DIIMINE(DITHIOLATE)PLATINUM(II) CHROMOPHORES: SYNTHESIS, SPECTROSCOPY, AND MATERIAL APPLICATIONS

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A series of 28 square-planar dithiol(diimine)platinum(II) chromophoric complexes have been synthesized, characterized, and evaluated for potential efficacy in sensitization of solid state photovoltaic devices to the near-infrared regions of the electromagnetic spectrum. The effect of molecular stacking in the solid state and self-association in solution are shown to influence spectral, electronic, and magnetic properties of the chromophores. Such properties are investigated in the pure form and as partners in donor-acceptor charge transfer adducts. Finally, selected chromophores have been incorporated into single layer schottky diodes as neat films and as dopants in multi-layer organic photovoltaic devices. Evaluation of the devices internal quantum efficiency and voltage-current was measured as proof of concept.
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CHAPTER 1
INTRODUCTION: BACKGROUND, MOTIVATION, AND OVERVIEW

1.1 Motivation and Necessity

The focus of investigation contained in this dissertation is one shared by many chemists, physicists, and material scientists. The liberation and harnessing of energy from renewable sources is beginning to be a desired method of electricity production in major consuming markets such as the United States and most industrialized societies. Driven by population growth and the modernization of newly developing countries, global energy use is expected to increase by over 50% by 2040 as reported by the United States Energy Information Administration.\textsuperscript{1} The growth of economies and stability of standards of living depend directly on the cost and availability of energy. However, the current paradigm for energy harvesting through the burning of fossil fuels has, in the last few decades, suffered some serious setbacks in its desirability as the dominant scheme of energy generation. The easy and accessible exothermic combustion reaction of hydrocarbons produces a multitude of undesirable byproducts. The most abundant of these are carbon dioxide, methane, nitrous oxide and sulfur oxides. The first three are known to be major contributors to the heating of Earth’s atmosphere as greenhouse gases. Nitrogen and sulfur oxides are responsible for the formation of acid rain which over time changes the pH of rivers and lakes making them unsuitable for plant or animal life and destroys farmland. Over half the production of these oxides in the United States is a result of fossil fuel combustion in power plants to produce electricity. Nitrogen and sulfur oxides along with other products of fossil fuel

\textsuperscript{1} DOE/EIA-0484(2013) U.S Energy information Administration
combustion like ozone and soot can cause permanent lung damage. Electricity production through fossil fuels accounts for the largest portion of these noxious and environmental hazards. The combination of the foreseeable increase in demand for energy coupled with negative repercussions of our current system on the air we breathe and the water we drink has prompted forward-thinking individuals and conglomerates to peruse other known but less reconnoitered methods to satisfy the energy thirst of the future. The combination of wind, geothermal, hydro, and solar energy may one day sate the hunger industrialized societies have for energy but currently these technologies fall far behind in meeting the massive amount demanded and provided by the burning of fossil fuels. Many of these emerging technologies are limited by the geographical conditions of the areas in which they are produced. Solar energy, that is producing energy directly from solar radiation, is the most promising as it occurs in the highest abundance far from the polar regions and close to the population centers of Earth.

1.2 A Brief Background in Photovoltics

Traditionally, solar technologies have focused on strictly inorganic materials relying on the built-in electric fields of highly pure crystalline silicon as a semiconductor to produce the charge separation needed to create a current upon absorption of light. It was discovered that n-type silicon wafers will develop a p-type skin when exposed to boron trichloride gas thus creating a junction capable of charge separation and delivery of electron-hole pairs to their

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respective electrodes. Excited electrons could move through the n-type material and holes in the opposite direction through the p-type. Coddled by the explosion of the inorganic semiconductor industry of the mid-to-late 20th century, fairly pure crystalline silicon was found to be a good method of producing immediately available energy. Efficiencies have now reached the Shockley-Queisser limit, the theoretical maximum for solar energy conversion in a single layer device, and other engineering techniques have been employed to boost output even further. However the cost of producing highly pure crystalline silicon materials made these technologies prohibitive at the consumer level needed for large scale applications. Also the energy requirements needed to produce crystalline silicon are enormous. The time needed for a crystalline Si photovoltaic cell to produce enough energy to offset the energy cost of its production has been estimated to be between 1.5 and 2 years depending on the location of the cell. Small hand-held devices, such as calculators and low voltage garden lights, are common on the market and affordable to most consumers, but the cost of large scale implementation of silicon solar panels to provide the majority of household power is a major investment that is incompatible in the current culture and economy. The need to reduce the cost of materials used in renewable resources is a major factor in how well these technologies take root and thrive in the current market. In 2007, energy generated from solar cells was selling for around $7 per peak watt and dependent on government subsidies to remain stable. To be competitive with fossil fuels on a large scale, a selling price of $2 per peak watt needs to be attained.

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6 Trends in Photovoltaic Applications, Survey report of selected IEA countries between 1992 and 2011, **2012**.
Many alternatives to the traditional silicon cells have been attempted. Other alternative inorganic materials, such as thin film CdTe, CdS, GaAs, and InP, are toxic and low in natural abundance. CdTe cells have been reported with efficiencies of 16.7% in the laboratory, but this efficiency is temperature dependent. Thin films of amorphous silicon have also been used but suffer from low efficiencies (about 5-7%) resulting from light degradation and silicon’s low deposition rates have led to a lack of commercial viability. Organic photovoltaic materials avoid many of these problems but efficiencies at the moment fall far short of what is needed to compete with crystalline silicon. Because the low absorption of most organic materials at long wavelengths and the action of electron-hole pairs carried to the electrodes in the same matrix that does the charge separation, desirable photocurrents and efficiencies have remained elusive.

