STUDIES ON HIGH POTENTIAL PORPHYRIN-FULLERENE
SUPRAMOLECULAR DYADS

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Photoinduced electron transfer in self-assembled via axial coordination porphyrin-fullerene dyads is investigated. Fullerene functionalized with imidazole and fullerene functionalized with pyridine is chosen as electron acceptors, while zinc pophyrin derivatives are utilized as electron donors. The electron withdrawing ability of halogen atoms make the porphyrin ring electrophilic, which explained the binding of (F<sub>20</sub>TPP)Zn with fullerene derivatives having the highest binding constant around 10<sup>5</sup>M<sup>-1</sup>. Another important observation is that the fullerene imidazole binding to zinc pophyrin had higher stability than fullerene pyridine-porphyrin dyad. Computational DFT B3LYP-21G(*) calculations are used to study the geometric and electronic structures. The HOMO and LUMO was found to be located on the porphyrin and fullerene entities, respectively. Photoinduced electron transfer is investigated by the steady-state absorption and emission, differential pulse voltammetry, and nanosecond and femtosecond transient absorption studies. The measurements provided the same conclusion that the increasing number of the halogen atoms on the porphyrin ring leads to the higher binding of porphyrin-fullerene supramolecular dyads and efficient charge separation and charge recombination processes.
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CHAPTER 1
INTRODUCTION

1.1 Introduction

Energy, an important factor of human being’s survival and the socio-economic development. With the development of society and population growth, the global energy consumption is increasing year by year. Large-scale use of fossil fuels has brought a series of environmental and ecological problems, and carbon dioxide emissions have led to a large number of serious issues in the form of greenhouse effect and global climate change.\(^1\) As a key part of sustainable development, new source of energy development has attracted the attention of general public and the governments.

![Figure 1.1 The principle of natural photosynthesis](image-url)

\(^1\)Reference or citation needed.
Photosynthesis is known to be the planet's most important chemical reactions, which keeps the balance of oxygen and carbon dioxide in the atmosphere, provides energy to living beings on the earth by converting light energy into chemical energy. In photosynthetic process, antenna system transfers the singlet excitation energy to the reaction center among the chromophores. To achieve the energy conversation, the reaction center absorbs the energy transferred from antenna system (Figure 1.1).²

Recently, artificial photosynthesis has become the focus of researchers around the globe. Serious shortage of non-renewable energy and the success of light into energy conversion by natural photosynthesis have stimulated scientists to harvest the ultimate energy source-solar energy.³ Therefore, artificial photosynthesis is a promising method to resolve the problem of inadequate energy. Consequently, a series of donor-acceptor systems have been designed to study the photo-induced energy and electron transfer reactions.⁴

1.2 Porphyrins as Electron Donors

Porphyrin is a fully conjugated macrocycle, which is composed of four pyrrole rings structurally similar to plant chlorophylls. The nitrogen atoms are located in the center of the ring, so that metal cations can easily chelate to form metalloporphyrins. Porphyrins with conjugated π electron system are well known electron donors, which is not only due to the delocalized π system that can cause minimal structure change during electrons transfer, but also due to the affluent redox properties.
Figure 1.2 The structure of the chlorophyll a and chlorophyll b

The green pigments found in chloroplasts of leaf cells, absorb light and use it to provide energy. Chlorophylls, the major component of chloroplast are Mg(II) complexes of cyclic tetrapyrroles. Another reason for choosing porphyrins as electron donor is the similar structure and properties as chlorophylls. The structure of the chlorophylls is shown in Figure 1.2. The highly conjugated macrocycle exhibits a strong absorption band at about 400 nm in the UV-Vis spectrum, and the band also called “Soret” band. In the high wavelength region of 450 nm to 700 nm, it shows several weak absorptions, known as Q bands. Intensity and wavelength of the absorption bands of porphyrins show slight changes because of different substituents on the porphyrin ring.
1.3 Fullerenes as Electron Acceptors

Fullerenes have been extensively used as electron acceptors in donor-acceptor electron transfer reactions.\textsuperscript{7-10} Fullerenes, \( \text{C}_{60} \) and \( \text{C}_{70} \) are pure carbon molecules composed of 60 and 70 carbon atoms (Figure 1.3). One of the important properties of fullerenes is their low reorganization energy due to their symmetric spherical structure, which stabilizes charged entities. Fullerenes have unique three-dimensional structures, suitable redox potentials and small reorganization energies, which is conductive to accelerate the charge separation process and extend the life time of charge separation state.

![The structure of \( \text{C}_{60} \)](image)

\textbf{Figure 1.3} The structure of \( \text{C}_{60} \)

Fullerene derivatives, \( \text{C}_{60}\text{Im} \) and \( \text{C}_{60}\text{Py} \), are very good electron acceptors and can bind to metal atom in porphyrins strongly. The structures of \( \text{C}_{60}\text{Im} \) and \( \text{C}_{60}\text{Py} \) are shown in Figure 1.4.
1.4 Photo-Induced Electron Transfer Theory

Due to the importance of the photo-induced reactions, the principles of the electron and energy transfer are necessary to understand. An electron gets excited from ground state to excited state by absorbing the light of chromophores. By exciting the fluorescence, the excited electron can get back to the ground state. There are two mechanisms during the photo-induced reaction, one is the electron transfer, and other is energy transfer. In an electron transfer process, the electron donor transfers an electron to the acceptor that has an empty lowest unoccupied orbital (LUMO). Upon charge separation, electron donor becomes a radical cation $D^+$ as a result of losing an electron, while the electron acceptor forms radical anion $A^-$. In the case of energy transfer process, the energy of excited electron by absorbing the light of chromophores is released to the acceptor. Thereby, the excited acceptor goes to an excited state, excited electron transferred from the excited state back to the ground state. For electron acceptor, it is
necessary to have low energy excited state. After accepting the excited energy from the donor, the energy acceptor populate its the singlet excited state.

With regard to in-depth understanding of electron transfer reaction, ‘Marcus theory’ has gained recognition and attention. Marcus theory provides the most valuable theoretical basis of photo-induced electron transfer process. According to Marcus theory, the rate of electron transfer depends on three elements, viz, the distance between the electron donor and acceptor, the activation energy, and reorganization energy.

\[ k_{\text{ET}} = k_{\text{el}} V_n \exp\left(-\Delta G^0 + \lambda\right)/4kBT \]  

(E.q. 1)

In equation 1, \( k_{\text{el}} \) is the electronic transmission coefficient, \( V_n \) is the frequency of nuclear motion through the transition state, \( \Delta G^0 \) is the standard Gibb’s free energy change for the overall electron transfer reaction, \( T \) is absolute temperature, \( B \) is the Boltzmann’s constant, and \( \lambda \) is the reorganization energy that consists of solvent-independent \( \lambda_i \) and solvent-dependent components \( \lambda_s \), shown in equation 2.

\[ \lambda = \lambda_i + \lambda_s \]  

(E.q. 2)

Solvent-independent is not influenced by surrounding medium. The dependence of the solvent reorganization energy is variational:

\[ \lambda_s = b f_s = b(1/n^2 - 1/\varepsilon_R) \]  

(E.q. 3)

In equation 3, the \( \varepsilon_R \) is the dielectric constant of solvents, \( f_s \) is a factor about the solvent polarity. The refractive index of solvents is \( n \). \( b \) is a coefficient which calculated by the following equation 4,

\[ b = q_e^2/4\pi\varepsilon_0 \left[ 1/2R_D + 1/2R_A - 1/R_{DA} \right] \]  

(E.q. 4)
$q_e$ is the charge of the atom, $\varepsilon_0$ is the permittivity of vacuum, $R_D$ is the radii of the donor, $R_A$ is the radii of the acceptor, and $R_{DA}$ is the center to center distance between the donor and the acceptor.

The free energy of activation is determined by the reorganization energy and energy changes. Equation 5 shown below is used to calculate the value of the activation energy.

$$\Delta G = -(\Delta G^0 + \lambda)^2/4\lambda$$  \hspace{1cm} (E.q. 5)

In Marcus curve, the relationship between driving force $\Delta G^0$ and the reorganization energy $\lambda$ shows a parabola, which also demonstrates various energy relationships in the reaction of donor-accepter system. The driving force has two aspects in Marcus curve, normal region ($-\Delta G^0<\lambda$) and inverted region ($-\Delta G^0>\lambda$). In the normal region, the rate of electron transfer increases along with driving force $-\Delta G^0$ increase; Furthest increasing of $-\Delta G^0$ lead to decrease in the rate of electron transfer, often called as ‘inverted region’. Upon reaching the point where $-\Delta G^0=\lambda$, the electron transfer rate attains a maximum.

1.5 Covalently and Non-Covalently Linked in D-A System

Donor-acceptor system is of great importance in artificial photosynthesis. For reasons discussed earlier, Porphyrin-fullerene based D-A systems are the most studied ones. 16-18 Two approaches are used to link porphyrins and fullerenes, namely, covalently and non-covalently linked ones.
Covalently linked donor-acceptor systems are accomplished generally through cycloaddition reactions. The 1, 3-dipolar cycloaddition reaction, which is a type of cycloaddition reactions, is found to be a popular synthesis method to connect porphyrins and fullerenes. D’Souza et al. has successfully synthetized a multi-triphenylamine-substituted porphyrin-fullerene dyad by using 1, 3-dipolar cycloaddition reaction (Figure 1.5). Porphyrins are modified by connecting three covalently linked triphenylamine entities at the meso position, and the fourth meso position is occupied by one fulleropyrrolidine. In this conjugated system, porphyrins with three triphenylamines work as electron donor, and fullerenes moiety act as electron acceptor. Owing to three triphenylamine entities acting as an antenna, to funnel the UV/Vis light to porphyrin entities and extended the delocalization becomes slower the charge recombination of the electron transfer system leading to long-lived charge separation states. The absorbance
and fluorescence spectra are used to analyze the absorption behavior. Also, cyclic voltammetry and nanosecond transient absorption spectrum are used to figure out the energy and kinetics of charge separation and recombination.\textsuperscript{20}

Non-covalently linked approach is also vital in building donor-acceptor system, which plays an important role in solar energy harvesting.\textsuperscript{21} Supramolecular interactions such as, hydrogen bonding, π-π interaction, rotaxane type binding, and axial ligation are few methods used for non-covalent donor-acceptor system.

