electron reversible, based on the peak-to-peak separation values, and the cathodic-to-anodic peak current ratio. During
the cathodic scan, dyad showed three reduction processes. Based on its monomers, the observed first two processes are assigned to the first and second reduction of axial AuPor\(^+\) unit, whereas the third process is assigned to the first reduction of AlPor. While in anodic scan, dyad reveals two oxidation processes in our experimental conditions and are assigned to the AlPor. As anticipated, the dyad exhibited a combination of processes from its monomeric porphyrin units without any perturbation in their redox potentials. Thus, the observed cyclic voltammograms and redox data suggest that the porphyrin units of the dyad do not influence one another significantly. However, the redox potentials of AuPor\(^+\)-Ph shifted positively compared with its precursor pentafluorophenyl substituted free-base porphyrin (H\(_2\)Por-Ph).\(^{52}\) This is due to the presence of positive charge (+3) on the Au centre, which make the porphyrin ring further electron deficient. Hence, AuPor\(^+\) reduces at lower and oxidizes at higher potentials. The TTF derivatives (TTF-py and TTF-Ph-py) show two processes corresponding to the first and second oxidation of TTF moiety. These results have been published elsewhere.\(^{50}\)

Figure 4.3.5. Cyclic voltammograms of (a) AlPor-Ph, (b) AuPor\(^+\)-Ph and (c) AlPor-Ph-AuPor\(^+\) with 0.1 M TBACIO\(_4\) in dichloromethane. Data were measured with ferrocene as an internal standard. Note that the oxidation at 0.48 V in all voltammograms is due to the internal standard ferrocene. Scan rate 25 mV/sec.
Figure 4.3.6 shows the energy level diagram of the dyad and its corresponding supramolecular triads. The redox potentials are used in combination with optical data to estimate the energies of the radical ion pair states ($E_{CS}$) and free energy change for the charge separation ($\Delta G_{CS}$) by using the Weller equation,\textsuperscript{65, 66}

$$E_{CS} = e\left[\frac{E_{1/2}(D^{*+}/D) - E_{1/2}(A/A^{*})}{(D^{*+} + D) - (A/A^{*})}\right] + G_S$$  \hspace{1cm} (1)

$$\Delta G_{CS} = E_{CS} - E_{0-0}$$  \hspace{1cm} (2)

where $E_{1/2}(D^{*+}/D)$ is the first oxidation potential of the donor, $E_{1/2}(A/A^{*})$ is the first reduction potential of the acceptor and $G_S$ is the ion-pair stabilization energy,

$$G_S = \frac{-e^2}{4\pi\varepsilon_0\varepsilon_S R_{D-A}}$$  \hspace{1cm} (3)

where $R_{D-A}$ is the centre-to-centre distance between the donor and acceptor,\textsuperscript{67} $\varepsilon_S$ is the dielectric constant of the solvent used for the optical and redox studies, in this case dichloromethane. The lowest excited singlet state energy ($E_{0-0}$) is estimated from the crossing point of absorption and fluorescence spectra and found to be 579 nm for AlPor.\textsuperscript{52} Since AuPor was found to be non-fluorescent, the lower energy band maxima at 554 nm of absorption spectrum is taken as its lowest excited singlet state. The peak maxima of phosphorescence band at 769 and 752 nm for AlPor-Ph and AuPor*-Ph, respectively (see Figure 4.3.7) are used to estimate the lowest excited triplet states. The calculated free energy levels suggest that the lowest excited singlet state of AlPor ($^1$AlPor*) can be involved in electron transfer and hole transfer with AuPor* and TTF, respectively in the triad. However, the sequence of these processes depends on their rates. The calculated energy levels suggest that the triplet-triplet energy transfer from AuPor* to AlPor and triplet hole transfer from the excited triplet state
[\textsuperscript{3}(\text{AuPor\textsuperscript{+}})\textsuperscript{*}] to AlPor are also energetically favourable. To verify these schemes, the steady-state fluorescence and the femtosecond transient absorption studies were performed.

Figure 4.3.6. Energy level diagram of the dyad and its corresponding supramolecular self-assembled triads in dichloromethane. Black solid lines represent electron transfer or hole transfer processes.

4.3.2.5 Fluorescence Spectroscopy

Figure 4.3.7 illustrates the fluorescence spectra of the dyad and its reference compounds in dichloromethane at room temperature and the data are summarized in Table 4.3.1. The AuPor\textsuperscript{+} was found to be non-fluorescent at room temperature in our experimental conditions. This is due to the heavy atom effect induced by the Au(III) metal ion. As a result, the first excited singlet state of AuPor\textsuperscript{+} [\textsuperscript{1}(\text{AuPor\textsuperscript{+}})\textsuperscript{*}] undergoes rapid intersystem crossing (ISC) to form the triplet state.\textsuperscript{56} The dyad fluorescence was measured with excitation wavelength of 550 nm, where 80\% of light is absorbed by AlPor. As shown in Figure 4.3.7, the dyad revealed two fluorescence bands, which are similar to its reference molecule AlPor-Ph. However, their intensities are strongly (nearly 88\%) quenched. Based on the energy level diagram (Figure 4.3.6), where the \textsuperscript{1}(\text{AuPor\textsuperscript{+}})\textsuperscript{*} is higher in energy than \textsuperscript{1}AlPor\textsuperscript{*}, and also due to a weak spectral
overlap between AlPor emission and AuPor absorption (Figure 4.3.511), the energy transfer from \(^1\text{AlPor}\) to \(^0\text{AuPor}\) can be safely ruled-out. On the other hand, the electron transfer from \(^1\text{AlPor}\) to \(^0\text{AuPor}\) is exergonic (\(\Delta G_{CS}\)) by \(-1.03\) eV. Therefore, the observed strong quenching is attributed to the electron transfer process. However, the heavy atom effect of Au metal cannot be neglected in the excited state properties.

![Emission spectra of AlPor-Ph-AuPor\(^+\) (green), AlPor-Ph (red) and AuPor\(^+\)-Ph (blue) in (a) dichloromethane at room temperature, excitation wavelength of 550 nm and (b) dichloromethane:ethanol (\(= 1:1\)) at 77 K, excitation wavelength of 520 nm.](image)

Figure 4.3.7. Emission spectra of AlPor-Ph-AuPor\(^+\) dyad with increasing amounts of pyridine-linked tetrathiafulvalene (TTF-py). The excitation wavelength was adjusted to the isosbestic point at 555 nm. In the absence of TTF-py, the dyad showed AlPor bands similar to its monomeric compound AlPor-Ph. However, their intensities were strongly quenched due to the electron transfer from \(^1\text{AlPor}\) to axial AuPor\(^+\). Upon addition of TTF-py, the fluorescence bands of AlPor were further quenched. These notable spectral changes suggest the formation of TTF-py→AlPor-Ph-AuPor\(^+\) triad in the solution. The complexation of AlPor-Ph-AuPor\(^+\) with TTF-py in solution was determined by means of Job’s plot based on the
change in fluorescence intensity. Figure 4.3.4b (inset) shows that a continuous variation plot of fluorescence intensity change vs $[\text{AlPor-Ph-AuPor}^+]/([\text{AlPor-Ph-AuPor}^+]+[\text{TTF-py}])$ in dichloromethane gave a maximal value of 0.5, indicating the formation of $\text{TTF-py} \rightarrow \text{AlPor-Ph-AuPor}^+$ complex with a coordination ratio at 1:1. To explain the possible quenching mechanism, various control titrations, TTF vs AlPor-Ph-AuPor$^+$ (Figure S12b) and pyridine vs AlPor-Ph-AuPor$^+$ (Figure S13b), were carried out where no change in fluorescence intensity was observed. On the other hand, titrations of TTF-py (or TTF-Ph-py) vs AlPor-Ph revealed a strong quenching in fluorescence bands of AlPor due to the hole transfer from $^1\text{AlPor}^*$ to TTF unit and these results are published elsewhere.\textsuperscript{47, 50, 52} Thus, the most likely explanation for quenching in triad is an intramolecular photoinduced hole transfer from $^1\text{AlPor}^*$ to TTF unit and this process was found to be exergonic ($\Delta G_{CS}$) by $-0.64$ eV. Similar results were found from the titrations of TTF-Ph-py vs AlPor-Ph-AuPor$^+$ (i.e. formation of triad TTF-Ph-py $\rightarrow$ AlPor-Ph-AuPor$^+$, Figure S10b). Due to an additional phenyl spacer between the TTF and py units, there is a decrease in the electronic coupling expected, which causes a slow down in hole transfer rate. Consistent with this expectation, the quenching is weaker. Therefore, the band shifts are more pronounced in the formation of triad TTF-Ph-py $\rightarrow$ AlPor-Ph-AuPor$^+$.

To investigate the possibility of hole transfer from $^3(\text{AuPor})^*$ to AlPor in the dyad, the steady-state fluorescence spectra were measured at low temperature. Figure 4.3.7b shows the emission spectra of the dyad AlPor-Ph-AuPor$^+$ and its reference monomers AlPor-Ph and AuPor-Ph in dichloromethane:ethanol (1:1) at 77 K. Spectra were measured with excitation at 520 nm where 82% and 18% light is absorbed by AuPor$^+$ and AlPor, respectively. The AlPor-Ph showed fluorescence bands at 597 and 654 nm, as well as phosphorescence bands at 710 and 769 nm.
In contrast, the AuPor+-Ph displayed only phosphorescence bands at 685, 704 and 752 nm, which were overlapped with AlPor phosphorescence bands. As anticipated, the dyad showed combination of bands, which corresponds to the fluorescence and phosphorescence of AlPor and AuPor+ entities. Furthermore, the fluorescence and phosphorescence bands are quenched by 51% and 14%, respectively. Based on the steady-state fluorescence studies at room temperature, it is reasonable to assign the quenching of AlPor fluorescence bands at 77K to the electron transfer from $^1$AlPor* to AuPor+. On the other hand, the singlet-singlet energy transfer from $^3$(AuPor+)* to AlPor and the hole transfer from $^1$(AuPor+)* to AlPor are not viable because gold(III) porphyrins are well known to have an extremely short-lived first excited singlet state.\(^{57}\) In contrast, gold(III) porphyrins typically have a long-lived (usually 1-2 ns, see Ref. 52) excited triplet state. Therefore, in combination with suitable energy levels it is likely that the triplet-triplet energy transfer and triplet hole transfer from AuPor+ to AlPor are possible in the investigated dyad at 77K. However, the results shown in Figure 4.3.7b did not indicate any substantial evidence for these processes, i.e. the phosphorescence intensity of AuPor+ was not varied significantly in presence of AlPor unit. Consequently, we can rule out the possibility of triplet-triplet energy transfer and triplet hole transfer from AuPor+ to AlPor moiety.

4.3.2.6 Femtosecond Transient Absorption Spectroscopy

Femtosecond transient absorption studies were performed in o-DCB (instead of low boiling dichloromethane) to secure evidence of electron transfer and hole transfer processes in the dyad and triads. Samples were excited using 400 nm wavelength light where the absorbance ratio of AlPor and AuPor+ is approximately 1:5. To help interpret the transient spectral data of charge separation products, spectroelectrochemical studies were performed on
AuPor+ in o-DCB, as shown in Figure 4.3.8. The one-electron reduced product of AuPor+ revealed peaks at 612, 645 (sh) and 790 nm. In addition, the Soret band of AuPor+ located at 409 nm revealed a red-shift of 7 nm and appeared at 416 nm. These processes were found to be fully reversible. Spectroelectrochemical data of AlPor and TTF have been reported previously.52

Figure 4.3.8. Spectral changes observed during the first reduction of AuPor+-Ph in o-DCB with 0.2 M TBAClO4.

Figure 4.3.9a shows the transient absorption spectrum of AuPor+ at the indicated delay times. In agreement with literature results,53 the instantly formed S1 and S2 states populated long-living triplet excited states via intersystem crossing process. Depleted bands at 520 and 552 nm corresponding to ground state bleaching of AuPor+ and positive peaks at 585 and 628 nm were observed. Owing to very low fluorescence quantum efficiency, no strong peaks corresponding to stimulated emission of AuPor+ was observed. As expected for the excited triplet state 3(AuPor+)*, the positive peaks decayed slowly as shown by the time profile of the 630 nm peak in the Figure 4.3.9b. The decay rate constant was found to be 1.77 x 10^8 s⁻¹ (time constant = 5649 ps) which could be considered as a lower limit since the decay process lasted
beyond the monitoring time window of the instrument being 3 ns. The transient absorption
spectrum of AlPor is shown Figure S14 (ESI), and it has been reported previously.52

Figure 4.3.9. Femtosecond transient absorption spectra of AuPor*-Ph in o-DCB at the excitation
wavelength of 400 nm.