One of the emerging technologies for the collection of energy directly from solar radiation has been the dye-sensitized solar cell (DSSC). By utilizing a metallorganic chromophore to absorb light and facilitate the charge separation, then allow the diverging hole-electron pair to be carried to the electrodes by the action of the semiconductor, the DSSC permits the engineer to optimize each component separately. The design of the chromophore can be tuned to absorb the maximum possible photons for the sun’s radiation then the electrochemical parameters of the semiconductor and electrodes can be optimized to match the needs of the chromophore to

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achieve the best mobility and stability. Already efficiencies of around 11% have been achieved using RuL₂(NCS)₂ where L=4,4’-dicarboxy-2,2’-bipyridine on TiO₂ with a I⁻/I₃⁻ redox couple to regenerate the oxidized dye.¹⁰ This model dye, commonly known as N3, has two absorption maxima that are harnessed to drive the DSSC circuit, one at 400 nm and another at 535 nm. Both excitations have molar extinction coefficients of around 1.4 x 10⁴ M⁻¹ cm⁻¹ and are characterized as a metal-to-ligand charge transfer (MLCT). The N3 dye has become the dominant prototype for the development of DSSCs and conditions including the semiconducting substrate and the redox couple have been optimized to match the electrochemical needs of this particular dye. The disadvantages of the DSSC is in its inherent manufacturing complexity and the instability of the I⁻/I₃⁻ redox couple. Other electrolyte systems have been studied to improve the long term stability including Co(III)/Co(II), SCN⁻/(SCN)₃⁻, SeCN⁻/(SeCN)₃⁻, and a few organic based systems, but overall performance suffers in cells containing N3 compared to the iodide/triiodide couple.¹¹

1.3 An Overview of this Research

In an attempt to circumvent the limitation of the DSSC modality occurring within the liquid redox couple, this original work attempts to return to the solid state theme but borrowing from the N3 the idea of using long wavelength absorptions of MLCT. The charge transfer in Pt(diimine)(dithiolate) has already been studied and its infamous “charge-transfer-to-diimine” has shown to be tunable to wavelengths comparable to N3. This charge transfer occurs to the

lowest occupied molecular orbital of the diimine (LUMO) analogous to the MLCT of N3. However, rather than originating from the highest occupied molecular orbital (HOMO) of the metal, the excitation arises from an orbital of mixed metal and dithiolate character.

In Chapter 2, square-planar platinum compounds with the general formula Pt(diimine)dithiolate have been studied to probe how the structure can be further modified from past work to achieve better coverage of the solar spectrum in dilute solutions, and promote intermolecular interactions in concentrated solutions and the solid state, which are capable of introducing new yet longer wavelength absorptions as a result of these interactions. Association between neighboring molecules is observed in concentrated solutions, as revealed through ultraviolet/visible absorption spectroscopy and in the solid state through both diffuse reflectance spectral measurements (solid-state absorption) and X-ray crystallographic determinations of the molecular structure and extended packing motifs thereof. A better understanding of the role of the ligands influence on the chromophore’s electronic absorption spectrum was elucidated by systematic variation around the metal center. Some modifications were also included to improve the solubility of the platinum chromophores for their use in solar cells that would be spin coated. The result of this work is essential to finding the best dyes or thin solid films for use in not only energy producing photovoltaic devices, but also the reduction/oxidation properties relevant to the use of these or similar complexes in organic light emitting diodes (OLEDs) and metal-organic

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field effect transistors (MOFETs). In Chapter 3, intermolecular interactions between the platinum chromophores and well-known organic electron acceptors have been studied. The similarity of the planar geometry between the selected acceptors and chromophores allowed investigation of the spatial stacking arrangements between the dyes and acceptors. Closely stacked alternating units of donors and acceptors are known to produce semiconducting materials and to broaden the absorption over the dye alone. These donor-acceptor charge transfers (DACT) red shifted the overall absorption of light often into the near-infrared region (NIR) and were observed by measurements of spectroscopic diffuse reflectance in solids. In solution, association between the donor-acceptor pair was studied and close interactions between the donor and acceptor were implied through coupling shown in 1-D and 2-D nuclear magnetic resonance. Also magnetic susceptibility measurements have been used to possibly detect partial oxidation of the platinum dye when forming closely stacked solids with the organic molecules as adducts. The strength of the various organic electron poor acceptors was manipulated by variation of the substituents on the aromatic core and then assessed by spectroscopic comparison along with literature reporting electrochemical data. Electron sharing between donor and acceptor can also be seen in the infrared spectrum stretching frequencies of the acceptor molecules. One of the appealing results of this close association between the dyes and the organic electron acceptor is that the acceptors often have functional groups that bind to

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TiO$_2$. Tight binding of the charge separation media to the inorganic semiconductor surface is a requirement in this type of solar cells to inject the excited electron into the circuit. This has been traditionally been accomplished in DSSCs by the use of an acid group on the dye. By providing an alternative injection route through the organic acceptor, one of the responsibilities of the dye is relieved and can be more fully functionalized to enhance desirable properties relevant to light absorption, sublimation/deposition (vapor pressure), and solubility.

In Chapter 4, the materials that seemed to be the most promising candidates for novel solar cells were incorporated into simple proof-of-concept devices and evaluated for photocurrent production. Internal photon-to-current efficiency of the cells were determined as well as the current-voltage parameters that are necessary to establish the overall efficiency of the device. Devices produced with locally available equipment are at least 1 cm$^2$, the minimum allowed for standardized testing. Collaborations with other labs produced smaller surface areas and serve as a promising goal to achieve as better equipment and facilities become available.