An increasing number of non-covalently linked systems through axial coordination have been developed.\textsuperscript{22-24} Metalloporphyrins with coordinative unsaturated metal cation accommodate one or two axial ligands, and pyridyl and imidazol normally used as ligands to link to porphyrin entity in axial linking way. The axial coordination is accomplished through linking the nitrogen of pyridyl and imidazole components to the metal center of metalloporphyrins.

D’Souza and co-workers devised a metal-ligand axial coordination approach to develop magnesium porphyrin-fullerene dyad (Figure 1.6). Meso-tetraphenylporphyrin (MgTPP) has been used as the electron donor, and \( \text{C}_{60} \) imidazole is used as an electron acceptor. Binding constant (\( K = (1.5 \pm 0.3) \times 10^4 \text{M}^{-1} \)), for the 1:1 complex of MgTPP and \( \text{C}_{60}\text{Im} \) has been reported based on Benesi-Hildebrand plot. This indicated a stable complex formation of porphyrin-fullerene dyad. By using the \textit{ab initio} B3LYP/3-21G (*) method, geometric and electronic structure of MgTPP-\( \text{C}_{60}\text{Im} \) dyad was probed. Electrochemical studies showed the redox behavior of the newly formed dyad, which indicated possibility of electron transfer from MgTPP to \( \text{C}_{60}\text{Im} \). The calculated free energy change for electron transfer is -0.90 eV. The charge separation rate was found to
be $1.1 \times 10^{10} \text{s}^{-1}$ relayed on the picosecond time-resolved emission study, suggesting the efficient charge separation. The nanosecond transient absorption study is used to obtain the rate of charge recombination, was found to be $8.3 \times 10^7 \text{s}^{-1}$.\textsuperscript{25}

**Figure 1.6** The structure of MgTPP axially ligated to $C_{60}\text{Im}$

In the present study, high potential porphyrin-fullerene supramolecular dyads have been investigated in detail and results discussed
CHAPTER 2
MATERIALS AND INSTRUMENTS

2.1 Materials and Synthesis

Chemical: Reagents were from Aldrich Chemicals whereas the bulk solvents utilized in the syntheses were from Fischer Chemicals.

2.1.1 Synthesis of (F$_{20}$TPP)Zn

Step I. Synthesis of 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin, (F$_{20}$TPP)H$_2$.

This was synthesized according to literature procedure.$^{26-27}$ Pyrrole (100 μL, 1.42 mmol) and pentafluorobenzaldehyde (278 mg, 1.42 mmol) were dissolved in 200 mL of dry CHCl$_3$, and the resultant mixture was stirred under argon for 1.5 h. BF$_3$O(Et)$_2$ (60 μL, 0.473 mmol) was then added. Porphyrin formation leveled off after 1 h. p-chloronil (265 mg, 1.07 mmol) was then added to the brown reaction mixture, and the resultant mixture was stirred at room temperature for 1 h. Triethylamine (66 μL, 0.473 mmol) was added, and the reaction mixture was stirred for 8 h and then concentrated. Column chromatography on silica gel with a mixture of hexane/chloroform (20:80 v/v) gave the final compound. Yield: 7%. $^1$H NMR (400 MHz, CDCl$_3$) in ppm: δ 8.8 (s, 8H, β pyrrole), 2.8 (s, 2H, -NH); $^{13}$C NMR (400 MHz, CDCl$_3$): δ = 161.1, 155.7, 143, 142.5, 136.7, 137.4, 134.8, 132.1, 120.7, 119.9, 107.7, 103.1 ppm, Mass: calculated, 974.55; found, 975.4

Step II. Synthesis of 5,10,15,20-tetrakis(pentafluorophenyl)porphyrinatozinc(II), (F$_{20}$TPP)Zn.

The structure of (F$_{20}$TPP) Zn is shown in Figure 2.1.
The free-based porphyrin from above (50 mg) was dissolved in CHCl$_3$ (10 mL), a few drops of saturated solution of zinc acetate in methanol was added, and the resulting mixture was refluxed for 2 h. The course of the reaction was followed by monitoring the disappearance of the intense visible band at 512 nm absorption band. At the end, the reaction was washed with water and dried over anhydrous Na$_2$SO$_4$. Chromatography on a silica gel column using CHCl$_3$ as eluent gave the final compound. Yield: 90%. $^1$H NMR (400 MHz, CDCl$_3$) in ppm: $\delta$ 8.9 (s, 8H, $\beta$ pyrrole); $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ = 143, 142.5, 138.6, 139, 134.8, 124.9, 123.8, 121.2, 115, 107.7 ppm, Mass calculated: 1037.94; found 1038.8

2.1.2 Synthesis of (CF$_3$TPP)Zn.

Step I. Synthesis of 5,10,15,20-tetrakis(4-(trifluoromethyl)phenyl)porphyrin, (CF$_3$TPP)$_2$. Pyrrole (100 μL, 1.42 mmol) and 4-(trifluoromethyl)benzaldehyde (247 mg, 1.42 mmol) were dissolved in 200 mL of dry CHCl$_3$, and the resultant mixture was stirred under argon for 1.5 h. BF$_3$.O(Et)$_2$ (60 μL, 0.473 mmol) was then added. Porphyrin formation
leveled off after 1 h. p-Chloronil (265 mg, 1.07 mmol) was then added to the brown reaction mixture, and the resultant mixture was stirred at room temperature for 1 h. Triethylamine (66 μL, 0.473 mmol) was added, and the reaction mixture was stirred for 8 h and then concentrated. Column chromatography on silica gel with a mixture of hexane/chloroform (40:60 v/v) gave the final compound. $^1$H NMR (400 MHz, CDCl$_3$) in ppm: δ 8.8 (s, 8H, β pyrrole), 7.59 (d, 8H, phenyl), 7.34 (d, 8H, Phenyl), -2.8 (s, 2H, -NH), $^{13}$C NMR (400 MHz, CDCl$_3$): δ = 161.1, 155.7, 145.6, 142.1, 141.3, 134, 137.4, 125, 124.1, 120.6, 103.1 ppm. Mass calculated: 886.73; found 887.64

Step II. Synthesis of 5,10,15,20-tetrakis(4-(trifluoromethyl)phenyl)porphyrinatozinc(II), (CF$_3$TPP)Zn.

The free-based porphyrin from above (60 mg) was dissolved in CHCl$_3$ (10 mL), a saturated solution of zinc acetate in methanol was added, and the resulting mixture was stirred overnight at room temperature. The course of the reaction was followed by monitoring the disappearance of the visible band at 516 nm. At the end, the reaction was washed with water and dried over anhydrous Na$_2$SO$_4$. Chromatography on a silica gel column using CHCl$_2$ as eluent gave the final compound. Yield: 94%. $^1$H NMR (400 MHz, CDCl$_3$) in ppm: δ 8.9 (s, 8H, β pyrrole), 7.57 (d, 8H, Ph), 7.31 (s, 8H, Phenyl), $^{13}$C NMR (400 MHz, CDCl$_3$): δ = 145.6, 139, 138.6, 134.9, 130.2, 124.9, 124.1, 123.8, 121.2, 115.4, 115 ppm. Mass calculated: 966.16; found 967.06. The structure of ((CF$_3$)$_4$TPP)Zn is shown in Figure 2.
2.1.3 Synthesis of (F₄TPP)Zn

Step I. Synthesis of 5,10,15,20-tetrakis(3-fluorophenyl)porphyrin, (F₄TPP)H₂.

Pyrrole (100 μL, 1.42 mmol) and 3-fluorobenzaldehyde (176 mg, 1.42 mmol) were dissolved in 200 mL of dry CHCl₃, and the resultant mixture was stirred under argon for 1.5 h. BF₃.O(Et)₂ (60 μL, 0.473 mmol) was then added. Porphyrin formation leveled off after 1 h. p-Chloronil (265 mg, 1.07 mmol) was then added to the brown reaction mixture, and the resultant mixture was stirred at room temperature for 1 h. Triethylamine (66 μL, 0.473 mmol) was added, and the reaction mixture was stirred for 8 h and then concentrated. Column chromatography on silica gel with a mixture of hexane/chloroform (30:70 v/v) gave the final compound. Yield: 23%. ¹H NMR (400 MHz, CD₃OD) in ppm: δ 8.86 (s, 8H, β pyrrole), 7.6-7.2 (m, 16H, phenyl), -2.79 (s, 2H, -NH), ¹³C NMR (400MHz, CDCl₃): δ = 162.8, 161.1, 155.7, 141.3, 137.4, 132.1, 120.7, 119.9, 114.7, 111.2, 103.1 ppm, Mass calculated: 686.7; found 687.58.
Step II. Synthesis of 5,10,15,20-Tetrakis(3-fluorophenyl)porphyrinatozinc(II), (F$_4$TPP)Zn.

The structure of (F$_4$TPP) Zn is shown in Figure 2.3.

![Figure 2.3 Structure of (F$_4$TPP)Zn](image)

The free-based porphyrin from above (50 mg) was dissolved in CHCl$_3$ (10 mL), a few drops of saturated solution of zinc acetate in methanol was added, and the resulting mixture was stirred overnight at room temperature. The course of the reaction was followed by monitoring the disappearance of the 512 nm absorption band. At the end, the reaction was washed with water and dried over anhydrous Na$_2$SO$_4$. Chromatography on a silica gel column using CHCl$_2$ as eluent gave the final compound. Yield: 95%. $^1$H NMR (400 MHz, CD$_3$OD) in ppm: δ 8.82 (s, 8H, β pyrrole), 7.6-7.10 (m, 16H, phenyl), $^{13}$C NMR (400MHz, CDCl$_3$): δ = 162.8, 141.6, 139, 138.6, 130.2, 124.9, 123.8, 121.2, 115, 114.7, 111.2 ppm, Mass calculated: 752.11; found 753.02

2.1.4 Synthesis of (Cl$_4$TPP)Zn

Step I. Synthesis of 5,10,15,20-tetrakis(4-chlorophenyl)porphyrin, (Cl$_4$TPP)H$_2$. 