Transient spectral features of AlPor-Ph-AuPor+ dyad are shown in Figure 4.3.10a where
in addition to the singlet and triplet features of AlPor and AuPor+, transient spectral features in
the 612 nm range and at the 655 nm range (shoulder band to the main 3(AuPor+)* peak)
corresponding to the formation of AuPor* and AlPor**, respectively, were clearly observed. That
is, evidence for charge separation in the AlPor-Ph-AuPor+ dyad resulting into the formation of
AlPor**-Ph-AuPor* radical ion was established. This charge separation could originate from
1AlPor* or 3(AuPor+)* , both having excited state energy sufficient to drive this process (Figure
4.3.6). The earlier discussed phosphorescence studies revealed absence of significant
quenching of 3(AuPor+)* in the dyad at 77 K (see Figure 4.3.7b), however, at elevated
temperature electron transfer could occur from this state as the transient peaks of 3(AuPor+)*
decays faster in the dyad than in pristine AuPor+. Additionally, no evidence for triplet-triplet
energy transfer from 3(AuPor+)* to AlPor was observed indicating such a process is not
competitive. By global fitting of the time profile of the 612 nm peak, time constants for charge

258
separation and charge recombination were obtained. A rise time of 3.16 ps resulted in a rate of charge separation, $k_{CS} = 3.17 \times 10^{11} \text{ s}^{-1}$, suggesting occurrence of ultrafast charge separation in the dyad. However, the decay was found to be biexponential (Figure 4.3.10d) with time constants of 27.26 and 2557 ps, resulting into rate of charge recombination, $k_{CR} = 3.67 \times 10^{10} \text{ s}^{-1}$ and $3.91 \times 10^{8} \text{ s}^{-1}$, respectively. The flexibility of the axially linked AlPor-Ph-AuPor$^+$ dyad has been attributed as possible cause of the biexponential decay. It is important to mention here that due to the strong overlap of spectral features of AuPor• and $^{3}$(AuPor$^+$)* in the 575-700 nm region, contributions of $^{3}$(AuPor$^+$)* in the long-living component cannot be ignored, although the time constant was lower than the time constant of pristine $^{3}$(AuPor$^+$)*.

Coordinating TTF-py or TTF-Ph-py to the Al centre of the dyad resulted in TTF-py→AlPor-Ph-AuPor$^+$ and TTF-Ph-py→AlPor-Ph-AuPor$^+$ triads. Figure 4.3.10b and c show the femtosecond transient spectral data of these triads. In both spectra, peak at 612 nm corresponding to AuPor• and at 650 nm corresponding to AlPor• and an additional peak in the 490 nm range corresponding to the formation of TTF• was observed. These observations are consistent with the formation of TTF•-py→AlPor-Ph-AuPor$^+$ and TTF•-Ph-py→AlPor-Ph-AuPor$^+$ distantly separated radical ion-pairs. By analysing the time profile of the 612 nm peak corresponding to AuPor• by global fitting (Figures 10e and f), time constants for charge separation and charge recombination were arrived. In the case of TTF-py→AlPor-Ph-AuPor$^+$ triad, a rise time of 18.5 ps was obtained resulting into $k_{CS} = 5.4 \times 10^{10} \text{ s}^{-1}$ while the biexponential decay with time constants of 1318 and 1468 ps resulted in $k_{CR}$ values of $7.59 \times 10^{8} \text{ s}^{-1}$ and $6.81 \times 10^{8} \text{ s}^{-1}$, respectively. For the TTF-Ph-py→AlPor-Ph-AuPor$^+$ triad, the rise and decay time constants of the 612 nm peak were found to be 61.2 and 1484 ps resulting into $k_{CS}$
of $1.64 \times 10^{10}$ s$^{-1}$ and $k_{CR}$ of $6.74 \times 10^{8}$ s$^{-1}$, respectively. For this triad, a monoexponential decay fit was satisfactory to evaluate $k_{CR}$.

Figure 4.3.10. Femtosecond transient absorption spectra of (a) AlPor-Ph-AuPor$^+$, (b) TTF-py→AlPor-Ph-AuPor$^+$ (3:1 ratio), and (c) TTF-Ph-py→AlPor-Ph-AuPor$^+$ (3:1 ratio) in o-DCB at the excitation wavelength of 400 nm. Figures d, e and f show the time profile of transient peaks of AlPor-Ph-AuPor$^+$, TTF-py→AlPor-Ph-AuPor$^+$ and TTF-Ph-py→AlPor-Ph-AuPor$^+$, respectively.
The formation of the final charge separation product in the triads, TTF*-py→AlPor-Ph-AuPor* and TTF*-Ph-py→AlPor-Ph-AuPor* deserve special mention. There are at least two routes to form these species, viz.,

Route 1:

\[ \text{TTF-AlPor-AuPor}^+ \xrightarrow{\text{photolysis}} \text{TTF-AlPor}^+\text{-AuPor} \xrightarrow{\text{hole transfer}} \text{TTF}^+\text{-AlPor-AuPor} \]

Route 2:

\[ \text{TTF-AlPor-AuPor}^+ \xrightarrow{\text{photolysis}} \text{TTF}^+\text{-AlPor} \xrightarrow{\text{electron transfer}} \text{TTF}^+\text{-AlPor-AuPor} \]

In the first route, the initial photo process involves charge separation in AlPor-Ph-AuPor upon photoexcitation (originating either from \(1^1\text{AlPor}^*\) or \(3(AuPor^+)^*\)) to yield AlPor*-AuPor* radical ion-pair. In the second step, AlPor* could undergo subsequent hole shift to TTF to yield the distinctly separated radical ion-pair, TTF*-AlPor-AuPor*. In the second route, the initial step involves formation of TTF*-AlPor* from \(1^1\text{AlPor}^*\) state. In the subsequent step, electron migration from AlPor* to AuPor+ takes place to yield TTF*-AlPor-AuPor* radical ion-pair as the final product. The determined \(k_{CS}\) values by monitoring the time profile of AuPor* for the triads are lower than that observed for the dyad but higher than the hole transfer rates from \(1^1\text{AlPor}^*\) to TTF in the TTF-py→AlPor-Ph and TTF-Ph-py→AlPor-Ph control dyads (see Table 4.3.2).\(^52\)

These results suggest route 1 to be the main electron transfer mechanism. Importantly, \(k_{CR}\) values for the distinctly charge separated states of the triads were found to be about two orders of magnitude lower than that observed for the dyad in the absence of coordinated TTF.

These results reveal successful charge stabilization in the self-assembled via axial position supramolecular triad.
Table 4.3.2. Transient data of investigated compounds in o-DCB.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\tau_{CS} (k_{CS})$</th>
<th>$\tau_{CR} (k_{CR})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlPor-Ph-AuPor⁺</td>
<td>$3.16 \text{ ps (}3.12 \times 10^{11} \text{ s}^{-1}\text{)}$</td>
<td>$27.26 \text{ ps (}3.67 \times 10^{10} \text{ s}^{-1}\text{)},$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2557 \text{ ps (}3.91 \times 10^{8} \text{ s}^{-1}\text{)}$</td>
</tr>
<tr>
<td>TTF-py→AlPor-Ph-AuPor⁺</td>
<td>$18.5 \text{ ps (}5.40 \times 10^{10} \text{ s}^{-1}\text{)}$</td>
<td>$1318 \text{ ps (}7.59 \times 10^{8} \text{ s}^{-1}\text{)},$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$1468 \text{ ps (}6.81 \times 10^{8} \text{ s}^{-1}\text{)}$</td>
</tr>
<tr>
<td>TTF-Ph-py→AlPor-Ph-AuPor⁺</td>
<td>$61.2 \text{ ps (}1.64 \times 10^{10} \text{ s}^{-1}\text{)}$</td>
<td>$1484 \text{ ps (}6.74 \times 10^{8} \text{ s}^{-1}\text{)}$</td>
</tr>
<tr>
<td>TTF-py→AlPor-Ph</td>
<td>$80 \text{ ps (}1.25 \times 10^{10} \text{ s}^{-1}\text{)}$</td>
<td>-</td>
</tr>
<tr>
<td>TTF-Ph-py→AlPor-Ph</td>
<td>$120 \text{ ps (}8.33 \times 10^{9} \text{ s}^{-1}\text{)}$</td>
<td>-</td>
</tr>
</tbody>
</table>

4.3.2.7 Role of Axial Porphyrin (H₂Por vs AuPor⁺) in dyads and triads

Noticeable differences were observed between the investigated compounds (AlPor-Ph-AuPor⁺ and TTF-Phₙ-py→AlPor-Ph-AuPor⁺, n = 0, 1) in the present study and the compounds (AlPor-Ph-H₂Por and TTF-Phₙ-py→AlPor-Ph-H₂Por, n = 0, 1) that we recently studied.⁴⁸ The singlet-singlet energy transfer was found to be the main quenching mechanism in dyad AlPor-Ph-H₂Por where the axial porphyrin (H₂Por) acted as an energy acceptor. However, the role of H₂Por as an energy acceptor was modulated into an electron acceptor by introducing the electron rich TTF molecule to the dyad, that is formation of triad TTF-Phₙ-py→AlPor-Ph-H₂Por.⁵² In the presence of TTF, the $^1\text{AlPor}^*$ state is rapidly quenched by the hole transfer to TTF unit before the transfer of excitation to H₂Por unit. The resulting primary radical pair TTF⁺⁺-Phₙ-py→AlPor⁺⁺-Ph-H₂Por ultimately undergoes a charge shift to H₂Por and generates a final radical pair TTF⁺⁺-Phₙ-py→AlPor-Ph-H₂Por⁺⁺. This way, the H₂Por entity in the triad was forced to participate as an electron acceptor rather than energy acceptor.
Interestingly, unlike the case of AlPor-Ph-H₂Por, photoexcitation of AlPor in the AlPor-Ph-AuPor⁺ dyad resulted in electron transfer process from ¹AlPor* to the axial porphyrin (AuPor⁺). The observed differences between the dyads (AlPor-Ph-H₂Por and AlPor-Ph-AuPor⁺) can be explained by the changes that occur in optical and redox properties of the axial porphyrin (AuPor⁺) due to gold(III) metalation. Upon gold(III) metalation, the spectral overlap between AlPor emission and AuPor⁺ absorption decreases, which prevents the energy transfer process from ¹AlPor* to AuPor moiety. Moreover, facile reduction of AuPor⁺ provides a large driving force for the electron transfer process from ¹AlPor* to AuPor⁺ moiety. Together with these alterations, electron transfer becomes a favourable process between AlPor to AuPor⁺ in newly synthesized AlPor-Ph-AuPor⁺ dyad and its corresponding triads (TTF-py→AlPor-Ph-AuPor⁺ and TTF-Ph-py→AlPor-Ph-AuPor⁺). Therefore, upon excitation, the initial charge separation occurs predominantly between the AlPor and AuPor⁺ units, which results in a primary radical pair (TTF-Phₙ-py→AlPor⁺⁺-Ph-AuPor*). In a consecutive step, the formed radical pair undergoes hole transfer to TTF unit to produce a spatially well-separated radical pair (TTF⁺⁺-Phₙ-py→AlPor-Ph-AuPor*, designated as route-1) with appreciable lifetimes.

4.3.3 Conclusion

The results presented above show the successful mimicking of vertical type photosynthetic reaction centre TTF-AlPor-AuPor⁺ by exploiting the unique properties of AlPor, AuPor⁺ and TTF entities. Ground state properties suggest that there are no intramolecular interactions between molecular components of the triads. However, due to a strong electron withdrawing nature of the axial AuPor⁺, which induces Lewis acid-base interactions between the Al centre of AlPor and fluorine atom of counter ion PF₆⁻, intermolecular interactions were
found in the dyad. Optical studies revealed that the excitation of AlPor in the triad resulted in ultrafast charge separation predominantly from AlPor to AuPor\(^*\) to generate the primary radical pair TTF\(^-\)AlPor\(^*\)-AuPor\(^*\), which eventually undergoes hole transfer to yield the final radical pair TTF\(^*\)-AlPor-AuPor\(^*\). The resulting TTF\(^*\)-AlPor-AuPor\(^*\) radical pair in the triad has two orders of magnitude slower recombination than the recombination of its parent dyad, i.e. AlPor\(^*\)-AuPor\(^*\). Therefore, these results establish the successful charge stabilization in vertical type self-assembled ‘D-AlPor-A’ supramolecular triads.

4.3.4 Experimental Section

4.3.4.1 Synthesis

All chemicals and solvents used in this study were purchased from either Sigma-Aldrich Chemical Co. or Alfa-Aesar. The synthesis of 5,10,15,20-tetra(phenyl)-porphyrinatoaluminum(III)hydroxide (AlPor-OH) and the reference compound AlPor-Ph have been previously reported.\(^48\) The pyridine appended tetrathiafulvalene derivatives (TTF-py and TTF-Ph-py) and precursor porphyrins (5-(4-methylcarboxyphenyl)-10,15,20-tri(pentafluorophenyl) porphyrin \(\text{H}_2\text{Por-Ph-COOCH}_3\), from now on referred to as \(\text{H}_2\text{Por-Ph}\)), 5-(4-carboxyphenyl)-10,15,20-tri(pentafluorophenyl)porphyrin \(\text{H}_2\text{Por-Ph-COOH}\)) have been reported elsewhere, Scheme S1.\(^50\) Gold(III) porphyrin derivatives, 5-(4-methylcarboxyphenyl)-10,15,20-tri(pentafluorophenyl)porphyrinatogold(III) \(\text{AuPor-Ph-COOCH}_3\cdot\text{PF}_6\), from now on referred to as \(\text{AuPor-Ph}\cdot\text{PF}_6\) and 5-(4-carboxyphenyl)-10,15,20-tri(pentafluorophenyl)porphyrinatogold(III) \(\text{AuPor-Ph-COOH}\cdot\text{PF}_6\), were prepared according to the reported methods,\(^62\) see supplementary information for details.
4.3.4.2 Preparation of AlPor-Ph-AuPor•PF₆

AlPor-OH (10 mg, 0.015 mmol) and AuPor-Ph-COOH•PF₆ (20 mg, 0.016 mmol) were dissolved in 10 mL of dry dichloromethane. The resulting solution was sonicated for 5 min and then stirred for 12 h at room temperature under nitrogen atmosphere. The solvent was removed under reduced pressure and washed with hexane to get the pure dyad as a purple solid. Yield: 27 mg (93%). Mass (ESI): m/z 1761.2504 [M−PF₆]⁺, calculated 1761.2516 for C₈₉H₄₀AlAuF₁₅O₂N₈. ¹H NMR (300 MHz, CD₃CN) ppm: 9.64 (s, 8H), 9.41 (bs, 2H), 9.04 (m, 10H), 8.29 (bs, 8H), 7.79 (m, 12H), 7.34 (bs, 2H), 5.01 (d, 2H, J = 9.0 Hz). ¹H NMR (CDCl₃, 300 MHz) ppm: 9.42 (bs, 4H), 9.10 (m, 10H), 8.82 (bs, 2H), 8.25 (m, 8H), 7.75 (m, 12H), 7.26 (bs, 2H), 5.60 (bs, 2H). ³¹P NMR (CDCl₃, 121 MHz) ppm: −143.33.