In Chapter 5, the overall conclusions from each chapter of this dissertation as well as some proposed ideas for the future direction of the research projects which can be investigated by future researchers are outlined.
CHAPTER 2
SYNTHESIS, SPECTROSCOPIC, AND CRYSTALLOGRAPHIC STUDIES OF
DIIMINE(DITHIOLATE)PLATINUM(II) CHROMOPHORES

2.1 Introduction

One of the major goals of this project is to develop a series of chromophores that extend the reach of solar absorption into the low-energy region of the visible spectrum and, if possible, the near infrared wavelengths. The strong charge transfer (CT) bands for many metallorganic complexes often cannot be harnessed due to culpable lower-lying d-d transitions, which can be populated instead of CT bands. The perceived colors of this class of complexes are the result of this symmetry forbidden d-d transition. Although far less intense than many of the ligand-to-metal, metal-to-ligand, intra- and inter-ligand charge transfers, the region of electromagnetic spectrum occupied by these photonic absorptions corresponds with the most apparent region in the output spectrum of our home planets’ nearest star. Although outside the scope and subject of this work, these comparatively less intense matter-energy transactions are easily detected by the human eye evolved to collect the spectrum of a G2V or yellow dwarf star as filtered through the local atmosphere. While the degree of saturation needed to stimulate the light collecting mechanics of the eye is sufficient to send the proper signals to the information processing centers of our brains, electronic devices are capable of collecting and processing a greater load and range of light energy. The research that follows will describe a method to increase both of these parameters for light harvesting.

The well-travelled organic chromophores represented by diimines, chiefly bichelating bipyridine ligands such as 2,2’-bipyridine (bpy) and 1,10-phenanthroline (phen), were shown to
provide promising photoconversion and charge-injection to an oxide nanoparticle such as TiO₂ when coordinated with appropriate metals in dye-sensitized solar cells (DSSCs).¹⁴ Such bipyridines and their derivatives still remain some of the most common organic ligands used in this technology. In this study, several embodiments of aforementioned diimine ligands have been used and modified along with other co-ligands for investigation in square-planer platinum systems. The tethering moiety that commonly exists in DSSC sensitzers (e.g., COOH) has been removed and replaced with a structure that either increases the complex’s solubility in organic solvents or its vapor pressure, thus increasing the ease of preparing the thin film of the solar cell via solution casting or thermal evaporation, respectively. For comparison, many non-carboxylated containing compounds of the same class have been studied and reported by Eisenberg and others investigating the basic photophysical and electrochemical properties of the neutral platinum(diimine)dithiolate complexes.¹⁵ The work in this dissertation, however, represents the first instance where such materials are actually used for solar cell devices. The Arakawa group has demonstrated that a carboxylated variety of these compounds are capable of sensitizing nanocrystalline TiO₂ in DSSC devices with Pt(4,4’-dicarboxy-2,2’-bipyridine)(quinoxaline-2,3-dithiolate).¹⁶ In this chapter, the structural and photophysical properties of a broad variety of such solar cell sensitizers will be classified, including incarnations known earlier but their crystal structures were not revealed, whereas Chapter 4 contains the


photocurrent and other device data. Conveniently, the physical tethering of the dye is not strictly needed for the solid-state device architecture in organic photovoltaics (OPVs) as it is in the solution-based DSSCs. Eisenberg and coworkers have shown the absorption energies can be tuned over a wide range of wavelengths and these absorptions are dependent on the polarity of the solvent. In most of these complexes the charge-transfer occurring in the ultraviolet or visible region was determined to be from a highest occupied molecular orbital (HOMO) with metal (d) and dithiolate (p-sulfur) mixed character to a lowest unoccupied molecular orbital (LUMO) contributed by the diimine π*-orbital. The electronic transition has been assigned as a mixed metal-ligand to ligand charge transfer (MML’CT), or as coined elsewhere “charge transfer to the diimine”. The energy of this CT transition can be tuned in two ways. First, by variation of the dithiolate to raise or lower the HOMO level of the transition as it is influenced by the electron donating or electron withdrawing properties of the dithiolate respectively. Secondly, the variation of the diimine to raise or lower the energy level of the LUMO as it is influenced by the electron donating or electron withdrawing properties of the diimine, respectively. This chapter contains all four of those situations, namely electron withdrawing groups on the dithiolate, electron donating groups on the dithiolate, electron donating groups on the diimine, and electron withdrawing groups on the diimine, both in isolation and in tandem (see Figure 2.1). However, the modification of the diimine to include ester functional group falls under the last category listed, that of electron withdrawing diimine substituents. The (1,2-benzenedithiolate)(2,2’-
bipyridine)platinum(II) complex, Pt(bpy)bdt, for example, can be assumed as a “middle of the road” model to represent a reference point for the four variations of the theme because of its high degree of planarity and lack of functional groups.

Figure 2.1: Electron donating groups added to the dithiolate ligand red shift the absorption compared to the unsubstituted complex (top left vs. top middle). Electron withdrawing groups added to the dithiolate ligand blue shift the absorption compared to the unsubstituted complex (top right vs. top middle). Electron withdrawing groups added to the diimine ligand red shift the absorption compared to the unsubstituted complex (bottom left vs. bottom middle). Electron donating groups added to the diimine ligand blue shift the absorption compared to the unsubstituted complex (bottom right vs. bottom middle).

The capacity to tune this charge-transfer to the π*-diimine is of interest to this study because it allows for the absorption of light to be shifted deep into the longer wavelengths of the visible spectrum and potentially into the near-infrared region of the solar radiation. As the electron-withdrawing abilities of the diimine substituents increase, the absorption of light energy is red shifted. These compounds tend to be darker in hue and of deep intensity. The “off-
black” colors of the solid compound and saturated solutions tend toward violet and indigo upon dilution, although spooky-forest green has also been observed in some compounds. The observed color is mainly a function of the low energy absorption band, but often higher energy absorptions can encroach into the visible region to provide additional variations of hue. These double visible absorptions result in the apparent green colors as both ends of the visible spectrum have maxima and the compound is more transparent to the middle region of visible wavelengths (see Figure 2.2). If the opposite approach is undertaken and the diimine substituents electron-donating properties are increased, the absorption of light energy is blue shifted. These compounds tend to be more a maroon or vinaceous color and of slightly less rich in intensity when compared to analogous chromophores that bear the electron-withdrawing functional groups on their diimines.