15
Pyrrole (100 μL, 1.42 mmol) and 4-chlorobenzaldehyde (199 mg, 1.42 mmol) were dissolved in 200 mL of dry CHCl₃, and the resultant mixture was stirred under argon for 1.5 h. BF₃·O(Et)₂ (60 μL, 0.473 mmol) was then added. Porphyrin formation leveled off after 1 h. p-Chloronil (265 mg, 1.07 mmol) was then added to the brown reaction mixture, and the resultant mixture was stirred at room temperature for 1 h. Triethylamine (66 μL, 0.473 mmol) was added, and the reaction mixture was stirred for 8 h and then concentrated. Column chromatography on silica gel with a mixture of hexane/chloroform (30:70 v/v) gave the final compound. Yield: 27%, ¹H NMR (400 MHz, CD₃OD) in ppm: δ 8.88 (s, 8H, β pyrrole), 7.4-6.9 (m, 16H, phenyl), -2.8 (s, 2H, -NH), ¹³C NMR (400 MHz, CDCl₃): δ = 161.1, 155.7, 142.1, 140.4, 137.4, 133.5, 132.1, 128.7, 127.8, 120.7, 119.5, 103.1 ppm, Mass calculated: 752.52; found 753.44

Step II. Synthesis of 5,10,15,20-tetrakis(4-chlorophenyl)porphyrinatozinc(II), (Cl₄TPP)Zn.

The free-based porphyrin from above (50 mg) was dissolved in CHCl₃ (10 mL), a saturated solution of zinc acetate in methanol was added, and the resulting mixture was stirred overnight at room temperature. The course of the reaction was followed by monitoring the disappearance of the 512 nm absorption band. At the end, the reaction was washed with water and dried over anhydrous Na₂SO₄. Chromatography on a silica gel column using CHCl₃ as eluent gave the final compound. Yield: 95%. ¹H NMR (400 MHz, CDCl₃) in ppm: δ 8.92(s, 8H, β pyrrole), 7.35-6.9(m, 16H, phenyl), ¹³C NMR (400 MHz, CDCl₃): δ = 140.4, 138.6, 139, 133.5, 128.7, 127.8, 124.9, 121.2, 115.4, 115 ppm, Mass calculated: 817.93; found 818.8. The structure of (Cl₄TPP) Zn is shown in Figure 2.4.
2.1.5 Synthesis of (TPP)Zn

Step I. Synthesis of 5,10,15, 20-tetra phenyl porphyrin, (TPP)H₂

In 200 mL of propionic acid, 18.9 mmol of (benzaldehyde) and 18.9 mmol (1.26 g) of pyrrole were added. The solution was refluxed for 45 minutes and the solvent was removed under reduced pressure. The crude product was then washed several times with methanol and dissolved in minimum amount of CHCl₃/hexane 1:1 and loaded on a basic alumina column and eluted with CHCl₃/hexane 1:1. Yield: 1.74 g (15 %). ¹H NMR (CDCl₃): δ (ppm) 8.85 (s, 8H, β-pyrrole), 8.13 (m, 6H o-phenyl H), 7.65 (m, 9H, m,p-phenyl H), -2.78 (s, br, 2H, imino H). Mass calculated: 614.74; found 615.6

Step II. Synthesis of 5,10,15, 20-tetra substituted porphyrinatozinc(II), (TPP)Zn.

The structure of (TPP)Zn is shown in Figure 2.5.
This was synthesized by metallation of above compound with zinc acetate. To 0.33 mmol (200 mg) of (TPP)H₂ in CHCl₃, excess of zinc acetate in methanol was added. The solution was stirred for 30 minutes and then concentrated and loaded on a basic alumina column and eluted with CHCl₃. Yield: 210 mg (93%). 1H NMR (CDCl₃): δ (ppm) 8.93 (s, 8H, β-pyrrole), 8.2 (d, 6H, o-phenyl H) and 7.74 (m, 9H, m,p-phenyl H). Mass calculated: 693.16; found 694.08.

2.2 Physical Methods

2.2.1 UV-Visible Absorption and Fluorescence Emission Spectroscopy

UV-visible absorption spectroscopy measured the absorbed energy at wavelength of the applied radiation. An optically watered quartz cell filled with pure solvent is used as reference sample to set as baseline. UV-visible absorption spectroscopy is a necessary method to detect the electronic coupling in a donor-acceptor system. The UV-visible-NIR spectral measurements were carried out with Shimadzu 2550 UV-Vis spectrophotometer or Jasco V-670 spectrophotometer.
The steady state fluorescence emission was monitored by using a Varian fluorescence spectrophotometer or a Horiba Jobin Yvon Nanolog UV-visible-NIR spectrophotometer.

2.2.2 Computational Studies

Computational study is used to gain insight into the molecular geometry and structure. Using B3LYP/3-21G (*) computational method, we investigated the complex geometry of porphyrins and fullerenes. The visualization of the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LOMO) were performed by Gausssvview software.

2.2.3 Differential Pulse Voltammetry (DPV)

Differential pulse voltammetry is a common electrochemical method, which superimposes a constant amplitude pulse voltage on the linear variation of the DC voltage. Differential pulse voltammetry not only has high accuracy (error 0.04 – 0.05 V) but also lower limits of detection to $10^{-7}$ to $10^{-8}$ M. DPV was recorded on a Princeton Applied Research potentiostat/galvanostat Model 263A. Three electrodes were needed in DPV measurement, which are: working electrode where potential was varied by time (platinum disc Ag/AgCl), reference electrode, counter electrode: Pt-wire. By collecting the first one-electron oxidation potentials of the donor, $E^+ (D)$, and the first one electron reduction potential of the acceptor, the free energy of charge separation (CS) and charge recombination (CR) for a donor-acceptor system was calculated by the Rehm-Weller equation (E.q. 6.7.) .
\[ \Delta G_{CR} = E^+(D) - E(A) + \Delta G_s \]  
\[ \Delta G_{CS} = -\Delta G_{CR} - E_{(0,0)} \]  
\[ E_{(0,0)} \text{ is the excited states of the donor. The value of } \Delta G_s \text{ is solvent dependent, which was calculated by following equation,} \]
\[ \Delta G_s = e^2/(4\pi\varepsilon_o)[(1/2R^+ + 1/2R^- - 1/R_{cc})/\varepsilon_R - (1/2R^+ + 1/2R^-)/\varepsilon_R] \]

In equation 8, \( R^+ \) and \( R^- \) are radii of cation and anion, \( R_{cc} \) is the center to center distance between donor and acceptor, and the \( \varepsilon_R \) is the dielectric constant of solvents.

### 2.2.4 Time-Resolved Emission Spectroscopic Techniques

Time-resolved emission measurement was used to monitor the electron transfer reaction, and obtain fluorescence decay of the excited molecule. By applying a pulsed laser to the molecule, the excited molecular decay to the ground state, was used to calculate the lifetime. In this project, five different porphyrins were monitored by time-resolved emission technique.

### 2.2.5 Femtosecond Transient Absorption Study

Femtosecond transient absorption measurements were recorded by using Femtosecond Laser Source by Coherent corporation involving diode-pumped, mode locked Ti:Sapphire laser and diode-pumped intra cavity doubled Nd:YLF laser to generate a compressed laser output of 1.45W. The rate of charge separation and charge combination is obtained by femtosecond transient absorption measurement, to prove the process of electron transfer in supramolecular systems.
2.2.6 Nanosecond Transient Absorption Study

Nanosecond transient absorption spectrum in the visible-NIR region were measured by means of laser-flash photolysis; 532 nm light from a Nd:YAG laser was used as the exciting source and a Ge-avalanche-photodiode module was used as a detector.
CHAPTER 3
HIGH POTENTIAL PORPHYRIN-FULLERENE IN SUPRAMOLECULAR DYADS

3.1 Introduction

Photosynthesis of green plants is fairly efficient energy conversion process. Since there is an energy shortage, mimicking photosynthesis for producing energy has become the focus of attention. Thus, synthesis and application of porphyrin and fullerene dyads has been undertaken to investigate photoinduced electron transfer. Porphyrins have been used as electron donors, due to their π conjugate structure and good absorbability. On the other hand, fullerene derivatives are used as electron acceptor. Metalloporphyrin axial ligated coordination by a fullerene functionalized to possess a nitrogenous ligand is the approach we used in present study. To get better understanding of the molecular geometry and electronic structure, B3LYP/3±21G(*) method has been used. UV-visible absorption and fluorescence emission measurement were used to analyze zinc porphyrins-C\textsubscript{60}Im/C\textsubscript{60}Py dyad systems. For purpose of probing the redox process, the differential pulse voltammetry approach is used. Femtosecond transient absorption and nanosecond transient absorption studies are performed to prove the occurrence of the charge transfer process, and to obtain the charge separation rate and charge recombination rate constants.

In the present study, halogen substituted porphyrin derivatives have been used, these are :

\[(F_{20}TPP)\text{Zn}-(5,10,15,20\text{tetrakis(pentafluorophenyl)}\text{porphyrinatozinc(II))},\]
\[((CF_3)TPP)\text{Zn}-(5,10,15,20\text{tetrakis\{4-(trifluoromethyl)phenyl\}porphyrinatozinc(II)}),\]
\[(F_4TPP)\text{Zn}-(5,10,15,20\text{tetrakis(3-fluorophenyl)}\text{porphyrinatozinc(II)}),\]
(Cl₄TPP)Zn-(5,10,15,20-tetrakis(4-chlorophenyl)porphyrinatozinc(II)), and (TPP)Zn-
(5,10,15,20-tetra phenyl porphyrinatozinc(II)). All the five substituted zinc porphyrins
were used to axial coordination of either C₆₀Im or C₆₀Py to form the dyads.