4.3.5 Supporting Information

Scheme 4.3.S1. Synthesis of gold(III) porphyrin derivatives. Reaction conditions: (i) BF₃•(OEt)₂, dichloromethane, 3 h, room temperature, N₂ (ii) p-chloranil, 12 h (iii) TFA, HCl, reflux, 48 h (iv) & (v) AuCl₃, AcOH, NaOAc, reflux, 16 h.
Scheme 4.3.S2. Synthesis of the investigated dyad AlPor-Ph-AuPor. Reaction conditions: dichloromethane, 12 h, room temperature, N₂.

Preparation of AuPor-Ph-COOH•PF₆. H₂Por-Ph-COOH (75 mg, 0.081 mmol), AuCl₃ (70 mg, 0.23 mmol) and NaOAc (260 mg, 3.23 mmol) were added to 10 mL of acetic acid. The resulting solution was refluxed for 16 h under nitrogen atmosphere. After reaction time, the reaction mixture was poured into water and extracted with dichloromethane. The collected organic layer was dried over Na₂SO₄ and then the solvent was removed under vacuum. The obtained solid was dissolved in methanol and precipitated with aqueous saturated NH₄PF₆. The obtained precipitate was collected by filtration and air-dried. The crude product was purified by silicagel column chromatography using dichloromethane:methanol (90:10) as an eluent. Yield: 20 mg (20%). ESI MS: m/z 1123.0444 for [M−PF₆]+, calculated 1123.0459 for C₄₅H₁₃AuF₁₅N₄O₂. ¹H NMR (300 MHz, CD₃CN): 9.69 (s, 4H), 9.62 (s, 4H), 8.61 (d, 2H, J = 7.8 Hz), 8.40 (d, 2H, J = 7.8 Hz). ³¹P
NMR (112 MHz, CD$_3$CN): -143.38 (sep). 1H NMR (CDCl$_3$, 300 MHz): 9.52 (d, 2H, J = 5.32 Hz), 9.47 (s, 4H), 9.39 (d, 2H, J = 5.32 Hz), 8.54 (d, 2H, J = 8.0 Hz), 8.25 (d, 2H, J = 8.0 Hz).

Figure 4.3.S1. $^1$H NMR (300 MHz) spectrum of AuPor-Ph-COOH.PF$_6$ in CD$_3$CN. Note that the peaks at 5.45 and 3.81 ppm are due to solvent impurities.

Figure 4.3.S2. $^{31}$P NMR (121 MHz) spectrum of AuPor-Ph-COOH•PF$_6$ in CD$_3$CN.
Preparation of AuPor-Ph-COOCH$_3$•PF$_6$. H$_2$Por-Ph-COOCH$_3$ (100 mg, 0.11 mmol), AuCl$_3$ (100 mg, 0.33 mmol) and NaOAc (300 mg, 3.65 mmol) were added to 10 mL of acetic acid. The resulting solution was refluxed for 16 h under nitrogen atmosphere. After reaction time, the reaction mixture was poured into water and extracted with dichloromethane. The collected organic layer was dried over Na$_2$SO$_4$ and then the solvent was removed under vacuum. The obtained solid was dissolved in methanol and was precipitated with aqueous saturated NH$_4$PF$_6$. The obtained precipitate was collected and air dried. The crude product was purified by silicagel column chromatography using dichloromethane:methanol (90:10) as an eluent. Yield: 34 mg (25%). FAB MS: m/z 1137.0607 for [M–PF$_6$]$^+$, calcualted 1137.0616 for C$_{46}$H$_{15}$AuF$_{15}$N$_4$O$_2$. $^1$H
NMR (300 MHz, CD$_3$CN): 9.68 (s, 4H), 9.61 (d, 2H, J = 6.0 Hz), 9.53 (d, 2H, J = 6.0 Hz), 8.56 (d, 2H, J = 6.0 Hz), 8.44 (d, 2H, J = 6.0 Hz), 4.12 (s, 3H).

Figure 4.3.S4. $^1$H NMR (300 MHz) spectrum of AuPor-Ph-COOCH$_3$•PF$_6$ in CD$_3$CN. Note that the peaks at 5.45 and 3.81 ppm are due to solvent impurities.
Figure 4.3.55. $^1$H NMR (300 MHz) spectra of AlPor-Ph-AuPor•PF$_6$ at ~1 mM (top) and ~2 mM (bottom) concentrations in CDCl$_3$. 
Figure 4.3.S6. $^1$H NMR (300 MHz) spectrum of AlPor-Ph-AuPor•PF$_6$ (~2 mM) in CD$_3$CN.
Figure 4.3.S7. $^1$H NMR (300 MHz) spectrum of TTF-py→AlPor-Ph-AuPor$^+$ in CDCl$_3$.

Figure 4.3.S8. $^1$H NMR (400 MHz) spectrum of 0.6 mM TTF-Ph-py→AlPor-Ph-AuPor$^+$ in CDCl$_3$. Note that peaks at 7.55, 7.26, 7.06 are to the solvent.
Figure 4.3.S9. UV-visible absorption spectra of TTF-py (orange) and TTF-Ph-py (maroon) in dichloromethane.

Figure 4.3.S10. (a) Absorption titrations and (b) fluorescence titration of AlPor-Ph-AuPor+ with TTF-Ph-py in dichloromethane. The inset shows the Benesi-Hildebrand plot of the change of absorbance at 603 nm. TTF-Ph-py was added up to $1.88 \times 10^{-3}$ M in 20 μL ($2.22 \times 10^{-4}$ M) increments to 1 mL ($6 \times 10^{-5}$ M) solution of dyad. The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.
Figure 4.3.S11. Spectral overlap between the AlPor emission (red) and AuPor$^+$ absorption (orange) spectra in dichloromethane.

Figure 4.3.S12. (a) Absorption titrations and (b) fluorescence titration of AlPor-Ph-AuPor$^+$ with TTF in dichloromethane. TTF was added up to $1.88 \times 10^{-3}$ M in 20 μL ($2.22 \times 10^{-4}$ M) increments to 1 mL ($6 \times 10^{-5}$ M) solution of dyad. The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.
Figure 4.3.S13. (a) Absorption titrations and (b) fluorescence titration of AlPor-Ph-AuPor⁺ with py in dichloromethane. Pyridine was added up to $3.80 \times 10^{-3}$ M to 1 mL ($2.4 \times 10^{-5}$ M) solution of dyad. The excitation wavelength was chosen at the isosbestic point, 555 nm, obtained from UV-visible titrations.

Figure 4.3.S14. (a) Femtosecond transient absorption spectra and (b) decay profile at 1247 nm of AlPor-Ph in o-DCB.
CHAPTER 5

SUBPHTHALOCYANINE-BASED MULTIMODULAR DONOR-ACCEPTOR CONJUGATES

5.1 Effect ofSpacer Connecting the Secondary Electron Donor Phenothiazine in Subphtalocyanine-Fullerene Conjugates in Promoting Electron Transfer Followed by Hole Shift Process*

5.1.1 Introduction

A firm understanding of the photochemical/photophysical processes of photosynthesis,¹⁻⁵ and mimicking them in synthetic model compounds⁶⁻²⁹ are key steps in light energy harvesting as low-cost alternative to fossil fuels.³⁰⁻³⁶ In natural photosynthesis, conversion of light energy into chemical energy involves the initial absorption and funneling of light energy of appropriate wavelengths by the antenna molecules to the reaction center. The second step involves photoinduced sequential electron transfer to generate long-lived charge-separated states by using the electronic excitation energy.⁸⁻¹² The antenna system consists of chlorophyll/carotenoid chromophore arrays that efficiently capture and transport energy via singlet-singlet energy transfer mechanism. The reaction center receives the excitation energy and converts it to chemical energy in the form of trans-membrane charge separation via a multistep electron-transfer process. Studies in designing donor-acceptor hybrids mimicking these features of photosynthesis hold promise in building optoelectronic and molecular switching devices,³⁷⁻⁴⁵ in addition to light energy harvesting applications.¹³⁻³⁶ A literature survey shows that in model compounds, spacers connecting the donor and acceptor pairs play a pivotal role in governing the efficiency and kinetics of photoinduced electron transfer; however,

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276
such information on spacers connecting the secondary electron donor/acceptor in creating the anticipated long-lived charge-separated states is not fully explored.

In model donor-acceptor hybrids, fullerenes (C₆₀ and C₇₀),⁴⁶-⁴⁸ have been widely utilized as electron acceptors while porphyrins⁴⁹-⁵⁰ and phthalocyanines⁵¹-⁵³ have been traditionally used as photosensitizer electron donors. Among the different properties of fullerenes, their favorable reduction potentials⁵⁴ and the small reorganization energy associated with electron transfer reactions⁵⁵ are important properties. In majority of the studies, it has been shown that the forward electron transfer (charge separation) occurs in the “normal region” of the Marcus parabola, while the charge recombination occurs in the “inverted region” of the Marcus parabola⁵⁶-⁵⁷ for donor-acceptor systems involving fullerene as an electron acceptor.⁹-²⁵ Recently, macrocyclic compounds other than porphyrin and phthalocyanines have been explored as photosensitizer electron donors or acceptors.²⁹,⁵⁸-⁶¹ Among these, subphthalocyanine (SubPc),⁶¹ little-cousin of phthalocyanine, has gathered much attention. SubPcs are 14 π-electron macrocycles made out of three 1,3-diiminoisoindole units N-fused around a central boron atom.⁶¹ Due to their synthetic versatility and interesting optical/redox/photophysical properties, they have been sought out in applications ranging from organic photovoltaics, nonlinear optics and developing artificial photosynthetic models.⁶¹-⁷¹

Few elegant donor-acceptor systems involving SubPc to probe photoinduced electron and energy transfer have been reported in the literature.⁶¹-⁶⁹ Simple dyads involving SubPc covalently linked to fullerene reveal singlet-singlet energy transfer to the fullerene entity,⁶⁵ however, by covalent attachment of secondary electron donor group(s), one can modulate their electronic properties to observe light-induced electron transfer.⁶⁵-⁶⁹ Recently, we
reported on a pentad featuring covalently linked SubPc-C\textsubscript{60} in which the SubPc was covalently linked to three easily oxidizable phenothiazine (PTZ) entities by flexible ether linkers (compound 1 in Scheme 5.1.1). The fullerene entity was covalently linked to SubPc unit using the central boron atom. In the present study, we have newly synthesized yet another pentad featuring SubPc, C\textsubscript{60} and phenothiazine as components (compound 2 in Scheme 5.1.1). Here the phenothiazine entities are directly linked to SubPc to make the macrocycle less flexible. Photoinduced electron transfer leading to long-lived charge separated states in these pentads are investigated using femtosecond and nanosecond transient absorption techniques in both polar benzonitrile and nonpolar toluene solvents. It is shown that in the case of 1 where the hole shifting agents are separated by a phenoxy linker, clear charge separation followed by hole shift leading to a long-lived charge-separated state is observed. However, in the case of 2, evidence for such sequential charge separation/hole shift was rather weak, primarily due to strong electronic interactions between SubPc and PTZ entities. Details of these findings are summarized below.

Scheme 5.1.1. Structures of the tris(phenothiazine)-SubPc-C\textsubscript{60} conjugates developed to probe the role of spacer connecting the primary electron donor (SubPc) to the hole shift agent (PTZ). Sequence of photochemical events are shown as (i), (ii), (iii). Abbreviations: CS = charge separation, CR = charge recombination, HS = hole shift.
5.1.2 Results and Discussion

5.1.2.1 Synthesis

The synthesis of pentad, 1 is given elsewhere. Scheme 5.1.2 outlines the synthesis of the pentad, 2 while the synthetic details are given in the Experimental Section. Briefly, first, chloro-[2,9,16-triiodo subphthalocyaninato]boron(III) was prepared by reacting 4-iodophthalonitrile and BCl₃, followed by chromatographic purification. Next, 4-formylphenoxy[2,9,16-triiodo subphthalocyaninato]boron(III) was obtained by reacting chloro-[2,9,16-triiodo subphthalocyaninato]boron(III) from the previous step with 4-hydroxybenzaldehyde in toluene followed by purification over silica gel column. The 4-formylphenoxy [2,9,16-tri(10H-phenothiazine)subphthalocyaninato]boron(III) was prepared by the reaction of 4-formylphenoxy[2,9,16-triiodo subphthalocyaninato]boron(III) with phenothiazine, Cu₂O and K₂CO₃ in o-dichlorobenzene. Finally, the 4-(1-methyl-3,4-[C₆₀]fulleropyrrolidine-2-yl)[2,9,16-tri(10H-phenothiazine)-subphthalocyaninato]boron(III) (pentad 2) was synthesized by reacting the formylphenoxy derivative from the previous step with sarcosine and fullerene in toluene according to Prato’s method followed by chromatographic purification over silica gel using a mixture of hot toluene:ethylacetate as eluent. The newly synthesized pentad was fully characterized by ¹H NMR, mass, absorption and electrochemical methods. The pentads were stored in dark and were freshly purified prior running spectral and photochemical measurements.
Scheme 5.1.2. Synthetic methodology developed for 2.