![Absorption spectra of Pt(dmbpy)bdt and Pt(dmecb)bdt](image)

**Figure 2.2:** Comparison of two extremes of the ligand modification: Pt(dmbpy)bdt [electron donation raising the LUMO] has a blue shifted absorption maximum in dilute dichloromethane solution and appears purple. Pt(dmecb)bdt [electron withdrawing lowering the LUMO] has a red shifted absorption maximum in dilute dichloromethane solution and appears green.
The energy of the CT transition in solution is influenced by the ligand field and this trend in the solid state continues. From the solid state of this class of chromophores another absorption emerges at longer wavelengths compared to their measurements in solution and can be correlated with the intermolecular Pt—Pt distance in the solid state. The solid state absorption is a more appropriate benchmark for evaluation than solution absorption as these complexes showed considerable solvothermic shifts dependent on the polarity of the solvent. This will be discussed further later in this chapter. Additionally, the ultimate use of these chromophores in solar cells is a solid state application where Pt—Pt distances would be at the shortest. The publication of the solid state properties these chromophores has scarcely been studied when compared to the amount of solution data to be found in the literature.19

In the solid state, the tendency of some Pt compounds (diimine/dichloride) to form linear chains of intermolecular Pt--Pt interactions was studied by Miskowski, Gray et al. in polypyridyl ligands.20 These authors showed that the energy of the absorption or emission of such complexes correlates with the distance between the Pt atoms in the chain. These “platinophilic bonding” interactions are stabilized by the overlap of the 5d(z^2) and 6d(p_z) orbitals on neighboring metal atoms in the chain. Data gathered from the few crystal structures of compounds forming linear platinum-platinum chains show these weak bonds are normally less than 3.5 Å in length and such

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intermolecular separation is affected by, among other things, steric bulk from the organic ligands and their attached substituents.\textsuperscript{21} In this study, anhydrous neutral compounds have been studied; therefore, other factors that may influence this weak intermolecular bonding interaction, such as the presence of a counter-ion or pH are minimized.

Figure 2.3: Structural diagrams of non-ester compounds used

Figure 2.4: Structural diagrams of ester containing compounds used

In this chapter, the discussion pertains to the molecular complexes whose chemical structures are shown in Figures 2.3-2.4. Figure 2.3 shows the compounds containing electron donating substituents or no substituents on the diimine, most of which are previously reported.
in the literature. Figure 2.4 shows the compounds in this study that have been modified to contain the electron-withdrawing ester substituents on the diimine that stabilize the LUMO participating in the CT to diimine and also improve solubility of the compound.

2.2 Experimental Section

2.2.1 Synthetic Details

2.2.1.1 Synthesis of 4,4′-Dicarboxy-2,2′-bipyridine (dcbpy)

4,4′-Dimethyl-2,2′-bipyridine was added to concentrated sulfuric acid and stirred until the organic molecule was completely solvated. Potassium dichromate was ground to a fine powder added in small amounts with deionized water while the solution stirred in a ice/water bath to maintain a temperature of 70-80°C. The dark green solution was stirred for three hours then poured over ice and filtered. The pale yellow-green chalky solid was washed with water and dried under vacuum. The product was refluxed for 4 hours in concentrated nitric acid. This solution was cooled to room temperature and diluted with ice. The pale yellow solution was allowed to sit in a refrigerator at 5°C for one hour. A fine white powder was collected by filtration and washed with water and then acetone then diethyl ether. The solid was dried under vacuum. Further purification by recrystallization in pyridine yielded colorless crystalline flakes that were used in subsequent synthetic procedures. (98% yield)

2.2.1.2 Synthesis of 4,4′-Dimethoxy-2,2′-bipyridine (dmecb) and Other Ester-substituted Bipyridine Ligands

4,4′-Dicarboxy-2,2′-bipyridine was dissolved in 20 mL of thionyl chloride and refluxed in an inert atmosphere for 2 hours. The volume of the yellow solution was reduced to dryness under gentle heating (50°C) and vacuum. The matte yellow solid was dried using these conditions for 24 hours.
A toluene-methanol mixture was prepared in a separate flask containing an argon environment using degassed and dried solvent. This solution was cannulated into the flask containing the acyl chloride under vacuum. An inert atmosphere was reintroduced to the reaction flask and the mixture was refluxed for five hours then cooled to room temperature. The faint pink solution was added to 30 mL of chloroform and washed with a saturated solution of sodium bicarbonate. The organic layer was then washed with a saturated solution of sodium chloride, dried with sodium sulfate, and filtered. The solution volume was evaporated using reduced pressure at room temperature. The white powder was then recrystallized in pyridine and methanol for use in subsequent synthetic procedures.

2.2.1.3 Synthesis of Dichloro(4,4'-dimethoxyester-2,2'-bipyridine)platinum(II) and Other Platinum Diimine Dichlorides

K2PtCl4 was dissolved in deionized water and heated to 60°C and dmecb (an equimolar amount) was dissolved in acetone at 60°C. The two solutions were mixed and refluxed for 8 hrs at 60-70°C. The yellow-orange water insoluble product was collected on a filter and washed with diethyl ether then hexanes to remove unreacted ligand. The product was then dissolved in dry and degassed dichloromethane and any insoluble material was removed by filtration. The solution was deep red to pale yellow depending on the concentration of the solution from high to low, respectively. A yellow-red compound was collected from the slow evaporation of dichloromethane.