3.2 Results and Discussion

3.2.1 Optical Absorption and Steady State Fluorescence Studies

Figure 3.1 shows the absorption spectra of (F₂₀TPP)Zn, ((CF₃)₄TPP)Zn, (Cl₄TPP)Zn, (F₄TPP)Zn, and (TPP)Zn in dichloromethane. (TPP)Zn, as a reference compound, shows the Soret band at 419 nm and a visible band located at 548 nm. Because of the presence of chlorine atoms on zinc porphyrin macrocycle, there is a small bathochromic shift Soret band at 420 nm and visible band at 549 nm. For fluorine atom substituted porphyrin derivations, a blue shift was observed. The Soret band and visible band of (F₄TPP)Zn and (CF₃TPP)Zn, were located at 418 nm and 547 nm respectively. Substitution of 20 fluorides in case of (F₂₀TPP)Zn showed drastic blue-shift of Soret band located at 414 nm.
Figure 3.1 Absorption spectra of \((\text{F}_{20}\text{TPP})\text{Zn}\), \((\text{CF}_3)_4\text{TPP})\text{Zn}\), \((\text{Cl}_4\text{TPP})\text{Zn}\), \((\text{F}_4\text{TPP})\text{Zn}\), and \((\text{TPP})\text{Zn}\) in dichloromethane

![Absorption spectra graph]

Figure 3.2 Steady state fluorescence spectra of \((\text{F}_{20}\text{TPP})\text{Zn}\), \(\lambda_{\text{ex}} = 414\) nm; \((\text{CF}_3)_4\text{TPP})\text{Zn}\), \(\lambda_{\text{ex}} = 418\) nm; \((\text{Cl}_4\text{TPP})\text{Zn}\), \(\lambda_{\text{ex}} = 420\) nm; \((\text{F}_4\text{TPP})\text{Zn}\), \(\lambda_{\text{ex}} = 418\) nm; and \((\text{TPP})\text{Zn}\), \(\lambda_{\text{ex}} = 419\) nm in dichloromethane

Figure 3.2 shows the steady state emission spectra of \((\text{F}_{20}\text{TPP})\text{Zn}\), \((\text{CF}_3)_4\text{TPP})\text{Zn}\), \((\text{Cl}_4\text{TPP})\text{Zn}\), \((\text{F}_4\text{TPP})\text{Zn}\), and \((\text{TPP})\text{Zn}\) in dichloromethane. Upon exciting the \((\text{TPP})\text{Zn}\) at 414 nm, the emission spectrum showed two peaks at 585 nm and 639 nm respectively. \((\text{Cl}_4\text{TPP})\text{Zn}\) when excited at 420 nm, revealed peaks located at 597 nm and 644 nm, which were blue shifted compared to the \((\text{TPP})\text{Zn}\). The emission spectrum of \((\text{F}_4\text{TPP})\text{Zn}\) shows two peaks at 595 nm and 642 nm, which indicated a blue shift, as compared to \((\text{TPP})\text{Zn}\). \((\text{CF}_3)_4\text{TPP})\text{Zn}\) upon excitation at 418 nm, also revealed a blue shift, whose peaks appeared at 596 nm and 643 nm. Since \((\text{F}_{20}\text{TPP})\text{Zn}\) has 20 fluorides substituted to zinc porphyrin, it showed a drastic blue shift of the fluorescence emission bands.
The trend in blue shift followed (TPP)Zn→(Cl₄TPP)Zn→(F₄TPP)Zn→((CF₃)₄TPP)Zn→(F₂₀TPP)Zn for both the absorbance and fluorescence emission and this could be attributed to the substitution effect in the macrocyclic ring of the zinc porphyrins.

3.2.2 Time-Resolved Emission Spectroscopic Study

The fluorescence lifetime τᵣ of the (TPP)Zn monitored at 595 nm showed a monoexponential decay, with a lifetime of 1.85 ns. The insert table in the Figure 3.3 shows the fluorescence lifetime of the (F₂₀TPP)Zn, ((CF₃)₄TPP)Zn, (Cl₄TPP)Zn, (F₄TPP)Zn. The values of the lifetime τᵣ are 1.22 ns, 1.91 ns, 1.0 ns, and 1.53 ns respectively. It was found that ((CF₃)₄TPP)Zn has relatively long-lived singlet excited state, which means ((CF₃)₄TPP)Zn is a better photosensitizer. The trend of better photosensitizer was ((CF₃)₄TPP)Zn> (TPP)Zn> (F₄TPP)Zn> (F₂₀TPP)Zn> (Cl₄TPP)Zn.

![Figure 3.3](image)

**Figure 3.3** The fluorescence decay of the substituted zinc porphyrins
3.2.3 Phosphorescence Study

(Cl₄TPP)Zn reveals phosphorescence maxima at 786 nm. The phosphorescence maxima of (F₄TPP)Zn occurred at 722 nm. For (F₂₀TPP)Zn, a low intensity phosphorescence band was observed at about 732 nm. This data was used to establish the triplet energy levels of porphyrin sensitizer in the present study, which is \( ^3(F_{20}TPP)Zn^* = 1.69 \text{ eV}, \quad ^3(F_4TPP)Zn^* = 1.6 \text{ eV}, \quad \text{and} \quad ^3(Cl_4TPP)Zn^* = 1.6 \text{ eV}. \)

![Figure 3.4](image.png)

**Figure 3.4** The phosphorescence spectrum of zinc porphyrin in dichlorobenzene of 77K

3.2.4 X-ray Crystallography Study

Although the structure of (5,10,15,20-tetrakis(pentafluoro-phenyl)porphyrinato)-zinc(II) n-hexane solvate has been known for a while, but a non-solvated molecule has not been reported by X-ray analysis before. This has been accomplished in the present study (Figure 3.5).

Suitable crystals of compound (F₂₀TPP)Zn were grown from hexane/dichloromethane (6:4) mixture for several days. The crystal structure
determination of the compound was carried out using a Bruker SMART APEX2 CCD-based X-ray diffractometer equipped with a low temperature device and a Mo-target X-ray tube (wavelength = 0.71073 Å). Measurements were taken at 200(2) K (crystals fall apart at 100K). Data collection, indexing, and initial cell refinements were carried out using APEX2\textsuperscript{31}, with the frame integrations and final cell refinements performed using SAINT\textsuperscript{32}. An absorption correction was applied using the program SADABS\textsuperscript{33}. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms in compound (F\textsubscript{20}TPP)Zn were placed in idealized positions and were refined as riding atoms. The structure was examined using the Addsym subroutine of PLATON to ensure that no additional symmetry could be applied to the models.\textsuperscript{34} Structure solution, refinement, graphics and generation of publication materials were performed using SHELXTL software.\textsuperscript{35-36} Refinement details and structural parameters for compound (F\textsubscript{20}TPP)Zn are summarized in Table 3.1.

**Table 3.1 Structure determination summary for (F\textsubscript{20}TPP)Zn**

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</table>

**Figure 3.5** ORTEP diagram. Thermal ellipsib of (F₂₀TPP)Zn
The molecule occupies a special position in the unit cell and has an almost flat core. Ph-rings (C11…C16 and C17…C22) are rotated out of that plane, forming dihedral angles of 78.2(1) and 78.7(1)°, respectively. Intermolecular contacts Zn1…F8/F8B (2.834 Å) and F3/F3A…F4/F4A (2.811 Å) link molecules in the crystal into a network (Figures 3.6 and 3.7). Interestingly, while in 1 fluorine atoms in $p$-positions of Ph-rings form short intermolecular contacts with Zn, in the earlier published structure the fluorine atoms in the $m$-positions of the phenyl cycle form even shorter intermolecular contacts (2.652 Å).^{31}

Figure 3.6 Fragment of the crystal packing with Zn1…F8/F8B contacts.
Figure 3.7 Crystal packing diagram along the $a$ axis. Dashed lines indicate intermolecular Zn…F and F…F contacts

3.2.5 Steady-State Absorption Spectral Studies
Figure 3.8 UV/Vis spectral changes observed during the formation of (a) (F20TPP)Zn-C60Im dyad and (b) (F20TPP)Zn-C60Py dyad in dichloromethane.

Figure 3.8(a) shows the UV/Vis titration spectral changes during the formation of both (F20TPP)Zn-C60Im dyad and (F20TPP)Zn-C60Py dyad in dichloromethane. Upon adding the calculated amount of C60Im to (F20TPP), the spectrum showed the red shift of the Soret and visible bands, suggesting the formation of the (F20TPP)Zn-C60Im dyad. As can be seen from the Figure 3.8(b), (F20TPP)Zn-C60Py dyad also reveal the red shift of the Soret and visible bands. From the Benesi-Hildebrand plot of the absorbance data, the formation constant $K$ for (F20TPP)Zn-C60Im and (F20TPP)Zn-C60Py dyad were $1.2 \times 10^5$ M$^{-1}$ and $9.1 \times 10^4$ M$^{-1}$ respectively. The value for the formation constant $K$ of axial coordination (F20TPP)Zn-C60Im dyad is higher compared the axially ligated dyad system of (F20TPP)Zn-C60Py.
Absorbance vs. wavelength, nm

(a)-i

(a)-ii

(b)-i

(b)-ii

I_0/(I_0-I)

1/c C 6 0 P yridine
Figure 3.9 The absorbance titration spectra of (a)-i ((CF$_3$)$_4$TPP)Zn-C$_{60}$Im, (a)-ii ((CF$_3$)$_4$TPP)Zn-C$_{60}$Py, (b)-i (Cl$_4$TPP)Zn-C$_{60}$Im, (b)-ii (Cl$_4$TPP)Zn-C$_{60}$Py, (c)-i (F$_4$TPP)Zn-C$_{60}$Im, (c)-ii (F$_4$TPP)Zn-C$_{60}$Py, (d)-i (TPP)Zn-C$_{60}$Im, and (d)-ii (TPP)Zn-C$_{60}$Py in dichloromethane
In Figure 3.9, spectral changes during the titration of, (a)-i ((CF$_3$)$_4$TPP)Zn with increasing addition of C$_{60}$Im (a)-ii ((CF$_3$)$_4$TPP)Zn upon increasing addition of C$_{60}$Py, (b)-i (Cl$_4$TPP)Zn with increasing addition of C$_{60}$Im (b)-ii (Cl$_4$TPP)Zn upon increasing addition of C$_{60}$Py, (c)-i (F$_4$TPP)Zn with increasing addition of C$_{60}$Im (c)-ii (F$_4$TPP)Zn upon increasing addition of C$_{60}$Py, (d)-i (TPP)Zn with increasing addition of C$_{60}$Im (d)-ii (TPP)Zn upon increasing addition of C$_{60}$Py, are shown.