5.1.2.2 Absorption, Fluorescence and Computational Studies

Figure 5.1.1a shows the absorption spectral features of the pentads in relation to the control compound, SubPc. SubPc revealed two absorption bands located at 314 and 568 nm, respectively. The phenothiazine peaks of the pentads were overlapped with the SubPc near-UV peak in the 315 nm range as revealed by the significant increase in intensity of this band. The pentads also revealed a sharp peak around 432 nm, characteristic of fulleropyrrolidine. The
fulleropyrrolidine near-UV bands were also overlapped with the SubPc and phenothiazine bands in the 315 nm range. Interestingly, the visible band of 1 was close to the SubPc visible band and appeared at 572 nm, indicating weak, if any, interactions with the appended phenothiazines. In contrast, the visible band of 2 was considerably more red-shifted accompanied by significant broadening, with a peak maxima located at 580 nm. The calculated full width at half maxima (FWHM) values for the visible band was found to be 1113, 1208 and 2177 cm\(^{-1}\) for SubPc, 1 and 2, respectively. The increased FWHM values of 2 suggest existence of intramolecular interactions between the directly linked phenothiazine entities and the SubPc \(\pi\)-system.

Figure 5.1.1. (a) Absorption spectrum normalized to the intense visible band, and (b) fluorescence spectrum obtained upon excitation at the visible peak maxima of SubPc, 1 and 2 in benzonitrile.
Figure 5.1.1b shows the fluorescence spectra of the pentads along with SubPc, excited at the visible band peak maxima. The control, SubPc revealed an emission band located at 584 nm when excited at 568 nm in benzonitrile. Interestingly, for both pentads 1 and 2 this emission was found to be quenched over 98%. Such quenching was also observed for 4-formylphenoxy-[2,9,16-tri(10-(4-phenoxy)-10H-phenothiazine)subphthalocyaninato]boron(III) and 4-formyl-phenoxy[2,9,16-tri(10H-phenothiazine)subphthalocyaninato]boron(III),\(^6\) that is, phenothiazine-SubPc without the appended fullerene. These results indicate photochemical reactions originating from the \(^1\)SubPc* with the covalently linked fullerene and phenothiazine entities.\(^7\) Changing the solvent from benzonitrile to less polar toluene had virtually no effect, that is, the SubPc emission was found to be quenched quantitatively for both conjugates. It may be mentioned here that under the experimental conditions, no emission of fulleropyrrolidine in the 720 nm range was observed, suggesting that excited state energy transfer from \(^1\)SubPc* to fullerene is a less likely quenching mechanism.\(^7\) Additionally, the fluorescence spectra recorded at the excitation wavelength of 400 nm (operating wavelength of our femtosecond transient spectrometer) also revealed similar quenching behavior. In a control experiment, 2-phenyl fulleropyrrolidine emission was also recorded that revealed emission at 720 nm (see Figure S1). This suggests that, at the excitation wavelength of 400 nm, both SubPc and C\(_{60}\) chromophores are excited.

Figure 5.1.2 shows the optimized structures of pentads 1 and 2 along with their frontier orbitals using B3LYP/3-21G(*) method.\(^7\) As pointed out earlier,\(^6\) owing to the flexible linkages, more than one energetically comparable conformers of the two regioisomers were possible. However, as shown in Figure 5.1.2a, the most stable isomer was one in which the SubPc and
the three phenothiazine entities formed a half-cage type structure leaving the fullerene on the top. Moving one of the phenothiazine units close to fullerene yielded a structure that did not reveal significant interactions with the fullerene. In the optimized structure, the highest occupied molecular orbital (HOMO) was found to be on one of the phenothiazine entities while the lowest unoccupied molecular orbital (LUMO) was found to be on the fullerene entity (Figure 5.1.2a right panel). For pentad 2 with directly linked phenothiazine entities on the periphery of SubPc, the half-cage type structure was flatter but still had a curvature due to the basic geometry of SubPc macrocycle (Figure 5.1.2b). There was no appreciable difference between the two structures when looking at the fullerene that was bound to the boron center of SubPc. Interestingly, HOMO of pentad 2 was found to be spread on the entire (PTZ)$_3$-SubPc segment of the pentad (see Figure 5.1.2b middle panel). This is in agreement with the optical absorption studies where intramolecular interactions between the phenothiazine entities with SubPc π-system were witnessed. The LUMO was found to be fully localized on the fullerene entity of the pentad (see Figure 5.1.2b right panel). Further electrochemical studies were performed to visualize the effect of such interactions on the redox behavior of the conjugate.
Figure 5.1.2. B3LYP/3-21G(*) optimized structures of pentads 1 and 2 (a and b, respectively). The frontier HOMO and LUMO for each optimized structure is shown on the right.

Table 5.1.1. Redox potentials in benzonitrile containing 0.1 M (tBu₄N)ClO₄ (V vs Ag/Ag⁺), HOMO and LUMO energies, and free-energy change associated with electron transfer of the studied dyads.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ox. Pot., [V]</th>
<th>Red. Pot., [V]</th>
<th>HOMO energies, [eV]</th>
<th>LUMO energies, [eV]</th>
<th>ΔGₛₛ, [eV] from (^1)SubPc*</th>
<th>ΔGₛₛ, [eV] from (^1)C₆₀*</th>
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<td>1</td>
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<td>-4.83</td>
<td>-3.23</td>
<td>-0.46[α]</td>
<td>-0.08[α]</td>
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<td>2</td>
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<td>-1.22</td>
<td>-5.62</td>
<td>-2.83</td>
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</table>

[α] For formation of (PTZ)₃-SubPc**-C₆₀**. [β] For formation of (PTZ)₂PTZ**-SubPc-C₆₀**. [γ] For formation of [(PTZ)₃-SubPc]**-C₆₀**.
5.1.2.3 Electrochemical Studies and Energy Level Diagram

Establishing the redox states of the donor and acceptor entities of the polyads (triads, tetrads, etc.,) and further utilization of this information to establish their energy states is important to unravel the mechanistic details of photoinduced electron transfer. With this in mind, we have performed electrochemical studies on the investigated pentads using differential pulse voltammetry (DPV) technique. The site of electron transfer for the different redox processes was arrived by performing control experiments involving SubPc, fulleropyrrolidine and phenothiazine precursors. Figure 5.1.3 shows the DPVs of pentads 1 and 2 in benzonitrile containing 0.1 M (t-Bu₄N)ClO₄. In agreement with the earlier reported cyclic voltammetry data,⁶⁹ pentad 1 revealed a multi-electron oxidation process located at 0.73 V vs. Ag/Ag⁺ due to oxidation of the three phenothiazine entities. The fulleropyrrolidine first reduction was located at -0.58 V vs. Fc/Fc⁺ while the second and third reductions were overlap of fulleropyrrolidine and SubPc reductions. A second oxidation was also observed at 1.10 V due to SubPc oxidation. Interestingly, for pentad 2, the multi-electron oxidation process was found to be anodically shifted by 70 mV compared to 1 as a result of the earlier discussed electronic interactions between phenothiazine and SubPc entities. Notably, there was no shift in the potential of C₆₀ reduction in 2 as compared to 1, and these potentials were close to the first reduction potential of pristine fulleropyrrolidine.²⁰ These results point out the fact that the fullerene entities in the triads are electronically isolated from both SubPc and phenothiazine entities. The first reduction of SubPc that was overlapped with the second reduction of fulleropyrrolidine in 1 was anodically shifted in 2 and appeared at -0.92 V. In summary, due to the electronic interactions between the phenothiazine and SubPc entities of 2 appreciable
changes in the redox potentials of both phenothiazine and SubPc (and not fulleropyrrolidine) were observed as compared to the redox potentials of 1 and the control compounds. These results indicate modulating energy states of pentad 2 to some extent as a result of intramolecular interactions between SubPc and phenothiazine as compared to that of pentad 1 wherein the three entities had no appreciable interactions with one another. The redox potentials are given in Table 5.1.1.

![Figure 5.1.3](image)

**Figure 5.1.3.** Differential pulse voltammograms (DPVs) corresponding to both oxidation and reduction processes of 1 and 2 in benzonitrile containing 0.1 M (t-Bu4N)ClO4. The DPV with an asterisk shows ferrocene oxidation (red curve) used as an internal standard. The vertical lines are drawn to compare the potentials of phenothiazine, and fulleropyrrolidine redox processes (see text for details). Scan rate = 5 mV/s, pulse width = 0.25 s, pulse height = 0.025 V. Potential vs. Ag/Ag+.

The free energy change for charge separation (ΔG_{CS}) from the singlet excited state of SubPc ($E_{0-0} = 2.1$ eV) to C60 and a hole shift from SubPc•• to phenothiazine in the pentads were
calculated using spectroscopic, computational and electrochemistry data following Rehm-Weller’s approach, according to equations 1-3.\textsuperscript{75-76}

\[
-\Delta G_{CR} = e(E_{ox} - E_{red}) \quad (1)
\]

\[
-\Delta G_{CS} = \Delta E_{00} - (-\Delta G_{CR}) \quad (2)
\]

where \(\Delta E_{00}\) and \(\Delta G_S\) correspond to the energy of \(^1\)SubPc* and electrostatic energy, respectively. The \(E_{ox}\) and \(E_{red}\) represent the oxidation potential of the electron donors (SubPc and phenothiazine) and the reduction potential of the electron acceptor (C\(_{60}\)), respectively. \(\Delta G_S\) refers to the static energy, calculated by using the ‘dielectric continuum model’ according to the following equation,

\[
-\Delta G_S = -(e^2/(4\pi \varepsilon_0))[((1/(2R_+)) + (1/(2R_-)) - (1/R_{CC})/\varepsilon_S - (1/(2R_+) + 1/(2R_-))/\varepsilon_R) \quad (3)
\]

where \(R_+\) and \(R_-\) are radii of the radical cation and radical anion, respectively; \(R_{CC}\) is the center-center distances between the donor (SubPc or phenothiazine) and C\(_{60}\), which were evaluated from optimized structures. The symbols \(\varepsilon_R\) and \(\varepsilon_S\) refer to solvent dielectric constants for electrochemistry and photophysical measurements, respectively.

These calculations revealed that the formation of \((\text{PTZ})_3\text{SubPc}^\text{**}-\text{C}_{60}^\text{●}-\text{SubPc-}\text{C}_{60}^\text{●}\) is exothermic in 1 in benzonitrile. The estimated \(\Delta G\) values were found to be -0.46 and -0.83 eV for the formation of \((\text{PTZ})_3\text{SubPc}^\text{**}-\text{C}_{60}^\text{●}\) and \((\text{PTZ})_2\text{PTZ}^\text{**}-\text{SubPc-}\text{C}_{60}^\text{●}\), respectively, from \(^1\)SubPc*, while these values were found to be -0.08 and -0.45 eV fo the formation of \((\text{PTZ})_3\text{SubPc}^\text{**}-\text{C}_{60}^\text{●}\) and \((\text{PTZ})_2\text{PTZ}^\text{**}-\text{SubPc-}\text{C}_{60}^\text{●}\), respectively from \(^1\)C\(_{60}\)*. For 2, where the \((\text{PTZ})_3\text{SubPc}\) primarily acts a single entity, the \(\Delta G\) value for the formation of \([(\text{PTZ})_3\text{SubPc}^\text{**}]-\text{C}_{60}^\text{●}\) was estimated to be -0.73 eV from \(^1\)SubPc* and -0.38 eV from \(^1\)C\(_{60}\)* (see Table 5.1.1).
The energy level diagram constructed using the spectral and electrochemical data is shown in Figure 5.1.4. At the excitation wavelength of 400 nm (wavelength of exciton laser from our femtosecond transient setup), both $^1$SubPc* and $^1$C$_{60}$* (via rapid internal conversion of the S$_2$ state of the excited C$_{60}$) are expected to form. Both $^1$SubPc* and $^1$C$_{60}$* could undergo a charge-separation process to yield (PTZ)$_3$-SubPc*-C$_{60}$* or could undergo competitive intersystem crossing the populate their respective triplet excited states ($^3$SubPc* triplet energy of ~1.45 eV and $^3$C$_{60}$* triplet energy = 1.50 eV). As discussed in the next section, the latter process (triplet population) seems to be inefficient for the studied conjugates. Formation of (PTZ)$_2$PTZ*-SubPc*-C$_{60}$ charge separated state from the initial $^1$SubPc* or $^1$C$_{60}$* is another option. Free-energy calculations suggest that this process is indeed a possibility for both conjugates from either of the excited singlet states. Under these circumstances, formation of the energetically favorable (PTZ)$_3$-SubPc*-C$_{60}$* could be anticipated. In the case of 1, where PTZ and SubPc are spatially separated by phenoxy groups, subsequent hole transfer to PTZ to yield (PTZ)$_2$PTZ*-SubPc*-C$_{60}$ as the final charge-separated species. This process would occur in competition with the (PTZ)$_3$-SubPc*-C$_{60}$* relaxing to $^3$SubPc*. The (PTZ)$_2$PTZ*-SubPc*-C$_{60}$ thus formed could relax directly to the ground state without populating any triplet states (see Figure 5.1.4 for relative energy levels). However, in the case of 2, where substantial electronic interaction between PTZ and SubPc entities is observed, the charge separation product [(PTZ)$_3$-SubPc]*-C$_{60}$* (shown in magenta in Figure 5.1.4) will have contributions of radical cation spread over the entire (PTZ)$_3$SubPc entity. Since (PTZ)$_3$SubPc largely acts as a single entity, no additional hole transfer process could be envisioned. The charge-separated state [(PTZ)$_3$-
SubPc$^{*+}$-$C_{60}^{*}$ would relax directly to the ground state or populate one of the intermediate triplet states, that is, $3^{*}$SubPc or $3^{*}$C$_{60}$ prior returning to the ground state.