2.2.1.4 Synthesis of Benzene-1,2-dithiolate(4,4'-dimethoxyester-2,2'-bipyridine)Platinum(II) and Other Platinum Diimine Dithiolates

Pt(dmecb)Cl2 was dissolved in dry degassed dichloromethane under argon. 1,2-benzenedithiol was added to an amount of absolute ethanol to achieve a (1:1) ethanol: CH2Cl2
solution. KHCO₃ stirred into suspension with the dithiol, the solution was then cannulated into
the platinum diimine dichloride solution. A dark product formed almost immediately and the
solution was stirred under argon and in the dark overnight. The solution volume was reduced
and the addition of excess hexanes produced a dark precipitate. This was filtered under an inert
atmosphere and washed with hexanes, then washed with diethyl ether and dried under vacuum
for 24 hours. The compound was purified by filtration over a bed of activated alumina and eluted
with dichloromethane. The eluted product was collected by evaporation of the solvent under
reduced pressure and addition of excess hexanes. The product was washed and dried again by
the procedure mentioned above.

2.2.2 Instrumentation

Electronic absorption measurements were collected on a PerkinElmer® Lambda™ 900
double beam UV-Vis-NIR spectrophotometer. Solution samples were prepared in volumetric
glassware using dry degassed solvents and then transferred to one millimeter, one centimeter or
ten centimeter Supersil quartz cuvettes for electronic absorption characterization. The solid
reflectance data were collected using the LabSphere integrating sphere accessory to the Lambda
900 spectrophotometer.

Infrared spectra for all compounds were recorded on a Nicolet 740 FT-IR
spectrophotometer. Background pellet consists of 0.2000 g of FT-IR grade KBr (Fluka) and the
sample pellet consists of approximately 1-2% sample, ground with KBr to equal 0.20 g.

Proton NMR was used to verify the purity of compounds in this study on a Varian VNMRS
500 MHz spectrometer. Between 5-20 mg of compound was dissolved in d₆-Chloroform, d₆-
DMSO, or d₆-Acetone (acquired from Cambridge Isotope Laboratories, Inc.) depending on the
best solubility or availability of the solvent and at least 265 scans were collected with 1.0 s relaxation delay in 5 mm NMR tubes (Wilmad). The spectra were referenced to the solvent peak without TMS (7.26 for d₆-Chloroform, 2.50 for d₆-DMSO, 2.05 for d₆-Acetone).

2.3  Results and Observations

2.3.1  Electronic Absorption Studies

2.3.1.1  Dilute Solution Studies and Absorption Band Assignments

Manipulation of the charge transfer band by variation of dithiolate ligand among compounds in the same diimine series studied results in a coarse tuning of energy associated with the “charge transfer to diimine”. In the Pt(dbbpy)L series(Figure 2.5a), the dithiolate quinoxiline-3,4,-dithiolate (qdt) whose comparable charge transfer is approximately 3120 cm⁻¹ (from 473 to 555 nm) blue shifted from the grouping of absorption maxima for the more electron donating dithiolates, 1,2-benzenedithiolate (bdt) and toluene-3,4-dithiolate (tdt). This group of maxima only varies about 320 cm⁻¹ (from 555 to 565 nm) corresponding to the compounds Pt(dbbpy)bdt and Pt(dbbpy)tdt respectively. The maleonitriledithiolate bearing chromophore absorption maxima is red shifted 1100 cm⁻¹ (from 473 to 499 nm) from Pt(dbbpy)qdt.

Both the qdt and mnt variety of Pt(dbbpy)dithiolate dyes exhibit a second absorption band that appears slightly more intense in the qdt compound (8760 vs 8530 L mol⁻¹ cm⁻¹) and about two-thirds as intense in the mnt compound (4250 vs 6680 L mol⁻¹ cm⁻¹) than the lowest energy bands. These bands border at the edge of visible and ultraviolet regions are too low in energy and not intense enough to be considered candidates for π-π* transitions, so cautiously they are labeled as ligand to ligand charge transfer. In the more polar Pt(dbbpy)bdt and Pt(dbbpy)tdt, weak bands are seen in the same region but are far less intense. These have been
assigned as spin-forbidden $\pi-\pi^*$ transitions from the triplet excited state of the diimine to the ground singlet state.

Figure 2.5: Normalized UV/Vis absorption spectrum in dichloromethane for dilute solutions (ca. $10^{-5}$ M) of Pt(dbbpy)bdt, Pt(dbbpy)tdt, Pt(dbbpy)mnt and Pt(dbbpy)qdt in: (a) the lower-energy region, and (b) the higher-energy region.

For the Pt(bpy)dithiolate series, the same progression of absorption energies is observed when the dithiolate ligand is varied while holding the diimine as bpy (Figure 2.6).
Figure 2.6: Normalized UV/Vis absorption spectrum in dichloromethane for Pt(bpy)tdt, Pt(bpy)bdt, Pt(bpy)mnt, and Pt(bpy)qdt in: (a) the lower-energy region, and (b) the higher-energy region.

That is, the energy of the “charge transfer to diimine” decreases from qdt > mnt > bdt > tdt. The effect of the methyl group on tdt versus bdt has a trifling effect in the Pt(dbbpy)dithiolate series.
only red shifting the absorption by 270 cm\(^{-1}\) (from 575 to 584 nm). The qdt complex from this series is blue shifted by the same amount from the low energy grouping by 3310 cm\(^{-1}\) to 483 nm. In this series, the lack of electron donating tert-butyl groups establishes a general basis to explore the electron withdrawing effects of the mnt ligand since only the HOMO energy is lowered according to Figure 2.1 (top right) in the Pt(bpy)mnt complex. The blue shift from the bdt complex to the mnt is 1620 cm\(^{-1}\) (to 526 nm).