The formation constant $K$ in Table 3.2 shows the order (F$_{20}$TPP)Zn>(((CF$_3$)$_4$TPP)Zn>(Cl$_4$TPP)Zn ≈ (F$_4$TPP)Zn>(TPP)Zn. For zinc porphyrin-C$_{60}$Py dyads, a similar trend was observed, suggesting the substituted ligand affects the formation of dyads. The fluorine atom has strong electron withdrawing ability; as a result the porphyrins with the fluorine atom revealed strong electrophilic effect. Thus, the more substituent F atom in the porphyrin, the higher formation constant was observed. C$_{60}$Im-(F$_{20}$TPP)Zn has the highest magnitude of formation constant, which attributed to the 20 fluorine atoms. In comparison of CF$_3$, the 12F connected with ZnTPP make the formation constant $K$ value smaller than the one of C$_{60}$Im-(F$_{20}$TPP)Zn dyad. The same reason can explain why the C$_{60}$Im- (F$_4$TPP)Zn dyad has the third highest $K$ value. For the five different substituted poyphyrrins, one with axial coordinate of C$_{60}$Im has higher formation constant value than the ones with C$_{60}$Py. That is, the imidazoly N to Zn atom has stronger binding affinity than the pyridyl N atom in the porphyrin core.
Table 3.2  Formation constant, $K$, calculated from Benesi-Hildebrand plots.

<table>
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<th>Donor</th>
<th>Acceptor</th>
<th>Formation constant, $K$</th>
</tr>
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<tbody>
<tr>
<td>(F$_{20}$TPP)Zn</td>
<td>C$_{60}$Im</td>
<td>$K=1.2\times10^5$ M$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>C$_{60}$Py</td>
<td>$K=9.1\times10^4$ M$^{-1}$</td>
</tr>
<tr>
<td>((CF$_3$)$_4$TPP)Zn</td>
<td>C$_{60}$Im</td>
<td>$K=3.0\times10^4$ M$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>C$_{60}$Py</td>
<td>$K=2.9\times10^4$ M$^{-1}$</td>
</tr>
<tr>
<td>(F$_{2}TPP$)Zn</td>
<td>C$_{60}$Im</td>
<td>$K=2.5\times10^4$ M$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>C$_{60}$Py</td>
<td>$K=2.2\times10^4$ M$^{-1}$</td>
</tr>
<tr>
<td>(Cl$_{4}$TPP)Zn</td>
<td>C$_{60}$Im</td>
<td>$K=2.4\times10^4$ M$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>C$_{60}$Py</td>
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</tr>
<tr>
<td>(TPP)Zn</td>
<td>C$_{60}$Im</td>
<td>$K=2.1\times10^4$ M$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>C$_{60}$Py</td>
<td>$K=1.2\times10^4$ M$^{-1}$</td>
</tr>
</tbody>
</table>

3.2.6 Steady State Fluorescence Study

Steady state fluorescence study is used to analyze the axial coordinated self-assembled dyads. Figure 3.10 shows the fluorescence spectrums of (a) (F$_{20}$TPP)Zn-C$_{60}$Im dyad and (b) (F$_{20}$TPP)Zn-C$_{60}$Py dyad. Upon adding calculated amounts of C$_{60}$Im or C$_{60}$Py to the (F$_{20}$TPP)Zn solution, the fluorescence intensity of the 585 nm and 639 nm bands decreased significantly. The fluorescence quenching of the (F$_{20}$TPP)Zn-C$_{60}$Im dyad was determined to be 80% while the fluorescence quenching of the (F$_{20}$TPP)Zn-C$_{60}$Py dyad was relatively smaller to be 78%. The binding efficiency of the (F$_{20}$TPP)Zn-C$_{60}$Im was higher than (F$_{20}$TPP)Zn-C$_{60}$Py dyad as verified by both absorbance titration and fluorescence titration experiments. The titration of the other four substituted porphyrins with C$_{60}$Im and C$_{60}$Py is shown in Figure 3.11.
Figure 3.10 The fluorescence spectral changes observed during the formation of (a) (F$_{20}$TPP)Zn-C$_{60}$Im dyad and (F$_{20}$TPP)Zn-C$_{60}$Py dyad in dichloromethane.
Figure 3.11 The fluorescence titrations of (a)-i ((CF<sub>3</sub>)<sub>4</sub>TPP)Zn-C<sub>60</sub>Im, \( \lambda_{ex} = 418 \) nm, (a)-ii ((CF<sub>3</sub>)<sub>4</sub>TPP)Zn-C<sub>60</sub>Im, \( \lambda_{ex} = 418 \) nm; (b)-i (Cl<sub>4</sub>TPP)Zn-C<sub>60</sub>Im, \( \lambda_{ex} = 420 \) nm, (b)-ii (Cl<sub>4</sub>TPP)Zn-C<sub>60</sub>Py, \( \lambda_{ex} = 420 \) nm; (c)-i (F<sub>4</sub>TPP)Zn-C<sub>60</sub>Im, \( \lambda_{ex} = 418 \) nm, (c)-ii (F<sub>4</sub>TPP)Zn-C<sub>60</sub>Im, \( \lambda_{ex} = 418 \) nm; and (d)-i (TPP)Zn-C<sub>60</sub>Im, \( \lambda_{ex} = 419 \) nm, (d)-ii (TPP)Zn-C<sub>60</sub>Im, \( \lambda_{ex} = 419 \) nm in dichloromethane

3.2.7 Computational Study

To secure a better understanding of intermolecular interactions and the electronic structures, B3LYP/3-21G (*) computational studies were performed.
Figure 3.12 B3LYP/3-21G (*) optimized structures of C$_{60}$Im bond substituted zinc porphyrins

Figure 3.12 shows the calculated B3LYP/3-2G(*) structures for the optimized structures of C$_{60}$Im bond substituted zinc porphyrins dyad. It is shown that the substituted porphyrin have axial ligation bond to fullerenes C$_{60}$Im.
Figure 3.13 (a) HOMO and LUMO of (TPP)Zn-C\(_{60}\)Im dyad, and (b) HOMO and LUMO of (TPP)Zn-C\(_{60}\)Py dyad

The highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of (TPP)Zn-C\(_{60}\)Im dyad are shown in Figure 3.13(a). HOMO is located in the (TPP)Zn porphyrin ring while LUMO is located in the C\(_{60}\)Im. The (TPP)Zn-C\(_{60}\)Py dyad was also studied, the HOMO is located in porphyrin ring and the LUMO is located in C\(_{60}\)Py, that shown in Figure 3.13(b).

As could been seen from Table 3.3, the binding energy of (TPP)Zn with C\(_{60}\)Im and C\(_{60}\)Py respectively are -20.10540438 and -17.69382262 kcal/mol. It is found that the axial coordination between the (TPP)Zn with C\(_{60}\)Im is better that (TPP)Zn-C\(_{60}\)Py dyad. This also confirmed the binding constant trend which the (TPP)Zn with C\(_{60}\)Im binds
shortage than the (TPP)Zn-C₆₀Py dyad. Computational results of the other four porphyrins were given in Table 3, which revealed a trend in the binding energy:

(F₂₀TPP)Zn > ((CF₃)TPP)Zn > (Cl₄TPP)Zn > (F₄TPP)Zn > (TPP)Zn.

### Table 3.3 The formation constant and binding energy for all investigated dyads

<table>
<thead>
<tr>
<th>Donor</th>
<th>Acceptor</th>
<th>Formation constant, $K$ (M⁻¹)</th>
<th>Binding Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(F₂₀TPP)Zn</td>
<td>C₆₀Im</td>
<td>$K=1.2x10^5$ M⁻¹</td>
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<tr>
<td></td>
<td>C₆₀Py</td>
<td>$K=9.1x10^4$ M⁻¹</td>
<td>-24.06862888</td>
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<tr>
<td>((CF₃)₄TPP)Zn</td>
<td>C₆₀Im</td>
<td>$K=3.0x10^4$ M⁻¹</td>
<td>-22.02721497</td>
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<tr>
<td></td>
<td>C₆₀Py</td>
<td>$K=2.9x10^4$ M⁻¹</td>
<td>-19.47707912</td>
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<tr>
<td>(F₄TPP)Zn</td>
<td>C₆₀Im</td>
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<td>-21.04754714</td>
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<td>C₆₀Py</td>
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<td>-18.9376092</td>
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<tr>
<td>(Cl₄TPP)Zn</td>
<td>C₆₀Im</td>
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<tr>
<td></td>
<td>C₆₀Py</td>
<td>$K=2.0x10^4$ M⁻¹</td>
<td>-18.49577976</td>
</tr>
<tr>
<td>(TPP)Zn</td>
<td>C₆₀Im</td>
<td>$K=2.1x10^4$ M⁻¹</td>
<td>-20.10540438</td>
</tr>
<tr>
<td></td>
<td>C₆₀Py</td>
<td>$K=1.2x10^4$ M⁻¹</td>
<td>-17.69382262</td>
</tr>
</tbody>
</table>

#### 3.2.8 Electrochemical Studies

Differential pulse voltammetry is used to evaluate the redox potentials of the newly assembled dyads. DPV experiments were performed in 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte in DCB, and the ferrence as the reference. Figure 3.14, shows two sets DPVs of the dyads, one for the zinc porphyrins with C₆₀Im (Figure 24 top), and the second one is zinc porphyrins with C₆₀Py (Figure 24 bottom).

For (F₂₀TPP)Zn, the first oxidation peak is located at 1.23 V and first reduction peak is at -0.98 V. Upon adding the C₆₀Im, the first oxidation peak is turn out to be at 1.29 V while the reduction of corresponding to C₆₀Im, appeared at -0.637 V. Similarly, adding C₆₀Py, the first oxidation peak is at 1.278 V and the first reduction peak is at -0.628 V.
Figure 3.14 Two sets of differential pulse voltammogram, for zinc porphyrins derivatives binding to C₆₀Im (top) and zinc porphyrins binding to C₆₀Py (bottom)
Table 3.4 shows the free energy changes of charge separation and charge recombination calculated using spectral and redox data. The (F$_{20}$TPP)Zn-C$_{60}$Im dyad has the lowest free energy change of charge separation. The calculated order of the free energy changes of charge separation is (F$_{20}$TPP)Zn-C$_{60}$Im < ((CF$_3$)$_4$TPP)Zn-C$_{60}$Im < (Cl$_4$TPP)Zn-C$_{60}$Im ≈ (F$_4$TPP)Zn < (TPP)Zn-C$_{60}$Im, it is to be conclude the substituted F atom lowers the free energy of charge separation, and the free energy of charge recombination increases by the increase number of F.

Table 3.4  Electrochemical redox potentials of the zinc porphyrin-fullerene dyads in DCB, 0.1M TBAPCl and free energy changes of charge separation and charge recombination.