Figure 5.1.4. Energy level diagram showing the various photochemical events of pentads 1 and 2 in benzonitrile. The magenta lines correspond to the energy of radical ion pairs formed by 2. Abbreviations: CS = charge separation, CR = charge recombination, ISC = intersystem crossing, IC = internal conversion, T = triplet state emission.

5.1.2.4 Pump-probe Transient Spectral Studies

In order to gather evidence for the formation of charge-separated species upon photoexcitation of the supramolecular conjugates and to evaluate kinetics of charge separation and recombination, transient absorption spectroscopic measurements both at the femto- and nanosecond time scales were performed. Two solvents, that is, polar benzonitrile and nonpolar toluene were used to rationalize the solvent effects under deaerated conditions. In addition, the precursor donor and acceptor entities were chemically oxidized or spectroelectrochemically
reduced for spectral identification. The spectroelectrochemically reduced, one-electron product of fulleropyrrolidine revealed a characteristic band around 1000 nm. In order to identify the spectral features of PTZ**, chemical oxidation of PTZ was performed using nitrosyl tetrafluoroborate (NOBF₄) as an oxidizing agent. As shown in Figure 5.1.S3a, chemical oxidation of phenothiazine revealed bands at 442 and 525 nm with two weak bands at 748 and 824 nm. Oxidation of 1 with increasing addition of NOBF₄, first, revealed the peaks expected for PTZ oxidation as shown in the differential absorption spectra (Figure 5.1.S3b). Further addition of the oxidizing agent caused bleaching of the SubPc peak at 572 nm with the appearance of a weak band at 630 nm in addition to broader spectral features in the 420-525 nm range. These results indicate first oxidation of PTZ entities followed by the SubPc entity in 1, as predicted by electrochemical and computational studies. Interestingly, when compound 2 was oxidized, bleaching of the broad SubPc peak at 580 nm accompanied by positive peaks at 450 and 680 nm were observed (Figure 5.1.S4). An isosbestic point at 520 nm was also observed. These results suggest that the oxidation product is [(PTZ)₃SubPc]** with the positive charge spread across different entities of (PTZ)₃SubPc as predicted by computational results.

Preliminary transient spectral data providing evidence of charge separation in 1 was earlier communicated by us. In this paper, additional mechanistic details are offered. Figure 5 shows transient absorption spectra of 1 in benzonitrile and toluene at different delay times. The 400 nm light excited both SubPc and fullerene entities having strong absorption in the visible region. On the basis of the MO energy diagram in Figure 5.1.4, visible light excitation of the central SubPc induces a charge-separation process from ¹SubPc* to C₆₀, which corresponds to an electron transfer from the LUMO of the excited SubPc to the LUMO of C₆₀, generating a
(PTZ)₃-SubPc*-C₆₀*- charge-separated state. This is conceivable since the fluorescence of SubPc is efficiently quenched by the connection of C60. Subsequently, an electron from the HOMO of PTZ unit transfers to the half-vacant HOMO of SubPc**, generating a (PTZ)₂PTZ**-SubPc-C₆₀*- charge-separated state in which the hole (radical cation) is localized on one of three PTZs as seen from the HOMO in Figure 5.1.2a. Alternatively, the ¹C₆₀* could also initiate the charge-separation process from the LUMO of excited C₆₀ to the LUMO of SubPc to generate a (PTZ)₃SubPc**-C₆₀*- charge-separated state. Subsequent hole transfer would result in a (PTZ)₂PTZ**-SubPc-C₆₀** charge-separated state. From the femtosecond transient spectra shown in Figure 5.1.5a, it was possible to secure evidence for the occurrence of these photochemical events in a step-wise fashion. First, bleaching of the peak at 565 nm, corresponding to ground state absorption of SubPc that recovered with time was observed, suggesting ¹SubPc* involvement in the photochemical events. A broad peak in the 880 nm range was also observed at an earlier time (see spectrum at 10 ps) that could be attributed to ¹C₆₀* formed by relaxation of the S₂ state to the S₁ state. The spectrum recorded at 10 ps delay time clearly revealed peaks at 1010 nm corresponding to C₆₀* and at 660 nm corresponding to SubPc**, providing evidence for the formation of a (PTZ)₃SubPc**-C₆₀*- charge-separated state. Fast decay of the peak at 660 nm resulted in simultaneous appearance of a peak in the 520 nm range (time constant = 30 ps in benzonitrile and 47 ps in toluene) corresponding to PTZ** (see spectrum recorded at 100 ps in Figures 5a and b), providing spectral proof for hole transfer. That is, formation of a (PTZ)₂PTZ**-SubPc-C₆₀*- charge-separated state was evident. Importantly, the recovery of the 570 nm depleted peak was faster than that observed in pristine SubPc due to an additional electron/hole transfer process, more so in benzonitrile than in toluene.
As pointed out earlier, in (PTZ)$_2$PTZ$^{**}$-SubPc-C$_{60}^+$, the electron and hole are separated by a longer distance over the central SubPc. As a consequence of this and the acceptor fullerene, the recombination process was found to be much slower than the charge-separation process with considerable radical peak intensities lasting over 3 ns, beyond the time window of the instrument. The rate of charge separation $k_{CS}$, determined by monitoring the C$_{60}^+$ peak at 1010 nm, was found to be $1.22 \times 10^{10}$ s$^{-1}$ in benzonitrile and $4.43 \times 10^9$ s$^{-1}$ in toluene, respectively. The rate constant for the decay process of C$_{60}^+$ representing charge recombination of the final...
charge-separation product, (PTZ)$_2$PTZ$^{\bullet\bullet}$-SubPc-C$_{60}$$^{\bullet\bullet}$, was found to be $1.31 \times 10^9$ s$^{-1}$ in benzonitrile and $1.21 \times 10^{10}$ s$^{-1}$ in toluene, respectively. Since the charge separation persisted beyond 3 ns, this rate could be considered as the upper limit.

![Femtosecond transient difference absorption spectra of 2 in (a) benzonitrile and (b) toluene. The samples were excited with 400 nm femtosecond (pulse width = 100 fs) laser pulses. The decay time profile of the C$_{60}$$^{\bullet\bullet}$ monitored at 1000 nm is shown on the right.](image)

Figure 5.1.6. Femtosecond transient difference absorption spectra of 2 in (a) benzonitrile and (b) toluene. The samples were excited with 400 nm femtosecond (pulse width = 100 fs) laser pulses. The decay time profile of the C$_{60}$$^{\bullet\bullet}$ monitored at 1000 nm is shown on the right.

Since the charge recombination persisted beyond 3 ns, further nanosecond transient spectra of 1 in both benzonitrile and toluene were recorded, as shown in Figure 5.1.56 (see nanosecond transient spectra of control compounds in Figure 5.1.55). At the delay time of 50 ns, the 660 nm band of SubPc$^{\bullet\bullet}$ was completely absent, indicating the presence of the (PTZ)$_2$PTZ$^{\bullet\bullet}$SubPc-C$_{60}$$^{\bullet\bullet}$ radical ion pair as the sole survivor and not the (PTZ)$_3$-SubPc$^{\bullet\bullet}$-C$_{60}$$^{\bullet\bullet}$
radical ion pair. However, the depleted peak of SubPc at 570 nm was also present, indicating forma-tion of \(^3\)SubPc\(^*\) species, perhaps due to the charge recombination of \((\text{PTZ})_3\)SubPc\(^*\)C\(_{60}\)\(^*\), as shown in Figure 5.1.4. The time profile of C\(_{60}\)\(^*\) at 1010 nm was monitored to calculate the charge recombination rates. From this, the lifetime of the radical ion pair, \(\tau_{\text{RIP}}\) was found to be 185 and 250 ns in benzonitrile and toluene, respectively, which resulted in values of \(k_{\text{CR}} = 5.41 \times 10^6\) s\(^{-1}\) and \(4.00 \times 10^6\) s\(^{-1}\) in the respective solvents. The magnitude of both \(\tau_{\text{RIP}}\) and \(k_{\text{CR}}\) followed a trend that con-formed with the predictions of the Marcus theory.\(^{56-57}\) Here, the \(k_{\text{CR}}\) values from the nanosecond transient data can be treated as lower limit of charge recombination in 1.

For compound 2, as mentioned earlier, the HOMO was spread over the entire \((\text{PTZ})_3\)SubPc entity (see Figure 5.1.2b), suggesting that the initial electron transfer product would be \([\text{(PTZ)}_3\text{SubPc}]^{1+}\cdot\text{C}_{60}\)\(^*\) in which the radical cation is spread over the \((\text{PTZ})_3\)SubPc entity. This seems to be the case as shown by the femtosecond transient spectra of 2 in benzonitrile and toluene, in Figure 5.1.6. In both solvents, the spectrum shown at 10 ps delay time revealed peaks corresponding to both \(^1\)SubPc\(^*\) (depleted peak at 585 nm) and \(^1\)C\(_{60}\)\(^*\) (880 nm peak), implying successful excitation of these sensitizers. Recovery/ delay of these peaks resulted in peaks corresponding to the charge-separated state. The spectral features corresponding to the cation radical were red-shifted with considerable spectral broadening and appeared in the 675–700 nm range. Unlike in 1 where a signal in the 520 nm range revealing the presence of PTZ\(^{1+}\) was observed, no clear signal was detected. The \(k_{\text{CS}}\) obtained from the kinetic fit of C\(_{60}\)\(^*\) was found to be \(3.43 \times 10^{10}\) s\(^{-1}\) and \(1.49 \times 10^{10}\) s\(^{-1}\) in benzonitrile and toluene, respectively, indicating fast charge separation. Interestingly, the process of charge recombination was almost fully completed by 3 ns (see spectra recorded at 3 ns delay time in Figure 5.1.6). The \(k_{\text{CR}}\)
calculated from the decay time profile of \( C_{60}^- \) was found to be \( 2.01 \times 10^9 \text{ s}^{-1} \) and \( 1.41 \times 10^9 \text{ s}^{-1} \) in benzonitrile and toluene, respectively. It is also important to note that the \( k_{CS} \) value for 2 was much higher than that of 1 in any given solvent, although the donor–acceptor distance between SubPc and \( C_{60} \) entities were the same in both conjugates.

Complementary nanosecond transient absorption spectra shown in Figure 5.1.7 revealed spectra of \( ^3\text{SubPc}^* \) and absence of \( C_{60}^- \) peak in the 1010 nm region, as predicted by the energy level diagram in Figure 5.1.4. That is, the \( [(\text{PTZ})_3\text{SubPc}]^{**-}C_{60}^- \) populated the \( ^3\text{SubPc}^* \) prior to returning to the ground state. This could also have any contributions from triplet–triplet energy transfer from \( ^3\text{C}_{60}^* \) (product of intersystem crossing of \( ^1\text{C}_{60}^* \)) to SubP (see Figure 5.1.4 for energy level diagram). From the decay profile of the 475 nm peak, time constants of 0.37 \( \mu \text{s} \) in benzonitrile and 0.53 \( \mu \text{s} \) in toluene were obtained.

![Figure 5.1.7](image)

Figure 5.1.7. Nanosecond transient absorption spectra of 2 in (a) benzonitrile and (b) toluene. The samples were excited with 532 nm nanosecond (pulse width = 8 ns) laser pulses. Figure b and c show the time profile of \( ^3\text{SubPc}^* \) monitored at 475 nm in toluene and benzonitrile, respectively.
5.1.3 Conclusions

The role of spacer linking the hole shifting agent to the primary electron donor in (PTZ)$_3$SubPc-C$_{60}$ donor–acceptor conjugates is investigated. In these compounds, the SubPc acted as a primary electron donor while the role of phenothiazines was that of a hole transfer agent with fullerene being the terminal electron acceptor. Intramolecular interactions between the phenothiazine and SubPc entities in 2, as a result of direct covalent bonding, were evidenced from absorption, computational, and electrochemical studies. Using femto- and nanosecond transient absorption techniques, evidence for charge separation, and kinetics of charge separation and recombination were obtained in both polar and nonpolar solvents. The spectral and kinetic data obtained by analyzing the time profiles of the radical ions revealed stabilization of the charge-separated state in 1 as a result of an electron transfer–hole shift mechanism. However, in the case of 2 due to direct linking of PTZ and SubPc, the sequential electron transfer-hole shift was not evident; consequently, the charge recombination process was rather rapid.

5.1.4 Supporting Information

![Fluorescence emission spectrum](image)

Figure 5.1.S1. Fluorescence emission spectrum of 2-phenyl fulleropyrrolidine (black), compound 1 (blue) and compound 2 (green) in benzonitrile at the excitation wavelength of 400 nm.
Figure 5.1.S2. B3LYP/3-21G(*) calculated (a) HOMO-2, (b) HOMO-1, (c) HOMO, (d) LUMO, (e) LUMO+1 and (f) LUMO+2 for the optimized structure of 2.
Figure 5.1.S3. Differential spectral changes observed during chemical oxidation using nitrosonium tetrafluoroborate of phenothiazine and 1 in benzonitrile.