For Pt(diimine)dithiolates containing the fused bipyridine ligand 1,10-phenanthroline (phen) the trend of decreasing absorption energy associated with the “charge transfer to the diimine” continues in the order of qdt > mnt > bdt > tdt (Figure 2.7). The electron donating methyl group of the tdt raises the energy of the HOMO located on the dithiolate by virtually the same amount as seen in the other series, red shifting the absorption maxima 300 cm\(^{-1}\) (from 572 to 582 nm). The qdt bearing chromophore in this series is blue shifted 3220 cm\(^{-1}\) (to 483 nm) and a shoulder appears at around 530 nm due to second charge transfer also assigned as a charge transfer to diimine. Pt(phen)mnt is red shifted from the qdt complexes maxima by only 660 cm\(^{-1}\) and blue shifted from the bdt maxima by 2360 cm\(^{-1}\) (to 499 nm). In comparison with the other series where the dithiolate is varied, this is a notable shift illustrating the strong influence of mnt on the HOMO energy when place in a system with phen. Strong ligand-to-ligand charge transfers are also observed for the mnt and qdt on the edge of the visible and ultraviolet regions (Figure 2.7b).

The Pt(dmbpy)dithiolate series behaves very similarly to the Pt(dbbpy)dithiolate series suggesting that the destabilizing effect on the LUMO of the diimine by the electron donating tert-butyl and methyl are very similar (Figure 2.8).
Figure 2.7: Normalized UV/Vis absorption spectrum in dichloromethane for Pt(phen)tdt, Pt(phen)bdt, Pt(phen)mnt, and Pt(phen)qdt in: (a) the lower-energy region, and (b) the higher-energy region.
Figure 2.8: Normalized UV/Vis absorption spectrum in dichloromethane for dilute solutions (ca. 10^{-5} M) of Pt(dmbpy)tdt, Pt(dmbpy)bdt, Pt(dmbpy)mnt in: (a) the lower-energy region, and (b) the higher-energy region.

Pt(dmbpy)mnt is blue shifted 2160 cm^{-1} (to 494 from 553 nm) from the bdt complex used as a comparison point (Figure 2.1). The effect of the electron donating methyl of the tdt has less effect on the HOMO energy than the same comparison made in the Pt(dbbpy)dithiolate series.
red shifting the maxima 260 cm\(^{-1}\) (to 561 from 553 nm). Also, a distinct ligand-to-ligand (dithiolate to diimine) charge transfer of near equal intensity is observed around 385 nm.

The first of the ester containing diimines studied in this work form the series Pt(dmecb)dithiolate (Figure 2.9). The previously observed trends regarding the HOMO energies still endures with the same progression as tdt(HOMO) > bdt (HOMO) > mnt (HOMO) > qdt (HOMO) resulting in decreases in absorption maxima as qdt > mnt > bdt > tdt. Also continuing is the very small effect of the methyl group of tdt has on stabilizing the HOMO compared to bdt. A red shift of 290 cm\(^{-1}\) (669 to 682 nm) from bdt to tdt is comparable to all other series that vary the dithiolate. The mnt and qdt of this series are both blue shifted 2360 and 3010 cm\(^{-1}\) respectively (to 579 and 557 nm). Equally as intense, a ligand-to-ligand charge transfer (LL’CT) band can be seen around 360 nm for Pt(dmecb)mnt and a strong LL’CT bands for the qdt complex at the border of the visible and ultraviolet regions.

In dilute solutions, Pt(disopcb)dithiolates follow the same trends established for all the series in this study (Figure 2.10). The tdt complex is red shifted 310 cm\(^{-1}\) (662 to 676 nm) from the bdt model. The mnt and qdt of this series are both blue shifted 2110 and 4390 cm\(^{-1}\) respectively (to 581 and 513 nm from 662 nm). The qdt complex of this series is ennobled as the highest energy absorption of any of the ester containing chromophores due to HOMO stabilizing effects of the dithiolate ligand. The addition of the isopropyl carbons to the ester improves solubility over the non-ester dyes, but tempers the electron withdrawing effects of this functional group thus the LUMO energy level is less stabilized than in the dmecb series. With the exception of the mnt bearing dye of this series, all of the absorption maxima are significantly blue shifted from their dmecb counterparts.
Figure 2.9: Normalized UV/Vis absorption spectrum in dichloromethane for dilute solutions (ca. 10^-5 M) of Pt(dmecb)tdt, Pt(dmecb)bdt, Pt(dmecb)qdt, Pt(dmecb)mnt in: (a) the lower-energy region, and (b) the higher-energy region.
Figure 2.10: Normalized UV/Vis absorption spectrum in dichloromethane for dilute solutions (ca. 10⁻⁵ M) of Pt(disopcb)tdt, Pt(disopcb)bdt, Pt(disopcb)qdt, Pt(disopcb)mnt in: (a) the lower-energy region, and (b) the higher-energy region.

Finally the Pt(dhepcb)dithiolates, synthesized for their excellent solubility, fall lockstep with the established trend regarding absorption energies of the CT band (Figure 11). The tdt
complex is red shifted 350 cm\(^{-1}\) (664 to 680 nm) from the bdt model. The mnt and qdt of this series are both blue shifted 2610 and 4320 cm\(^{-1}\) respectively (to 566 and 516 nm from 664 nm). All of the complexes of this series are slightly blue shifted from their dmecb counterparts. Again this illustrates the long alkyl groups of the ester mitigating the LUMO stabilization provided by the ester group. These compounds should be ideal for solution processed photovoltaics based on their solubility, wide range of absorption in the visible region, and high extinction coefficients (\(\varepsilon = 11600 \text{ L mol}^{-1} \text{ cm}^{-1}\) for Pt(dhepcb)tdt).