<table>
<thead>
<tr>
<th>Donor</th>
<th>Acceptor</th>
<th>Formation constant, $K$</th>
<th>1$^{st}$ ox.</th>
<th>1$^{st}$ red.</th>
<th>$\Delta G_{CS}$</th>
<th>$\Delta G_{CR}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(F$_{20}$TPP)Zn</td>
<td>C$_{60}$Im $K=1.2x10^5$ M$^{-1}$</td>
<td>1.285</td>
<td>-0.637</td>
<td>-0.098</td>
<td>-1.922</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C$_{60}$Py $K=9.1x10^4$ M$^{-1}$</td>
<td>1.278</td>
<td>-0.628</td>
<td>-0.114</td>
<td>-1.906</td>
<td></td>
</tr>
<tr>
<td>((CF$_3$)$_4$TPP)Zn</td>
<td>C$_{60}$Im $K=3.0x10^4$ M$^{-1}$</td>
<td>0.892</td>
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<td>-0.382</td>
<td>-1.619</td>
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</tr>
<tr>
<td></td>
<td>C$_{60}$Py $K=2.9x10^4$ M$^{-1}$</td>
<td>0.89</td>
<td>-0.722</td>
<td>-0.389</td>
<td>-1.612</td>
<td></td>
</tr>
<tr>
<td>(F$_4$TPP)Zn</td>
<td>C$_{60}$Im $K=2.5x10^4$ M$^{-1}$</td>
<td>0.84</td>
<td>-0.68</td>
<td>-0.49</td>
<td>-1.52</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C$_{60}$Py $K=2.2x10^4$ M$^{-1}$</td>
<td>0.775</td>
<td>-0.74</td>
<td>-0.495</td>
<td>-1.515</td>
<td></td>
</tr>
<tr>
<td>(Cl$_4$TPP)Zn</td>
<td>C$_{60}$Im $K=2.4x10^4$ M$^{-1}$</td>
<td>0.816</td>
<td>-0.685</td>
<td>-0.489</td>
<td>-1.501</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C$_{60}$Py $K=2.0x10^4$ M$^{-1}$</td>
<td>0.831</td>
<td>-0.665</td>
<td>-0.494</td>
<td>-1.496</td>
<td></td>
</tr>
<tr>
<td>(TPP)Zn</td>
<td>C$_{60}$Im $K=2.1x10^4$ M$^{-1}$</td>
<td>0.683</td>
<td>-0.729</td>
<td>-0.589</td>
<td>-1.412</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C$_{60}$Py $K=1.2x10^4$ M$^{-1}$</td>
<td>0.71</td>
<td>-0.701</td>
<td>-0.59</td>
<td>-1.411</td>
<td></td>
</tr>
</tbody>
</table>

3.2.9  Femtosecond Transient Absorption Study

To obtain the rate of charge separation and charge recombination, femtosecond transient absorption studies were performed using a 400 nm 100 fs laser excitation source
in toluene. Figure 3.15, shows the femtosecond transient absorption spectra of the (TPP)Zn-C$_{60}$Im dyad. Upon the 400 nm excitation, the peak appeared at 680 nm is contributed to be the (TPP)Zn$^+$ while the peak at 1010 nm is corresponded to the C$_{60}$Im$^-$, suggesting the intramolecular electron transfer to yield ZnTPP$^+$- C$_{60}$Im$^-$ radical ion-pair. By recording kinetics of the radicals, evidence for long lived charge separated state was obtained. That is, the charge separation rate constant, $k_{CS}$, is found to be $0.57 \times 10^{10}$ s$^{-1}$, and charge recombination rate, $k_{CR}$, calculated to be $6.25 \times 10^8$ s$^{-1}$.
**Figure 3.15** The femtosecond transient absorption spectra of the \((\text{TPP})\text{Zn-C}_6\text{Im}\) dyad. The lower panels show kinetics decay curves monitored at different wavelength in toluene.

The dyad \((\text{TPP})\text{Zn-C}_6\text{Py}\) was also studied. Under the same experimental conditions, Figure 3.16 shows peaks at 630 nm and 1020 nm respectively due to the \((\text{TPP})\text{Zn}^+\) and \(\text{C}_6\text{Py}^-\). Charge separation for the \((\text{TPP})\text{Zn}^+\cdot\text{C}_6\text{Py}^-\) dyad system is to be 126 ps, which is smaller than the charge separation of \((\text{TPP})\text{Zn}^+\cdot\text{C}_6\text{Im}^-\) dyad (175 ps). The rate constants for charge separation and charge recombination are \(0.79 \times 10^{10} \text{ s}^{-1}\) and \(6.34 \times 10^8 \text{ s}^{-1}\), respectively.
Figure 3.16 The femtosecond transient absorption spectra of the (TPP)Zn-C$_{60}$Py dyad.

The lower panels show time profile of the bands at the indicated wavelength in toluene.
Figure 3.17, shows the femtosecond transient absorption spectra of axially ligated dyad system of (Cl₄TPP)Zn-C₆₀Im in toluene. With 400 nm laser excitation, the (Cl₄TPP)Zn⁺ reveals at 680 nm, and the peak at 1010 nm due to the C₆₀Im⁻. The shift of the (Cl₄TPP)Zn⁺ peak is because the chlorine substituted to pophyrin ring. The charge separation rate is calculated to be 0.98×10¹⁰ s⁻¹, while the charge combination rate is 8.1×10⁸ s⁻¹. Chlorine substituted to zinc porphyrin, which make the porphyrin moiety electron deficient. The (Cl₄TPP)Zn⁺ donates electron faster than the (TPP)Zn⁺- C₆₀Im⁻ system, which makes the charge separation rate of (Cl₄TPP)Zn⁺ - C₆₀Im⁻ is higher than (TPP)Zn⁺- C₆₀Im⁻ dyad. The charge recombination is 8.1×10⁸ s⁻¹; it is found that the chlorine increase the kₐ value compared the (TPP)Zn-C₆₀Im dyad.

![Graph 1](image1.png)

**Figure 3.17** The femtosecond transient absorption spectra of the (Cl₄TPP) Zn-C₆₀Im dyad. Time profile of the 1010 nm band is shown in the right hand panel in toluene

Chlorine substituted porphyrin axially ligated to C₆₀Py is studied using femtosecond pump probe technique with 400 nm laser excitation. As can be seen from
the Figure 3.18, peaks at 460 nm and 672 nm corresponding to \((\text{Cl}_4\text{TPP})\text{Zn}^+\), and peak at 1020 nm corresponding to \(\text{C}_{60}\text{Py}^-\) were observed. Charge separated rate constant, \(k_{\text{CS}}\) was calculated to be \(1.11 \times 10^{10} \text{ s}^{-1}\), and the charge recombination rate constant was calculated to be \(8.36 \times 10^8 \text{ s}^{-1}\). It confirmed the same trend discussed earlier, the chlorine substitution slowed down the charge separation rate and increased the charge recombination rate, compared to \((\text{TPP})\text{Zn-}\text{C}_6\text{Py}\) dyad.

**Figure 3.18** The femtosecond transient absorption spectra of the \((\text{Cl}_4\text{TPP})\text{Zn-C}_6\text{Py}\) dyad. Time profile of the 1020 nm band is shown in the right hand panel in toluene.

Using the femtosecond transient absorption measurement with 400 nm laser excitation, the supermolecular dyads of \(((\text{CF}_3)_4\text{TPP})\text{Zn-C}_6\text{Im}\) and \(((\text{CF}_3)_4\text{TPP})\text{Zn-C}_6\text{Py}\) are investigated. Figure 3.19, shows the femtosecond transient spectrums of (top) the \(\text{C}_6\text{Im}-(\text{CF}_3)_4\text{TPP})\text{Zn}\) dyad and (bottom) \(\text{C}_6\text{Py}-(\text{CF}_3)_4\text{TPP})\text{Zn}\) dyad, respectively.
In ((CF$_3$)$_4$TPP)Zn-C$_{60}$Im dyad system, the peak at 680 nm is attributed to ((CF$_3$)$_4$TPP)Zn$^+$ cation while of the peak is at 1020 nm is due to C$_{60}$Im$^-$ anion. The charge separated rate constant, $k_{CS}$ was calculated to be $2.1 \times 10^{10}$ s$^{-1}$, and the charge recombination rate constant was calculated to be $9.8 \times 10^8$ s$^{-1}$.

In case of ((CF$_3$)$_4$TPP)Zn-C$_{60}$Py dyad, charge separation peaks at 680 nm and 1020 nm corresponding to ((CF$_3$)$_4$TPP)Zn$^+$ and C$_{60}$Py$^-$ were observed. Charge separation rate, $k_{CS}$, is found to be $2.63 \times 10^{10}$ s$^{-1}$, and charge recombination rate, $k_{CR}$, is calculated to be $10.3 \times 10^8$ s$^{-1}$.

By comparing the $k_{CS}$ and $k_{CR}$ values for the two sets of supermolecular dyads, the electron transfer rate is faster in axial coordination to C$_{60}$Im than the ((CF$_3$)$_4$TPP)Zn-C$_{60}$Py dyad due to the stronger binding affinity of the N atom in imidazole to Zn. The electron withdrawing nature of the fluorides on Zinc porphyrin make the electron separation faster in ((CF$_3$)$_4$TPP)Zn fullerene dyad than in (TPP)Zn fullerene dyad.
Figure 3.19  The femtosecond transient absorption spectra of (top) the ((CF$_3$)$_4$TPP)Zn-C$_{60}$Im dyad and (bottom) ((CF$_3$)$_4$TPP)Zn-C$_{60}$Py dyad in toluene.

Figure 3.20 (left), shows the femtosecond transient absorption spectra of axially ligated dyad system of (F$_{20}$TPP)Zn and C$_{60}$Im in toluene. Supramolecular dyad system of (F$_{20}$TPP)Zn-C$_{60}$Im was photoexcited with a 400 nm laser. Charge separated radical ion peak of (F$_{20}$TPP)Zn$^+$ is at 680 nm, and the anion radical ion peak at 1010 nm is observed. Charge separation rate constant, $k_{CS}$ is calculated to be $3.8 \times 10^{10}$ s$^{-1}$, while the charge recombination rate constant, $k_{CR}$ is calculated to be $10.4 \times 10^8$ s$^{-1}$. It is shown to be the charge separation is short lived. The charge separated states of the (F$_{20}$TPP)Zn$^+$ and C$_{60}$Im$^-$ recombined in less than 3 ns.