Figure 5.1.S4. Differential absorption spectral changes observed during chemical oxidation of 2 in benzonitrile. Nitrosonium tetrafluoroborate was used as an oxidizing agent.
Figure 5.1.S5. Nanosecond transient absorption spectra of (a) 2-phenyl fulleropyrrolidine, (b) SubPc, and (c) (PTZ)$_3$SubPc (precursor compound of 1) in toluene at the indicated delay times. The samples were excited with 532 nm nanosecond (pulse width = 8 ns) laser pulses. The right hand panels show the time profile monitored at 700 nm, 455 nm and 456 nm of the corresponding transient absorption spectra shown in left.
Figure 5.1.S6. (a) Nanosecond transient absorption spectra of 1 in benzonitrile at the indicated delay times. The samples were excited with 532 nm nanosecond (pulse width = 8 ns) laser pulses. Figure b and c show the time profile of the $C_{60}^+$ monitored at 1000 nm in benzonitrile and toluene, respectively.
Figure 5.1.S7. \(^1\)H-NMR spectrum of 4-formylphenoxy\([2,9,16\text{- triiodo subphthalocyaninato}\] boron(III) in CDCl\(_3\).

Figure 5.1.S8. \(^1\)H-NMR spectrum of 4-formylphenoxy\([2,9,16\text{- tri(10H-phenothiazine) subphthalocyaninato}\] boron(III) in CDCl\(_3\).
Figure 5.1.S9. $^1$H-NMR spectrum of $\mathbf{2}$ in CDCl$_3$.

Figure 5.1.S10. MALDI-TOF-mass spectrum of $\mathbf{2}$. 
5.2 Tuning Optical and Electron Donor Properties by Peripheral Thio-Aryl Substitution of Subphthalocyanine: A New Series of Donor-Acceptor Hybrids for Photoinduced Charge Separation*

5.2.1 Introduction

Building donor-acceptor systems designed to mimic the photosynthetic reaction center events, and efficiently convert light energy into other forms (electricity or fuel) with the intermediate charge separated state has been one of the goals of modern supramolecular chemistry.1-31 Various conjugated macromolecules including porphyrins, phthalocyanines, and BF$_2$-chelated dipyrrromethenes (BODIPY) have been widely used as the primary building blocks because of their excellent photophysical and photochemical properties.32-37 Subphthalocyanine (SubPcs),38 unique ring reduced member of common phthalocyanine family with a bowl shaped nonplanar structure, is a 14 $\pi$-electron aromatic compound comprised of three N-fused diiminoisoindole units and an axial ligand around a tetra coordinated boron atom. Because of the different $\pi$-conjugated skeleton, and shape and structure of SubPc from the commonly used porphyrins and phthalocyanines, these molecules show distinct optical and electronic properties. Consequently they have been utilized as organic functional materials in optoelectronic and light energy harvesting systems.39-52

SubPcs display light absorption properties in the UV-visible region for the context of solar energy conversion. In particular, they exhibit an intense absorption in the 570 nm region with the excitation coefficient in the order of 50,000 M$^{-1}$ cm$^{-1}$. The high electronic excitation energy, exceeding 2.0 eV, can thus be useful for promoting efficient exergonic electron transfer process. In addition, the rigid nonplanar SubPc core shows small stokes shift and low

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reorganization energy useful to observe long-lived charge separated states. Furthermore, the optoelectronic and light absorption features of SubPc can be finely tuned by varying their axial ligands and peripheral chemical modifications. In this regard, the axial halogen atom of SubPc can easily be replaced by oxygen nucleophiles, particularly phenol, and this has been a convenient reaction strategy for the axial modification and introduction of diverse functional groups to further enhance the stability and solubility of SubPcs.39-52

Recently, significant efforts have been made to develop various types of near-infrared (near-IR) sensitizers due to their potential applications in various fields in chemistry, physics and biology.53 Near-IR sensitizers are especially important for light energy harvesting applications where sunlight carries over 50% of its radiation. Generally, porphyrins, phthalocyanines and BODIPYs have been used to synthesize near-IR sensitizers after structural modifications and central metal atom variations.54-57 Most of the phthalocyanines reveal their intense visible-band absorption around 650 – 700 nm.35-37 Recently, it has been demonstrated that by introducing phosphorus(V) into the central cavity and peripheral substitution of electron donating substituents (Group: 16 S and Se), the phthalocyanine visible-band could be red-shifted beyond 1000 nm through the synergistic effects.58 Inspired by this, in the present study, we have utilized the approach of peripheral modification of SubPc using six entities of electron donor thiotolualyl and thionaphthyl groups. Such ring modification is expected not only to red-shift the absorption and emission but also improve the electron donor ability of SubPc (facile oxidation). To verify this hypothesis, a new series of donor-acceptor dyads using fullerene (C60) as an electron acceptor have been constructed and photoinduced electron transfer events have
been systematically investigated using steady-state and time-resolved emission, and transient absorption techniques operating at different time scales.

Figure 5.2.1 shows the structure of the dyads constructed using the peripherally modified SubPc using six entities of thio-aryl substituents. Here, the central SubPc macrocycle in each dyad bears a C₆₀ as an electron acceptor at the axial position connected through covalent bonding between B and O atom, while the α and β hydrogens from the peripheral positions of SubPc macrocycle have been replaced either by thiotolualyl or thionaphthyl entities. For dyads 1 and 2, the six β-hydrogens of the SubPc macrocycle have been replaced by 4-thiotolualyl and 2-thionaphthyl substituents, respectively. For dyads 3 and 4, the six β-hydrogens of the SubPc macrocycle have been substituted either with 4-thiotolualyl or 2-thionaphthyl groups, respectively. Finally, for dyad 5, the six β-hydrogens have been replaced by 1-thionaphthyl entities. The newly synthesized dyads, 1 - 5 along with their control compounds, 1c – 5c (see Schemes 1 and 2 for structures) have been fully characterized by NMR (¹H and ¹³C), MALDI-TOF-mass, absorption and emission spectroscopy, and electrochemistry. The dynamics of photoinduced electron transfer processes within the dyads has been studied and confirmed by both femto- and nanosecond transient absorption spectroscopy in polar solvents.
Figure 5.2.1. Structures of newly synthesized SubPc-C₆₀ dyads with peripherally modified SubPc with thio-aryl entities. Structure of pristine SubPc used as control is also shown.

5.2.2 Results and Discussion

5.2.2.1 Synthesis

The synthesis of all the derivatives have been achieved by following the procedure outlined in Schemes 1 and 2. Scheme 5.2.1 describes the procedure developed for the synthesis of SubPc-C₆₀ dyads, 1 and 2, where the thio-aryl substituents are attached at the α–positions of SubPc macrocycle. Scheme 5.2.2 describes the procedure developed for the synthesis of SubPc-C₆₀ dyads, 3-5, where the thio-aryl substituents are attached at the β–positions of the SubPc macrocycle. Generally, the most convenient route for the synthesis of SubPc has been refluxing of target phthalonitrile in the presence of BX₃ (X = Cl or Br) to promote cyclotrimerization to form the SubPc macrocycle. Thus, for the modification of peripheral positions of the SubPc, the key step was to design and synthesize various substituted phthalonitriles as precursors. For dyads 1 and 2, first, 2,3-dicyanohydroquinone was tosylated to obtain 3,6-ditosylated phthalonitrile using tosyl chloride in the presence of triethylamine (TEA) and
dimethylaminopyridine (DMAP). Next, the 3,6-ditosylated phthalonitriles were converted into
dithio-aryl substituted phthalonitrile, 1a and 2a by the application of base catalyzed
nucleophilic substitution reaction in the presence of 4-methylbenzenethiol and 2-
naphthalenethiol, respectively. Next, compounds 1a and 2a were refluxed in the presence of
BCl₃ in p-xylene solution for about an hour to obtain the respective SubPc-Cl, 1b and 2b
derivatives. The reactive chlorine atom in 1b and 2b was subsequently replaced by 4-formyl
phenoxide group by the treatment of 4-hydroxybenzaldehyde in toluene to obtain compounds
1c and 2c, respectively. Finally, 1c and 2c were treated with C₆₀ and sarcosine in toluene
following standard Prato’s 1,3-dipolar cycloaddition reaction of fullerene to obtain the desired
compounds 1 and 2.⁵⁹

Scheme 5.2.1. Synthetic scheme adopted for dyads 1 and 2.

For the syntheses of dyads, 3-5, a procedure outlined in Scheme 5.2.2 was adopted.
Here, 4,5-difluoro phthalonitrile was used for the preparation of phthalonitrile precursors
which were later used for the formation of SubPc macrocycles. By the application of base
catalyzed nucleophilic substitution reaction in DMSO, treatment of 4,5-difluorophthalonitrile
with 4-methylbenzenethiol, 2-naphthenethiol and 1-naphthenethiol, compounds 3a, 4a and
5a were respectively obtained. The SubPc derivatives, 3b, 4b and 5b were synthesized by
reacting the respective phthalonitrile with BCl₃ in p-xylene. This was followed by replacing the
axial chloride with 4-formylphenoxide to obtain compounds 3c, 4c and 5c. Finally, dyads 3, 4
and 5 were synthesized by reacting the corresponding aldehyde derivative with C₆₀ and
sarcosine in toluene. Details of syntheses along with NMR (¹H and ¹³C) and MALDI-Mass
spectra are given in the Supporting Information (SI). The purity of the newly synthesized
compounds was checked by thin-layer chromatography and were stored in dark to prevent any
photodecomposition.

Scheme 5.2.2. Synthetic scheme adopted for dyads 3 - 5.
5.2.2.2 Optical Absorption and Emission Studies

Figure 5.2.2a shows the normalized absorption spectrum of dyads 1 and 3 along with control compounds 1c and 3c, and tri(ter-butyl)boron subphthalocyanine chloride (SubPc), as a reference compound, in o-dichlorobenzene (DCB). Absorption bands of pristine SubPc were located at 572 and 320 nm while that of peripherally modified SubPcs, 1c and 3c, the spectra revealed the expected red-shifted absorption bands located at 656 and 602 nm, respectively. This large change in absorption was presumably due to strong ground state intramolecular interactions involving thio-aryl substituents. The dyads, 1 and 3, which bears C\textsubscript{60} on the top of the SubPc macrocycle revealed absorption maxima at 649 nm and 606 nm, respectively, in addition to the signature sharp band of fulleropyrrolidine at 432 nm. There was a significant increase in absorption in the 300 to 350 nm range due to various substituents and C\textsubscript{60} absorption in this region as shown in Figure 5.2.2a. The spectral features for 2c and 2 were similar to 1c and 1 having substituents at the α-positions, while those of 4c and 5c were close to 3c, and of dyads 4 and 5 were close to 3 having substituents at the β-positions of SubPc macrocycle. The spectral data is listed in Table 5.2.1 while spectra of dyads 2, 4 and 5 along with their control compounds is shown in Figure S1 in SI. It is important to note that the spectral perturbations were the highest for α-substituted derivatives while such effects were relatively less for β-substituted derivatives. This could also be said for the peak width. For example, the full width at half maxima (FWHM) values of the visible band of SubPc, 3c and 1c were found to be 1183, 1090 and 2062 cm\textsuperscript{-1}, respectively. That is peaks of 1c and 1 revealing higher spectral width compared to those of 3c and 3. The nature of the thio-aryl substituents,
whether thiotolualyl or thionaphthyl for given type of ring substituion, had minimal influence on the spectral properties.

![Absorption and Emission Spectra](image)

**Figure 5.2.2.** a) Absorption and b) emission spectra of compounds 1 and 3 along with control compounds 1c and 3c, and the reference compound, SubPc in DCB. The compounds were excited at the most intense visible band peak maxima of a given compound.

The steady-state fluorescence spectral studies of the newly synthesized SubPc derivatives along with their control compounds were performed in o-DCB as shown in Figure 5.2.2b for representative compounds, while the data for the entire series is given in Table 5.2.1 (see Figure S1b in the Supporting Information for fluorescence of 2, 4, 5 and corresponding control compounds). Complementary to the absorption properties, compounds 1c ($\lambda_{exc} = 656$ nm) and 3c ($\lambda_{exc} = 602$ nm) along with reference compound SubPc ($\lambda_{exc} = 568$ nm) reveal emission at 691, 621 and 582 nm with fluorescence quantum yields ($\Phi_f$) of 0.07, 0.25 and 0.25, respectively. That is, the most red-shifted emission in the case of 1c compared to 3c and SubPc.
were observed. The emission of 1c extends all the way to 800 nm. On the other hand, due to
the presence of C_{60}, the emission of SubPc is quenched over 95% in case of dyads 1 and 3.
Similar observations were also made for compounds 2, 4, and 5 along with their control
compounds, 2c, 4c and 5c in DCB. That is, near-IR emission in the case of 2c (covering until 800
nm) and red-shifted emission in the case of 4c and 5c (emission extended to 750 nm), as a
result of peripheral thio-aryl substitution was observed. Upon attaching the electron-acceptor
fullerene, much of the emission was quenched revealing occurrence of excited state events in
these donor–acceptor dyads. Changing the solvent to a slightly more polar benzonitrile
revealed similar spectral trends. It should be mentioned here that direct excitation of SubPc in
the dyads revealed no emission in the 720 nm range corresponding to \(^1\text{C}_{60}\) suggesting singlet–
singlet energy transfer may not be one of the quenching mechanisms.