Figures 2.5-2.11 illustrate the blue shifting effects of the electron withdrawing cyano group of the maleonitrile dithiolate (mnt) and the quinoxaline of the quinoxaline 2,3-dithiolate (qdt) on the visible absorption peak compared to the unsubstituted 1,2-benzenedithiolate (bdt). Also a small red shifting influence from the electron donating methyl substituent of the 3,4-toluenedithiolate (tdt). The charge-transfer to the diimine peak maxima for the compounds lacking any diimine substituents, Pt(bpy)mnt and Pt(phen)mnt, are shifted to approximately 1620 and 2560 cm\(^{-1}\) higher in energy respectively from the analogs for who’s dithiolate (bdt) is attached to a simple benzene ring and bears no electron donating or withdrawing groups. These two compounds represent the minimum and maximum blue shifting effects provided by the mnt for the Pt(diimine)mnt series. The same comparisons made for the electron withdrawing quinoxaline series shows the minimum and maximum shifts for the Pt(diimine)qdt series to be 3000 cm\(^{-1}\) for Pt(dmecb)qdt and 7300 cm\(^{-1}\) for Pt(bpy)qdt when compared to the bdt analog. The electron donating tdt shifts the charge transfer to the diimine absorbance peak 258 cm\(^{-1}\) lower in energy from the bdt analog of Pt(dmbpy)tdt, the minimum effect of the tdt dithiolate.
Figure 2.11: Normalized UV/Vis absorption spectrum in dichloromethane for dilute solutions (ca. 10^{-5} M) of Pt(dhepcb)tdt, Pt(dhepcb)bdt, Pt(dhepcb)qdt, and Pt(dhepcb)mnt in: (a) the lower-energy region, and (b) the higher-energy region.
The maximum effect of the tdt ligand compared to the bdt analog is 354 cm\(^{-1}\) for Pt(dhepcb)tdt vs Pt(dhepcb)bdt. Figure 2.12 lists all charge transfer to diimine absorptions shifts from one dilute CH\(_2\)Cl\(_2\) solution to another and the inset table in Figure 2.12 summarizes the minimum and maximum shifts for each series when compared to their non-substituent bearing counterparts (bpy for diimines and bdt for dithiolates). A common feature in these series that is notable among the variants that bear mnt or qdt moieties in this work (Figure 2.5) is the ascension of a short wavelength band into the visible region. One would be attempted to assign these bands to diimine-localized \(\pi-\pi^*\) transitions, which represent the conventional assignment for the second-lowest energy group of electronic transitions in this family of complexes. However, that assignment would be counterintuitive given that the same diimine (dbbpy) is used for all complexes in Figure 2.5, which then should attain the same absorption maximum for the diimine-localized \(\pi-\pi^*\) transition in each complex. Therefore, I propose that with the poorer dithiolate electron donors that bear electron-withdrawing N-heterocyclic (qdt) or cyano groups conjugated to the dithiolate, the HOMO would no longer be an admixed metal-dithiolate orbital but instead a metal-localized orbital with the HOMO-1 being the thiolate orbital. Thus, the shorter-wavelength absorption band that appears in the visible region of such complexes that contain mnt or qdt is now assigned to a thiolate-to-diimine charge transfer (LL’CT) while the lowest-energy band is assigned to metal-to-ligand charge transfer (MLCT), whereas the above assignment with admixed HOMO pertains to only the better electron-donating dithiolates such as bdt and tdt. This proposed new assignment is illustrated in Figure 2.13.
Figure 2.12: Shifts in dilute dichloromethane solution absorption maxima reported in cm⁻¹. The highlighted values are estimated values. Positive values represent a blue shift and negative values represent a red shift comparing the vertical (side) entries to the top horizontal (top) entries.
Figure 2.13: (Left) Orbital diagram illustrating the mixing of Pt(d) and S(π) orbitals to form one of mixed character that originates the MMLL'CT present in Pt(diimine)dithiolates with electron donating substituents attached to the ditiolate (Right) Orbital diagram illustrating the non-mixed of Pt(d) and S(π) orbitals proposed for Pt(diimine)dithiolates with electron withdrawing substituents on the dithiolate ligand that would produce two distinct charge transfer bands, one metal centered and the other ligand centered.

This is barely observed in the non-methylated Pt(bpy)bdt, but is seen in the very similar Pt(phen)mnt and Pt(phen)qdt (Figure 2.7). The introduction of the bridging carbons on the diimine of 1,10-phenanthroline reduces the internal vibrations of these compounds, thus preserving the rigidity of the molecule and integrity of these transfers.

A comparison of the two series containing the methyl and t-butyl groups (Figures 2.8 & 2.5) illustrate that the effects of the diimine and the dithiolate cannot be considered additive. Both Pt(dbppy)bdt and Pt(dbppy)ttdt have peak maxima around 555nm. Pt(dmbpy)bdt and Pt(dmbpy)ttdt also share the same absorptions energies even though the methyl group should be more strongly donating to the aromatic ring than the tert-butyl through hyper conjugation.

All charge transfers of the lowest energy have been determined to be of a mixed metal-ligand to ligand character. The bathochromic shift in absorption energy observed in the qdt species is due to the increasing stability of the HOMO located on the mixed platinum-sulfur orbitals. The resonance stabilization energy of the qdt ligand is difficult to counter weight (Figure 2.16). The addition of strongly electron withdrawing groups to the diimine moiety slightly red
shifts the maximum and only in the most extreme case of LUMO stabilization by the dimethoxyester is there any significant reduction in energy.

It can be seen in Figure 2.14 that the electron withdrawing properties of the ester functional group subdued by the extended alkyl chains of the isopropyl and heptyl moieties. One consequence of this blue shift is low energy absorptions appear as shoulders in the major visible spectrum peaks. These shoulders occur approximately 2200 cm\(^{-1}\) red shifted from the lowest intramolecular absorption and is attributed to intermolecular charge transfer possible in the dimer for solutions or in extended stacks for solid samples.

The effects of variation of the substituents at the 4,4' position of the 2,2'-bipyridine ligand can be seen in figures 2.14-2.17. As the functional group donates electrons to the ring, the energy level of the LUMO is raised; therefore, the absorption peak is blue shifted to higher values. Electron withdrawing substituents, which are esters in this study but theoretically could be amides or any of the well-known electron withdrawing functional groups, stabilize the LUMO energy and as a result red shift the absorption energy of the CT. A general trend can be observed for the CT energy in all the series where the diimine is varied of dmbpy > dbbpy > phen > bpy > disopc > dhepc > dmebc with the exception of the series containing the mnt dithiolate where the Pt(disopcb)mnt possesses the lowest energy charge transfer.
Figure 2.14: Normalized Pt(L)qdt UV/Vis absorptions of dilute CH₂Cl₂ solutions (~10⁻⁵ M). L has been varied to show the effect of the diimine on the charge transfer band.