Figure 3.20 (right), shows the femtosecond data for the (F$_{20}$TPP)Zn and C$_{60}$Py dyad under similar experiment conditions with (F$_{20}$TPP)Zn and C$_{60}$Im dyad. The peak at 690 nm is due to the (F$_{20}$TPP)Zn$^+$ and the character peak at 1020 nm is assign to the
C$_{60}$Py$^-$ anion. Charge separation rate constant and the charge recombination rate constant is to be 5x10$^{10}$ s$^{-1}$ and 10.58x10$^8$ s$^{-1}$, respectively. A short lived charge separation is also found in the (F$_{20}$TPP) Zn and C$_{60}$Py dyad system.

Figure 3.20 The femtosecond transient absorption spectra of (left) the (F$_{20}$TPP)Zn-C$_{60}$Im dyad and (right) (F$_{20}$TPP)Zn-C$_{60}$Py dyad in toluene

Table 3.5 Femtosecond data of the porphyrins with C$_{60}$Im, both $k_{CS}$ and $k_{CR}$ values have been calculated based on Femtosecond transient data

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda$ monitored</th>
<th>Fit</th>
<th>$\tau$ value</th>
<th>$k_{CS}$</th>
<th>$k_{CR}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(TPP)Zn-C$_{60}$Im</td>
<td>1010 rise</td>
<td>Mono</td>
<td>175 ps</td>
<td>0.57 x10$^{10}$ s$^{-1}$</td>
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</tr>
<tr>
<td></td>
<td>1010 decay</td>
<td></td>
<td>1600 ps</td>
<td>6.25 x 10$^8$ s$^{-1}$</td>
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</tr>
<tr>
<td>(Cl$<em>4$TPP)Zn-C$</em>{60}$Im</td>
<td>Rise</td>
<td></td>
<td>120 ps</td>
<td>0.98 x10$^{10}$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1010 decay</td>
<td></td>
<td>1230 ps</td>
<td>8.1 x10$^8$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>(F$<em>4$TPP)Zn-C$</em>{60}$Im</td>
<td>Rise</td>
<td></td>
<td>108 ps</td>
<td>1.38 x10$^{10}$ s$^{-1}$</td>
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</tr>
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<td>Rise</td>
<td></td>
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<td></td>
<td>1010 decay</td>
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<td>1000 ps</td>
<td>9.8 x10$^8$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>(F$<em>{20}$TPP)Zn-C$</em>{60}$Im</td>
<td>Rise</td>
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<td>3.8 x 10$^{10}$ s$^{-1}$</td>
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</tr>
<tr>
<td></td>
<td>1010 decay</td>
<td></td>
<td>960ps</td>
<td>10.4 x10$^8$s$^{-1}$</td>
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</tr>
</tbody>
</table>
Table 3.6 Femtosecond data of the porphyrins with C$_{60}$Py, both $k_{CS}$ and $k_{CR}$ values have been calculated based on Femtosecond transient data in this table

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>λ monitored</th>
<th>Fit</th>
<th>$\tau$ value</th>
<th>$k_{CS}$</th>
<th>$k_{CR}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(TPP)Zn-C$_{60}$Py</td>
<td>1020(rise)</td>
<td>Mono</td>
<td>126 ps</td>
<td>0.79x10$^{10}$ s$^{-1}$</td>
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<tr>
<td></td>
<td></td>
<td>Decay</td>
<td>1575 ps</td>
<td></td>
<td>6.34x10$^{8}$ s$^{-1}$</td>
</tr>
<tr>
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<td>Decay</td>
<td>1195 ps</td>
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<td>8.36x10$^{8}$ s$^{-1}$</td>
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<tr>
<td>(F$<em>4$TPP)Zn-C$</em>{60}$Py</td>
<td>1020nm(rise)</td>
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<td>Decay</td>
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<tr>
<td>((CF$_3$)$<em>4$TPP)Zn-C$</em>{60}$Py</td>
<td>1020nm(rise)</td>
<td>Mono</td>
<td>38 ps</td>
<td>2.63x10$^{10}$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Decay</td>
<td>975 ps</td>
<td></td>
<td>10.3x10$^{8}$ s$^{-1}$</td>
</tr>
<tr>
<td>(F$<em>{20}$TPP)Zn-C$</em>{60}$Py</td>
<td>1020nm(rise)</td>
<td>Mono</td>
<td>20 ps</td>
<td>5 x 10$^{10}$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Decay</td>
<td>945 ps</td>
<td></td>
<td>10.58x10$^{8}$ s$^{-1}$</td>
</tr>
</tbody>
</table>

Based on femtosecond data, $\tau_{CS}$, $k_{CS}$, $\tau_{CR}$ and $k_{CR}$ have been calculated as shown in Table 3.5. The short lived charge separation is the (F$_{20}$TPP)Zn-C$_{60}$Im, and the long lived charge separation is found to be (TPP)Zn-C$_{60}$Im have been observed. It is concluded that the trend of the charge separation is (TPP)Zn-C$_{60}$Im< (Cl$_4$TPP)Zn-C$_{60}$Im< (F$_4$TPP)Zn-C$_{60}$Im < ((CF$_3$)$_4$TPP)Zn-C$_{60}$Im< (F$_{20}$TPP)Zn-C$_{60}$Im.

Based on femtosecond data, $\tau_{CS}$, $k_{CS}$, $\tau_{CR}$ and $k_{CR}$ have been calculated as shown in Table 3.6. Similar to the substituted zinc porphyrins with C$_{60}$Im, the trend (TPP)Zn-C$_{60}$Py < (Cl$_4$TPP)Zn-C$_{60}$Py < (F$_4$TPP)Zn-C$_{60}$Py < ((CF$_3$)$_4$TPP)Zn-C$_{60}$Py< (F$_{20}$TPP)Zn-C$_{60}$Py is also found in the supermolecular substituted zinc porphyrins with C$_{60}$Py system.

It is clear that the electron withdrawing group affects the rate of electron transfer, in other words, the electron withdrawing group make the porphyrin strong electrophilic.
Meanwhile, the number of the fluorine or chlorine substituted to zinc porphyrin also increases the electron transfer rates both in the formed and reverse direction.

### 3.2.10 Nanosecond Transient Absorption Studies

Figure 3.21 shows the nanosecond transient absorption spectrum of (TPP)Zn-C₆₀Im dyad in toluene at 120 ns and 220 ns time intervals. Absorption band at 700-780 nm corresponding to the triplet state of (TPP)Zn ($^3\text{ZnTpp}^*$) and the triplet state of C₆₀Im ($^3\text{C₆₀Im}^*$) were observed at 220 ns. Owing to the absorption of (TPP)Zn, the depleted peak showing at 800 nm was also observed. The region of the 1000-1050 nm at 120 ns, as the evidence for the formation of the C₆₀Im$^-$ and (TPP)Zn$^+$ radical pair, was observed. The decay around the 1000-1050 region is not that obvious, is attributed to the tail of the absorption 850nm.

![Figure 3.21](image)

**Figure 3.21** The nanosecond transient absorption spectra of adding the C₆₀Im to (TPP)Zn in toluene
Upon adding the C$_{60}$Py to (TPP)Zn, the band at 860 nm was observed contributed to the triplet state of $^3$C$_{60}$Py* and $^3$(TPP)Zn* at 450 ns, and the band at 1000-1050 nm was generated due to the formation of the C$_{60}$Py$^-$ and (TPP)Zn$^+$, which shown in Figure 3.22. The charge recombination rate $k_{CR}$ in (TPP)Zn-C$_{60}$Py dyad is to be $10 \times 10^6$ s$^{-1}$ and the decay lifetime at 1000 nm is 0.1 µs, which suggests faster recombination process than the one in (TPP)Zn-C$_{60}$Im dyad system.

**Figure 3.22** The nanosecond transient absorption spectra of adding the C$_{60}$Py to (TPP)Zn in toluene

Four chlorine substituted to zinc porphrin ring is to form (Cl$_4$TPP)Zn. In the (Cl$_4$TPP)Zn-C$_{60}$Im dyad in toluene, the band at 710-780 nm in the nanosecond transient was observed corresponding to the triplet state of $^3$C$_{60}$Im* and $^3$(Cl$_4$TPP)Zn*. The band at 970-1030 nm, C60Im$^-$, was observed at 120 ns, revealing the formation of the C$_{60}$Im anion radical and (Cl$_4$TPP)Zn cation radical. The charge recombination rate is calculated...
to be $15.3 \times 10^6$ s$^{-1}$. The lifetime of the decay was 65 ns. Figure 3.23 shows the nanosecond transient absorption spectra of (left) (Cl$_4$TPP)Zn-C$_{60}$Im dyad.

Nanosecond Transient Absorption study of the dyad of the (Cl$_4$TPP)Zn with C$_{60}$Py is also investigated, the spectra is shown in Figure 3.23 (right). After coordinating the C$_{60}$Py to (Cl$_4$TPP)Zn, the transient band in the region at 720-780 nm is found because of the triplets of the two radical, $^3$C$_{60}$Py$^*$ and $^3$(Cl$_4$TPP)Zn$^*$. The formation of the C$_{60}$Py$^-$ and (Cl$_4$TPP)Zn$^+$ is proved by the band at 970-1020 nm by 90 ns. The lifetime of the 1000 nm decay is 50 ns. The charge recombination rate is calculated to be $20 \times 10^6$ s$^{-1}$. The (Cl$_4$TPP)Zn-C$_{60}$Im dyad is faster than (Cl$_4$TPP)Zn-C$_{60}$Py dyad.