5.2.2.3 Electrochemical Studies and Energy Level Diagram

The optical absorption and emission studies revealed that having thio-aryl substituents
on either a or b positions of the SubPc macrocycle lowers the HOMO–LUMO gap, more so for
the a-substituted derivatives. This could be a consequence of altering the HOMO and LUMO
energy levels. In order to gain better understanding, electrochemical studies using differential
pulse voltammetry (DPV) were performed. Figure 5.2.3 shows the DPVs in DCB containing 0.1M
(n-Bu\(_4\)N)ClO\(_4\) while the data of compounds 1c–5c and dyads 1–5 along with pristine SubPc
without thio-aryl substituents are given in Table 5.2.1. The site of electron transfer for each
redox couple, arrived by performing control experiments, is also labeled. Facile oxidation and
reduction compared to that of pristine SubPc upon thio-aryl substitution was evident for the
series of compounds. For 1c and 2c, having thio-aryl substituents at the \(\alpha\)-positions, this effect
was much more pronounced compared to those of $3c$–$5c$. That is, the oxidation potential was lowered by 110–120 mV while the reduction potential was lowered by 150–160 mV for $1c$–$2c$ while for $3c$–$5c$, lowering of oxidation potential was less than 30 mV but the reduction potential was lowered as much as 200 mV (see Table 5.2.1). In essence, HOMO–LUMO gap followed the order $1<2<3<5<SubPc$, a trend that agreed well with the optical HOMO–LUMO gap.

Table 5.2.1. Spectral (absorption and fluorescence), electrochemical redox potentials, [a] and free-energy change associated with electron transfer data of the investigated compounds in $o$-DCB.

<table>
<thead>
<tr>
<th>Cmpd</th>
<th>$\lambda_{abs}$ [nm]</th>
<th>$\lambda_{fl}$ [b] [nm]</th>
<th>$\tau$ [b] [ns]</th>
<th>$\Delta E_{\infty}$ [c] [eV]</th>
<th>$\Phi$ [d]</th>
<th>$E_{ox}$ [V]</th>
<th>$E_{red}$ [V]</th>
<th>$-\Delta G_{CS}$ [e] [eV]</th>
<th>$-\Delta G_{CR}$ [e] [eV]</th>
</tr>
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<tbody>
<tr>
<td>SubPc</td>
<td>568</td>
<td>582</td>
<td>1.86</td>
<td>2.13</td>
<td>0.25</td>
<td>0.59</td>
<td>-1.54</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1c</td>
<td>656</td>
<td>691</td>
<td>1.53</td>
<td>1.80</td>
<td>0.07</td>
<td>0.49</td>
<td>-1.37</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>2c</td>
<td>653</td>
<td>690</td>
<td>0.97</td>
<td>1.79</td>
<td>0.05</td>
<td>0.48</td>
<td>-1.38</td>
<td>---</td>
<td>---</td>
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<tr>
<td>3c</td>
<td>602</td>
<td>621</td>
<td>1.88</td>
<td>1.97</td>
<td>0.25</td>
<td>0.61</td>
<td>-1.34</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>4c</td>
<td>611</td>
<td>629</td>
<td>2.47</td>
<td>1.96</td>
<td>0.26</td>
<td>0.58</td>
<td>-1.32</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>5c</td>
<td>607</td>
<td>625</td>
<td>1.63</td>
<td>1.97</td>
<td>0.17</td>
<td>0.59</td>
<td>-1.33</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1</td>
<td>649</td>
<td>690</td>
<td>&lt;0.1</td>
<td>1.80</td>
<td>&lt;5×10$^{-4}$</td>
<td>0.50</td>
<td>-1.10</td>
<td>1.61</td>
<td>0.19</td>
</tr>
<tr>
<td>2</td>
<td>653</td>
<td>692</td>
<td>&lt;0.1</td>
<td>1.79</td>
<td>&lt;5×10$^{-4}$</td>
<td>0.48</td>
<td>-1.13</td>
<td>1.59</td>
<td>0.20</td>
</tr>
<tr>
<td>3</td>
<td>606</td>
<td>610</td>
<td>&lt;0.1</td>
<td>1.97</td>
<td>&lt;5×10$^{-4}$</td>
<td>0.62</td>
<td>-1.12</td>
<td>1.71</td>
<td>0.26</td>
</tr>
<tr>
<td>4</td>
<td>609</td>
<td>611</td>
<td>&lt;0.1</td>
<td>1.96</td>
<td>&lt;5×10$^{-4}$</td>
<td>0.59</td>
<td>-1.13</td>
<td>1.69</td>
<td>0.27</td>
</tr>
<tr>
<td>5</td>
<td>605</td>
<td>607</td>
<td>&lt;0.1</td>
<td>1.97</td>
<td>&lt;5×10$^{-4}$</td>
<td>0.60</td>
<td>-1.14</td>
<td>1.71</td>
<td>0.26</td>
</tr>
</tbody>
</table>

[a] In DCB containing 0.1 M (TBA)ClO$_4$. [b] For SubPc 561 nm nanoLED, for $1c$, $2c$, $1$ and $2$ 624 nm nanoLED and $2c$, $3c$, $4c$, $2$, $3$, and $4$ 561 nm nanoLED excitation sources were used. [c] $(\Delta E_{\infty}=1240/\lambda_{abs}+1240/\lambda_{fl})/2$ [d] SubPc was used as a standard [e] The free energy change for charge separation ($-\Delta G_{CS}$) from the singlet excited state of SubPc derivatives within the dyad was calculated using spectroscopic, and electrochemistry data following Rehm–Weller’s approach, according to the following equations:$^{61}$ $-\Delta G_{CR}=E_{ox}-E_{red}+\Delta G_{S}$ and $-\Delta G_{CS}=\Delta E_{\infty}-(-\Delta G_{CR})$ in which $\Delta E_{\infty}$ and $\Delta G_{S}$ correspond to the energy of singlet excited state of SubPc and electrostatic energy, respectively. $E_{ox}$ and $E_{red}$ represent the oxidation potential of the electron donor (SubPc) and the reduction potential of the electron acceptor ($C_60$), respectively. $\Delta G_{S}$ was calculated according to dielectric continuum model $\Delta G_{S}=\alpha e^2/4\pi\varepsilon_0[(1/2R_++1/2R_-)\Delta(1/\varepsilon_R)-1/R_{CC}\varepsilon_R]$. $\varepsilon_0$ and $\varepsilon_R$ are the vacuum permittivity and dielectric constant, respectively, of the solvent used for photochemical and electrochemical studies. $R_+$ and $R_-$ represent radii of the cation and anion, respectively. $R_{CC}$ is the center-to-center distance between donor and acceptor entities of the dyad (distance between boron and the center of fullerene is 9.2 Å).
As shown in Figure 5.2.3, in the case of the dyads 1–5, within the monitored potential window, there were no appreciate changes in the first, second, and third reduction potentials involving fullerene reductions, and these values agreed well with the reduction potentials of pristine fulleropyrrolidine. This observation suggests lack of intramolecular interactions between the fullerene and SubPc entities of the dyad, which are separated by over 9 Å. Notable changes were seen for the oxidation and reduction peaks corresponding to SubPc entity. The SubPc first oxidation potential followed the trend 1,2<3–5, while for SubPc reduction this trend was 3–5<1,2, similar to that observed for the series of control compounds 1c–5c. The HOMO–LUMO gap of the dyads, that is, the potential difference between the first oxidation potential of SubPc and first reduction potential of C60, was also evaluated. A lower gap for dyads 1 and 2 (gap ca. 1.63 eV) compared to dyads 3–5 (gap ca. 1.74 eV) was evident from such calculations.

![Differential pulse voltammograms of the indicated compounds](image)

Figure 5.2.3. Differential pulse voltammograms of the indicated compounds (see Scheme 5.2.1 for structures) in o-DCB, 0.1 M (n-Bu4N)ClO4. Scan rate = 5 mV/s, pulse width = 0.25 s, pulse height = 0.025 V.
An energy level diagram was established using the spectroscopic and electrochemical data, and the calculated free energy changes for charge separation and charge recombination, according to Rehm–Weller approach\textsuperscript{61} (see Table 5.2.1 footnote for the pertinent equations). As can be seen in Figure 5.2.4, the energy levels indicating the singlet excited state of SubPc and charge-separated states in o-DCB were different for dyads 1 and 2 (green lines) than those of dyads 3–5 (shown by pink lines). The energy of the charge-separated state generated in dyads 3–5 is higher by about 0.1 eV than those generated by dyads 1–2, and are higher than the triplet excited state energy of both \(^3\)SubPc\textsuperscript{*},\textsuperscript{43} and \(^3\)C\(_{60}\)\textsuperscript{*}. Under such conditions, the charge-separated state could return to the ground state by populating one of the triplet states. It may be mentioned here that the energy of the charge-separated state would be slightly lower (ca. 20 mV) in polar benzonitrile, due to different degrees of solvation of the charge-separated states. However, their relative positions with respect to the excited SubPc and C\(_{60}\) levels (both singlet and triplet states) would not alter due to small change in magnitude of the energy levels caused by solvent polarity effects. In order to verify these predictions, and secure evidence of charge separation in these dyads in solvents of varying polarity, transient absorption studies at different time scales (femto- to millisecond) were performed as summarized in the following section.
5.2.4 Transient Absorption Studies

First, femtosecond transient spectral properties of peripherally functionalized SubPcs were performed in $\alpha$-DCB and benzonitrile. Figure 5.2.5 shows transient spectra of SubPc derivatives in benzonitrile. The $\beta$-thio-aryl-functionalized SubPcs, immediately after excitation (400 nm of 100 fs pulses), revealed transient peaks corresponding to singlet excited SubPc (see spectrum recorded at 25 ps delay time in Figure 5.2.5a and b). Compound 1c revealed peaks at 522, 693, and 997 nm and a negative peak at 650 nm with contributions from ground-state bleaching and stimulated emission.
Figure 5.2.5. Femtosecond transient difference absorption spectra of compounds 1c-5c at the indicated delay times in Ar-saturated benzonitrile.

Similarly for compound 2c, positive peaks were found at 502, 719, and 997 nm and the negative peak at 645 nm. At later times, decay of the positive peaks and recovery of the negative peak was accompanied by new peaks at 722 and 1194 nm for 1c and at 509, 733 and 1184 nm for the case of 2c was observed. These new peaks have been assigned to the triplet-state transitions of SubPc formed through an intersystem crossing process that was confirmed by performing nanosecond transient absorption studies (vide supra). Similar spectral features were observed in o-DCB also (see Figure 5.2.S1 in the Supporting Information).

For β-thio-aryl-substituted SubPcs the spectral features were almost similar. For 3c, positive peaks at 482, 720 and 961 nm and a negative signal at 602 nm were observed. Decay of the positive peaks and recovery of the negative peak was accompanied by new weak spectral features at 551 and 653 nm, which could be attributed to $^3\text{SubPc}^*$ transitions. Similar spectral
trends were also observed for other derivatives in both benzonitrile (see Figure 5.2.5c and d) and o-DCB (see Figure 5.2.52 in Supporting Information). In summary, successful excitation of SubPcs to initially populate the $^1\text{SubPc}^*$ followed by the intersystem crossing process to populate the $^3\text{SubPc}^*$ state in the investigated solvents was observed.

The femtosecond transient absorption studies also provided evidence for the occurrence of photoinduced charge separation in these dyads. Figure 5.2.6a and b show the femtosecond transient spectra of $\alpha$-substituted dyads 1 and 2 in benzonitrile. For dyad 1, the transient peaks of the instantaneously formed $^1\text{SubPc}^*$ decayed rapidly with the occurrence of new peaks at 488, 710, 1005, 1126 and 1488 nm. Additionally, the recovery of the negative peak at 645 was much faster than that seen for 1c in the same solvent. These observations support charge separation from the $^1\text{SubPc}^*$ leading to the formation of $\text{SubPc}^{**}$–$\text{C}_{60}^*$ charge-separated state. The transient peaks at 490, 710, 1126 and 1475 nm have been attributed to the presence of $\text{SubPc}^{**}$, while the 1005 nm peak was assigned to $\text{C}_{60}^*$.
Figure 5.2.6. Femtosecond transient absorption difference spectra of compounds 1-5 at the indicated delay times in Ar-saturated benzonitrile.

Although different in peak intensity, since 1c also had peaks in this spectral region, the spectra of 1 and 1c at the same concentration and at a delay time of 100 ps (where charge separation was fully established) was compared, as shown in Figure 5.2.7a. Such comparison confirmed that the transient peaks observed for 1 in the spectral region of SubPc\(^{**}\) (490, 710, 1126 and 1475 nm), while the 1005 nm peak was due to C\(_{60}\)\(^{-}\) (the noisy peak in the 730–800 nm range is due to extreme detector sensitivity and change of detectors from visible to near IR). With time, peaks corresponding to the charge-separated state in Figure 5.2.6a and b decayed with the appearance of new peak at 1190 nm corresponding to the formation of \(^{3}\text{SubPc}\)\(^{*}\). That is, population of the triplet excited state of \(^{3}\text{SubPc}\)\(^{*}\) by the radical ion-pair prior returning to the ground state as predicted by the energy level diagram in Figure 5.2.4 was witnessed.
Figure 5.2.7. Femtosecond transient difference absorption spectra of a) 1 (magenta) and 1c (wine) at a delay time of 100 ps, and b) 3 (magenta) and 3c (wine) at the delay time of 250 ps in Ar-saturated benzonitrile.

For β-substituted SubPc-C$_{60}$ dyads charge separation from the singlet excited state of SubPc was also evident. That is, recovery of the depleted peak at 602 nm was much faster than that observed in the case of control SubPcs. In addition, the cation and anion radical peaks at their expected wavelength region were observed. Spectral data for dyads 3–5 in benzonitrile is shown in Figure 5.2.6c–e, while comparison of spectral data of 3 and 3c at a delay time of 250 ps is shown in Figure 5.2.7b. Such analysis clearly revealed SubPc$^{*+}$ peak in the 660 nm range and C$_{60}^{*-}$ peak at 1005 nm, confirming charge separation from $^1$SubPc$^*$ in these dyads. The transient spectral data for dyads 1–5 in o-DCB is shown in Figure S3 in the Supporting Information, which also confirms charge separation in this solvent. The peaks corresponding to the charge-separated state decayed with time with the appearance of new peak in the 1165 nm range for 1 and 2, representing formation of $^3$SubPc$^*$ (see spectrum at 3 ns delay time). The kinetics of charge separation ($k_{CS}$) and charge recombination ($k_{CR}$) were evaluated by monitoring the growth the decay of the radical anion peak at 1005 nm, and are given in Table
5.2.2. The magnitude of $k_{CS}$ indicated fast charge separation, while the $k_{CR}$ was one-to-two orders of magnitude smaller than $k_{CS}$, a trend predicted for fullerene based donor–acceptor systems,\cite{13,14,15,16,17,18,19,20} and the expected solvent polarity trends within the experimental errors. In summary, successful occurrence of photoinduced electron transfer in peripherally modified with thio-aryl entities SubPc axially bound to fullerene in polar solvent has been demonstrated.

Table 5.2.2. Kinetics of charge separation, $k_{CS}$ and charge recombination, $k_{CR}$ of the investigated $\alpha$- and $\beta$-thio aryl substituted SubPc covalently linked to C$_{60}$.[a]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$k_{CS}$ [s$^{-1}$]</th>
<th>$k_{CR}$ [s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>benzonitrile</td>
<td>$3.4 \times 10^{10}$</td>
<td>$1.5 \times 10^{9}$</td>
</tr>
<tr>
<td></td>
<td>o-dichlorobenzene</td>
<td>$2.4 \times 10^{10}$</td>
<td>$9.3 \times 10^{8}$</td>
</tr>
<tr>
<td>2</td>
<td>benzonitrile</td>
<td>$5.9 \times 10^{10}$</td>
<td>$1.3 \times 10^{9}$</td>
</tr>
<tr>
<td></td>
<td>o-dichlorobenzene</td>
<td>$1.1 \times 10^{10}$</td>
<td>$1.3 \times 10^{9}$</td>
</tr>
<tr>
<td>3</td>
<td>benzonitrile</td>
<td>$6.3 \times 10^{10}$</td>
<td>$7.4 \times 10^{8}$</td>
</tr>
<tr>
<td></td>
<td>o-dichlorobenzene</td>
<td>$6.0 \times 10^{10}$</td>
<td>$2.1 \times 10^{9}$</td>
</tr>
<tr>
<td>4</td>
<td>benzonitrile</td>
<td>$1.5 \times 10^{10}$</td>
<td>$7.5 \times 10^{8}$</td>
</tr>
<tr>
<td></td>
<td>o-dichlorobenzene</td>
<td>$1.4 \times 10^{10}$</td>
<td>$1.2 \times 10^{9}$</td>
</tr>
<tr>
<td>5</td>
<td>benzonitrile</td>
<td>$2.9 \times 10^{10}$</td>
<td>$2.4 \times 10^{8}$</td>
</tr>
<tr>
<td></td>
<td>o-dichlorobenzene</td>
<td>$1.4 \times 10^{10}$</td>
<td>$4.3 \times 10^{8}$</td>
</tr>
</tbody>
</table>

[a] Experimental uncertainty = $\pm 10\%$

In order to establish the return path of the charge-separated states of these dyads, nanosecond transient absorption studies were performed. First, transient spectra of the control compounds 1c–5c were recorded; however, the transient signals were found to be weak implying inefficient population of $3\text{SubPc}^*$ in these compounds. Next, the dyads 1–5 were excited using 550 nm excitation, in which only SubPc had major absorbance. As predicted from femtosecond transient data recorded at higher delay times, dyads 1 and 2 revealed peaks in the range of 508, 755, 996, and 1190 nm, and a negative peak at 650 nm corresponding to $3\text{SubPc}^*$ (Figure 5.2.8a and b). For dyads 3–5 these peaks were in the 490, 730, and 990 nm range, and a negative peak at 610 nm corresponding to $3\text{SubPc}^*$ (Figure 5.2.8c–e). These spectra were
sufficiently different from that of fulleropyrrolidine, $^3\text{C}_{60}^*$, indicating the population of low-lying $^3\text{SubPc}^*$ instead of $^3\text{C}_{60}^*$ (see Figure 5.2.4 for energy level diagram). The signal intensities of $3\text{SubPc}^*$ in both types of dyads, namely, $\alpha$- or $\beta$-substituted, were better defined than those observed in $1\text{c}–5\text{c}$. These results suggest that populating $^3\text{SubPc}^*$ by the process of charge recombination is much more efficient than by direct excitation. The decay time constants for the $^3\text{SubPc}^*$ signal in these dyads were in the range of 35–50 $\mu$s.

![Graphs showing transient difference absorption spectra of dyads 1-5 at various delay times in Ar-saturated benzonitrile.](image)

Figure 5.2.8. Nanosecond transient difference absorption spectra of dyads 1-5 at the indicated delay times in Ar-saturated benzonitrile.

5.2.3 Conclusions

A series of SubPcs modified by peripheral substitution of thio-aryl groups to improve their light-harvesting properties, namely, red-shifted absorbance and emission, have been newly designed and synthesized. Greater spectral modulation in the case of $\alpha$-substituted SubPc derivatives compared to the $\beta$-substituted derivatives was witnessed. Electrochemical
studies revealed perturbation of both HOMO and LUMO levels and better electron-donor properties of thio-aryl substituted SubPcs. Next, the modified SubPcs were successfully utilized to build donor-acceptor dyads through the central boron atom with the well-known electron acceptor C₆₀. Both steady-state and time-resolved emission studies revealed quenching of SubPc in these dyads due to the occurrence of excited state events, and the free-energy calculations performed using spectroscopic and electrochemical redox data along with the control experiments suggested photoinduced charge separation to be the likely quenching mechanism. Subsequent studies performed using transient absorption techniques operating at different time scales provided spectral proof of charge separation. Kinetic analysis of the data revealed ultrafast charge separation and relatively slow charge recombination in these dyads, properties relevant to solar energy harvesting. Further studies along these lines are in progress.

5.2.4 Supporting Information

Figure 5.2.S1. Absorption (a) and emission (b) spectrum of compounds 2, 4 and 5 along with control compounds 2c, 4c and 5c, and the reference compound, SubPc in DCB. The compounds were excited at the most intense visible band peak maxima of a given compound.
Figure 5.2.52. Femtosecond transient difference absorption spectra of compounds 1c-5c at the indicated delay times in Ar-saturated o-DCB.

Figure 5.2.53. Femtosecond transient absorption difference spectra of compounds 1-5 at the indicated delay times in Ar-saturated o-DCB.
Figure 5.2.S4. Spectral changes observed during first electrochemical oxidation of (a) 2c and (b) 4c in benzonitrile.

Figure 5.2.S5. $^1$H-NMR spectrum of dyad 1 in CDCl$_3$. 
Figure 5.2.S6. $^{13}$C-NMR spectrum of dyad 1 in CDCl$_3$.

Figure 5.2.S7. MALDI-mass spectrum of compound 1.

Figure 5.2.S8. $^1$H-NMR spectrum of dyad 2 in CDCl$_3$. 
Figure 5.2.S9. $^{13}$C-NMR spectrum of dyad 2 in CDCl$_3$.

Figure 5.2.S10. MALDI-mass spectrum of compound 2.

Figure 5.2.S11. $^1$H-NMR spectrum of dyad 3 in CDCl$_3$. 
Figure 5.2.S12. $^{13}$C-NMR spectrum of dyad 3 in CDCl$_3$.

Figure 5.2.S13. MALDI-mass spectrum of compound 3.

Figure 5.2.S14. $^1$H-NMR spectrum of dyad 4 in CDCl$_3$. 
Figure 5.2.S15. $^{13}$C-NMR spectrum of dyad 4 in CDCl$_3$.

Figure 5.2.S16. MALDI-mass spectrum of compound 4.
Figure 5.2.S17. MALDI-mass spectra of compound 5.
CHAPTER 6

SUMMARY

The utilization of fossil fuel to fulfill the global energy demand though promotes economic development, it also presents a great threat to the environment let alone its deposits are getting exhausted. Hence, there’s a need to find renewable sources of energy that could supply the current and future energy demand while mitigating the existing condition of the earth. Along with the other sources of renewable energy, solar power has gained great interest in the past decades due to the vast abundance of sunlight and the carbon-free energy that it generates. The artificial capture and harvest of light energy has been patterned with the intricate pigment-protein complexes of plants. Although the current artificial photosynthetic apparatuses showed promising results, it still doesn’t come close to the efficiency that plants possess when it comes to absorbing, funneling, and converting light to chemical energy. However, this only proves that we still have a great deal of work to do in designing and constructing artificial photosynthetic systems of high quantum efficiency.

The result of the current research hopes to enrich the database on the design and assembly of light harvesting systems for artificial photosynthetic applications. Here, various multimodular antenna-reaction center mimics were characterized, and the photophysical and photochemical events were investigated in order to elucidate the photodynamic mechanisms (i.e., photoinduced energy and electron transfer) in these systems. The different modes of interaction between the electron donor and acceptor, and their arrangements were probed to determine its effects towards energy and electron transfer. Furthermore, the extent of charge stabilization with the employment of multiple electron donors was also examined along with
the variation of spacer lengths between the photoactive components. Finally, the impact of the modulation of the photophysical and redox properties of the photoactive components towards photoinduced electron transfer was also investigated.

The utilization of BODIPY as the antenna system and the employment of ferrocene (Fc) as secondary donor did prove to be effective, in not only capturing light but also in stabilizing the charge separated states. For a simple ZnP:C60Im, the rate constant for charge recombination was determined to be $8.40 \times 10^9$ s$^{-1}$; however, the self-assembled Fc-(ZnP:C60Im)-BODIPY multimodular donor-acceptor photosystem afforded to slow down the rate of charge recombination by about an order of 4, $k_{CR} = 1.44 \times 10^5$ s$^{-1}$. The results confirm that the presence of Fc afforded the spatially separated radical ion pair Fc$^+$(ZnP:C60•)$^-$-BODIPY. Moreover, the employment of multiple Fc units, and varying the linking mode (i.e., directly or with phenyl spacer) exhibited different mechanisms for charge stabilization. In directly linked Fc, initial electron transfer from Fc to ZnP yielding Fc$^+$-ZnP$^+$ was observed as manifested by the 680 nm peak corresponding to ZnP$^+$. Afterwards with the addition of C60Im, a peak at 1020 nm for C60$^+$ was observed. The phenyl-Fc on the other hand, didn’t reveal any peak at 680 nm; however, upon addition of C60Im showed reduction of the $k_{CR}$ value which indicates that the participation of Fc in the charge stabilization process is through hole shifting. These results tell us that interaction of the secondary donor towards the primary electron donor-acceptor system is dependent on the length of the spacer.

Evidence on the distance dependence of sequential electron transfer is further demonstrated by the aluminum(III) porphyrin-based multimodular photosystem composed of vertically positioned tetrathiafulvalene appended with pyridine and phenylpyridine, and a
covalently linked benzonate appended fullerene of varying phenyl spacer length. The transient absorption studies and time-resolved EPR showed the formation of the TTF**-AlP-C₆₀* radical ion pair with a lifetime of about 60-130 ns.

Substitution of the porphyrin macrocyle with fluorine atoms proved to modify its redox properties permitting it to serve as an electron acceptor as depicted by its lowered first reduction potential. Further lowering of its reduction potential was obtained by its metalation with gold(III) rendering a positive charge on the porphyrin macrocycle. Evidence of sequential electron transfer in the free-base porphyrin triad was confirmed indirectly by monitoring the AlP** band at ~570 and ~610 nm. While for the gold(III) porphyrin triad, it was confirmed through the AuP* peak at 612 nm. Charge stabilization in both triads with the addition of TTF was indeed observed with 1393-1484 ps lifetimes.

The influence of spacers towards the rates of electron transfer and charge stabilization was extended in subphthalocyanine-fullerene conjugates employing three phenothiazine (PTZ) secondary electron donors. Optical transient absorption studies suggests that electronic coupling in directly linked SubPc and PTZ is relatively moderate as manifested by the weak charge stabilization of the radical ion pair, where the C₆₀* decayed almost completely by 3 ns. However, long-lived charge separated states was observed in the phenoxy linked PTZ with a lifetime 185 and 250 ns in benzonitrile and toluene, respectively.

Modulation of the electronic properties of the SubPc core was also studied through its thio-aryl substitution at the α- and β-positions. The SubPc derivatives displayed redshifted Q bands indicative of electronic perturbation. Furthermore, photoinduced electron transfer was
also observed from the transient absorption peak at 1010 nm which corresponds to the $C_{60}^-$ radical anion with $k_{CR}$ values from $2.4 \times 10^8 - 2.5 \times 10^9$ s$^{-1}$.

The various factors that affect the rate of energy transfer, charge separation and charge recombination in antenna-reaction center photosystems were demonstrated in the current research. Furthermore, charge stabilization of the radical ion pair was also illustrated with the synthesis of multi-donor-acceptor conjugates that exhibits electron migration and hole transfer processes. Although the current donor-acceptor systems can still be improved by varying the type of molecular spacer used; instead of phenyl spacers, acetylene linkers could be used. The multiple antenna system and the secondary electron donors could be utilized in order to maximize light absorption. Again, it is our hopes that the multicomponent donor-acceptor photosystems studied here have enriched the database on antenna-reaction center mimics and will be helpful in the preparation and fabrication of a full-scale artificial photosynthetic apparatus.
APPENDIX

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336


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