**Figure 3.23** The nanosecond transient absorption spectra of (left) (Cl$_4$TPP)Zn-C$_{60}$Im dyad and (right) (Cl$_4$TPP)Zn-C$_{60}$Py dyad in toluene

Fuuorine substituted zinc porphyrin-C$_{60}$ dyads were studied using the nanosecond transient absorption technique. The Figure 3.24 (top) shows the nanosecond transient absorption spectrums of (F$_4$TPP)Zn-C$_{60}$Im and (F$_4$TPP)Zn-C$_{60}$Py dyads. A absorption band at 720-780 nm was observed at 250 ns, which is identified the triplet states of $^3$(F$_4$TPP)Zn$^*$ and $^3$C$_{60}$Im$^*$. At 108 ns, the band at 1000 nm provided evidence of the
formation of the \((\text{F}_4\text{TPP})\text{Zn}^+\text{-C}_6\text{Im}^-\) radical ion pairs. Similar bands were observed for \((\text{F}_4\text{TPP})\text{Zn-C}_6\text{Py}\) dyad spectra shown in Figure 3.24 (bottom). It was found that the band at 750-780 nm was observed at 200 ns and the band at 1000 nm was formed at 95 ns, which corresponded to the triplets states and the formation of the ion pairs, respectively. The significant decay at 1000 nm of the \((\text{F}_4\text{TPP})\text{Zn-C}_6\text{Im}\) dyad showed a quick-rise decay compared to the decay for the \((\text{F}_4\text{TPP})\text{Zn-C}_6\text{Py}\) dyad. The estimated charge recombination rates of the \((\text{F}_4\text{TPP})\text{Zn-C}_6\text{Im}\) dyad and \((\text{F}_4\text{TPP})\text{Zn-C}_6\text{Py}\) dyad were \(18.5 \times 10^6 \text{ s}^{-1}\) and \(23.8 \times 10^6 \text{ s}^{-1}\) respectively.
Figure 3.24 The nanosecond transient absorption spectra of (top) (F₄TPP)Zn-C₆₀Im dyad and (bottom) (F₄TPP)Zn-C₆₀Py dyad in toluene at the excitation wavelength of 532 nm.

Figure 3.25 (top) shows the absorption spectrum of ((CF₃)₄TPP)Zn-C₆₀Im dyad. At 68 ns, the decay band at 1000 nm was shown in the spectrum, which contributed to the formation of the radical ions. The band at 1000 nm diminished at 140 ns, and the band at 750-780 nm ((CF₃)₄TPP)Zn-C₆₀Im corresponding to the triplet states of the ³((CF₃)₄TPP)Zn* and ³C₆₀Im*. The charge recombination rate was 10.2x10⁸ s⁻¹. In the case of ((CF₃)₄TPP)Zn-C₆₀Py in Figure 3.25(bottom), the charge recombination rate is calculated to be 11 x10⁸ s⁻¹ which is based on the calculation of the decay at 1000 nm that is due to the formation of the ((CF₃)₄TPP)Zn⁺-C₆₀Im⁻ radical ion pairs. After 240 ns, the band at 1000 nm completely disappeared.
Figure 3.25 The nanosecond transient absorption spectra of (top) the \((\text{CF}_3)_4\text{TPP})\text{Zn-C}_60\text{Im}\) dyad and (bottom) \((\text{CF}_3)_4\text{TPP})\text{Zn-C}_60\text{Py}\) dyad in toluene at the excitation wavelength of 532 nm.
Table 3.7 Kinetic parameters, $\tau_{CS}$ and $k_{CS}$ calculated using femtosecond transient technique, $\tau_{CR}$ and $k_{CR}$ using nanosecond transient technique

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda$ monitored</th>
<th>Fit</th>
<th>$\tau_{value}$</th>
<th>$k_{CS}$</th>
<th>$k_{CR}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(TPP)Zn-C$_{60}$Im</td>
<td>1010 rise</td>
<td>Mono</td>
<td>175 ps</td>
<td>$0.57 \times 10^{10}$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>(TPP)Zn-C$_{60}$Im</td>
<td>Decay</td>
<td></td>
<td>0.12 $\mu$s</td>
<td></td>
<td>$8.33 \times 10^{5}$ s$^{-1}$</td>
</tr>
<tr>
<td>(Cl$<em>4$TPP)Zn-C$</em>{60}$Im</td>
<td>Rise</td>
<td></td>
<td>120 ps</td>
<td>$0.98 \times 10^{10}$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>(Cl$<em>4$TPP)Zn-C$</em>{60}$Im</td>
<td>Decay</td>
<td></td>
<td>65 ns</td>
<td></td>
<td>$15.3 \times 10^{6}$ s$^{-1}$</td>
</tr>
<tr>
<td>(F$<em>4$TPP)Zn-C$</em>{60}$Im</td>
<td>Rise</td>
<td></td>
<td>108 ps</td>
<td>$1.38 \times 10^{10}$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>(F$<em>4$TPP)Zn-C$</em>{60}$Im</td>
<td>Decay</td>
<td></td>
<td>54 ns</td>
<td></td>
<td>$18.5 \times 10^{6}$ s$^{-1}$</td>
</tr>
<tr>
<td>((CF$_3$)$<em>4$TPP)Zn-C$</em>{60}$Im</td>
<td>Rise</td>
<td></td>
<td>46 ps</td>
<td>$2.1 \times 10^{10}$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>((CF$_3$)$<em>4$TPP)Zn-C$</em>{60}$Im</td>
<td>Decay</td>
<td></td>
<td>32 ns</td>
<td></td>
<td>$31 \times 10^{6}$ s$^{-1}$</td>
</tr>
<tr>
<td>(F$<em>{20}$TPP)Zn-C$</em>{60}$Im</td>
<td>Rise</td>
<td></td>
<td>26 ps</td>
<td>$3.8 \times 10^{10}$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>(F$<em>{20}$TPP)Zn-C$</em>{60}$Im</td>
<td>Decay</td>
<td></td>
<td>980 ps</td>
<td></td>
<td>$10.2 \times 10^{8}$ s$^{-1}$</td>
</tr>
</tbody>
</table>

Table 3.8 Kinetic parameters, $\tau_{CS}$ and $k_{CS}$ calculated from femtosecond transient technique, $\tau_{CR}$ and $k_{CR}$ from nanosecond transient technique

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda$ monitored</th>
<th>Fit</th>
<th>$\tau_{value}$</th>
<th>$k_{CS}$</th>
<th>$k_{CR}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(TPP)Zn-C$_{60}$Im</td>
<td>1020(rise)</td>
<td>Mono</td>
<td>126 ps</td>
<td>$0.79 \times 10^{10}$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>(TPP)Zn-C$_{60}$Im</td>
<td>Decay</td>
<td></td>
<td>0.1 $\mu$s</td>
<td></td>
<td>$10 \times 10^{6}$ s$^{-1}$</td>
</tr>
<tr>
<td>(Cl$<em>4$TPP)Zn-C$</em>{60}$Im</td>
<td>1020nm(rise)</td>
<td>Mono</td>
<td>90 ps</td>
<td>$1.11 \times 10^{10}$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>(Cl$<em>4$TPP)Zn-C$</em>{60}$Im</td>
<td>Decay</td>
<td></td>
<td>50 ns</td>
<td></td>
<td>$20 \times 10^{6}$ s$^{-1}$</td>
</tr>
<tr>
<td>(F$<em>4$TPP)Zn-C$</em>{60}$Im</td>
<td>1020nm(rise)</td>
<td>Mono</td>
<td>65 ps</td>
<td>$1.52 \times 10^{10}$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>(F$<em>4$TPP)Zn-C$</em>{60}$Im</td>
<td>Decay</td>
<td></td>
<td>42 ns</td>
<td></td>
<td>$23.8 \times 10^{6}$ s$^{-1}$</td>
</tr>
<tr>
<td>((CF$_3$)$<em>4$TPP)Zn-C$</em>{60}$Im</td>
<td>1020nm(rise)</td>
<td>Mono</td>
<td>38 ps</td>
<td>$2.63 \times 10^{10}$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>((CF$_3$)$<em>4$TPP)Zn-C$</em>{60}$Im</td>
<td>Decay</td>
<td></td>
<td>27 ns</td>
<td></td>
<td>$37 \times 10^{6}$ s$^{-1}$</td>
</tr>
<tr>
<td>(F$<em>{20}$TPP)Zn-C$</em>{60}$Im</td>
<td>1020nm(rise)</td>
<td>Mono</td>
<td>20 ps</td>
<td>$5 \times 10^{10}$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>(F$<em>{20}$TPP)Zn-C$</em>{60}$Im</td>
<td>Decay</td>
<td></td>
<td>900 ps</td>
<td></td>
<td>$11 \times 10^{8}$ s$^{-1}$</td>
</tr>
</tbody>
</table>

As can be seen from Table 3.7, the substituted zinc porphyrin derivatives with C$_{60}$Im showed the decay lifetime $\tau_{value}$ trend: (TPP)Zn-C$_{60}$Im > (Cl$_4$TPP)Zn-C$_{60}$Im > (F$_4$TPP)Zn-C$_{60}$Im > ((CF$_3$)$_4$TPP)Zn-C$_{60}$Im > (F$_{20}$TPP)Zn-C$_{60}$Im. On the other hand, the trend for the decay lifetime $\tau_{value}$ of the substituted zinc porphyrin derivatives with C$_{60}$Py in Table 3.8 was (TPP)Zn-C$_{60}$Py > (Cl$_4$TPP)Zn-C$_{60}$Py > (F$_4$TPP)Zn-C$_{60}$Py >
((CF_3)_4TPP)Zn-C_{60}Py > (F_{20}TPP)Zn-C_{60}Py. The electron withdrawing substitutes make both the charge
CHAPTER 4

SUMMARY

The self-assembled via axial coordination of substituted zinc porphyrin-fullerene dyads is investigated in this thesis. Based the optical absorption and steady state fluorescence studies of the different porphyrins, the photosensitizing electron ability of zinc porphyrin has been evaluated. X-ray and computational measurements are performed to get better understanding of the geometry and electronic structures of the dyads. The formation constants were calculated according Benesi-Hildebrand plots using optical absorption data. The fluorescence quenching suggested occurrence of electron transfer processes. Both UV-Vis absorption and fluorescence studies revealed a trend in which the binding between the substituted zinc porphyrins and fullerenes increased with increasing the electron deficient substitutes on the zinc porphyrins. Occurrence of photoinduced electron transfer was established from time-resolved emission and transient absorption studies. The charge separation and charge recombination was witnessed for dyads with porphyrins bearing electron withdrawing halogen substitution. Halogen substituted on porphyrins promoted both charge separation and charge recombination process as observed from the kinetic data. The outcome of the present study is indicative of using these donor-acceptor dyads for building higher energy harvesting devices.
REFERENCES


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