Figure 2.15: Normalized Pt(L)mnt UV/Vis absorptions of dilute CH₂Cl₂ solutions (~10⁻⁵ M). L has been varied to show the effect of the diimine on the charge transfer band.
Figure 2.16: Normalized Pt(L)bdt UV/Vis absorptions of dilute CH₂Cl₂ solutions (≈10⁻⁵ M). L has been varied to show the effect of the diimine on the charge transfer band.

Figure 2.17: Normalized Pt(L)tdt UV/Vis absorptions of dilute CH₂Cl₂ solutions (≈10⁻⁵ M). L has been varied to show the effect of the diimine on the charge transfer band.
2.3.1.2 Solid State Diffuse Reflectance Studies

Comparisons of dilute solution absorption spectra to solid state diffuse reflectance spectra illustrate the ability of this class of chromophores to act often as the near-infrared absorber this study has pursued. This property is observed obviously in the solid state, but also to a lesser extent in the spectra of the more concentrated solutions as the molecules self-associate to form dimers or larger oligomers. This low energy absorption is due to intermolecular interactions becoming more probable as concentration is increased, hence red shifting the absorption bands affected by association to approach the limiting case represented by the neat solid. In Chapter 3, the consequence of this property in terms of how it can be exploited for thin film-based organic solar cells is discussed. The presence of the lower energy absorption cutoff with significant red shift from the absorption edge of the solution spectra is observed in the solid-state diffuse reflectance spectra of all the Pt(diimine)dithiolate complexes (Figures 2.18-2.25). The significant broadening and lowering of resolution of the individual absorption bands is an expected outcome for solid low-dimensional materials that exhibit significant intermolecular interactions, as the underlying electronic structure description becomes that of band structure as opposed to discrete molecular orbital description due to the increased density of states.

Table 2.1 gives a complete comparison of the absorption bands for all compounds studied in this work. The general trend to lower energy absorptions in the solid state is established and is consistent with the position that closely associated molecules in the solid state give rise to new absorptions. The red shift of the absorption cutoffs of the solid verses the solution varies from as small as 1160 cm\(^{-1}\) for Pt(bpy)tdt to as large as 4650 cm\(^{-1}\) for Pt(dhepcb)qdt.
Figure 2.18: Pt(dmeč)bdt diffuse reflectance vs. dilute CH₂Cl₂ solution (~10⁻⁵ M)

Figure 2.19: Pt(disopcb)qdt diffuse reflectance vs. dilute CH₂Cl₂ solution (~10⁻⁵ M)

Figure 2.20: Pt(dbbpy)qdt diffuse reflectance vs. dilute CH₂Cl₂ solution (~10⁻⁵ M)

Figure 2.21: Pt(dmbpy)bdt diffuse reflectance vs. dilute CH₂Cl₂ solution (~10⁻⁵ M)
The band gap ($E_g$) for the solid materials generally exhibits the same general trend for the solution absorption maxima in that the most red shifted absorptions correspond to the complexes that
exhibit the most electron releasing dithiolates and most electron withdrawing diimines (Table
2.1).

Table 2.1: Comparison of solution absorption maxima vs. solid state absorption maxima and
solid absorption cutoffs for the (diimine)(dithiolate)platinum(II) complexes studied in this
dissertation. \(E_g\) has been calculated from the solid state absorption cut-off.

<table>
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<th>Compound</th>
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<th>Solid</th>
<th>Solid</th>
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<tr>
<td></td>
<td>(\lambda_{\text{max}}) (/nm)</td>
<td>(\lambda_{\text{max}}) (/nm)</td>
<td>(\lambda_{\text{cutoff}}) (/nm)</td>
<td>(E_g) (/eV)</td>
</tr>
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<td>580</td>
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<tr>
<td>Pt(dbbpy)bdt</td>
<td>555</td>
<td>570</td>
<td>727</td>
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<td>1.69</td>
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<tr>
<td>Pt(dmbpy)bdt</td>
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<td>570</td>
<td>727</td>
<td>1.71</td>
</tr>
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<td>451</td>
<td>847</td>
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2.3.1.3 Oligomerization of Pt(diimine)dithiolates in Solution

The effects of aggregation on the absorption band shift can also be observed best in the
concentrated solutions of the Pt(diimine)dithiolates that bear esters. The additional solubility provided by this functional group attached to each pyridine ring allows the preparation of solutions that are concentrated enough to allow extensive aggregation in solution. Such aggregation has been shown before in platinum(II) compounds containing the heptanoic ester functionalized bipyridine with the dithiolate moiety replaced by dichloride in a previous Ph.D. dissertation from the Omary group,\(^\text{22}\) whereas extending the concept to dithiolated species should have desirable consequences toward organic solar cell applications given the much lower-energy absorptions rendered by the charge transfer absorption bands into the NIR region. Aggregation in solution, indeed, does occur when the dithiolate is present on the compound resulting in a red shifted absorption in solution for the primary MMLL’CT and the appearance of a small shoulder at beyond 600 nm in a dichloromethane solution. Figure 2.26 illustrated this aggregation associated charge transfer for an ester containing diimine compound at several concentrations.

A strict interpretation of Beer’s law should allow the prediction that the extinction coefficient for any given wavelength should be the same for a given compound. Therefore a plot like figure 2.26b should have identical profiles for each concentration. However, there are slight positive deviations from Beer’s Law at low energy wavelengths around 640 nm accompanied by negative deviations at the absorptions at the maxima and the shoulder around 575 nm as concentrations of Pt(disopcb)qdt increase. Normally deviations from Beer’s law do not occur at

concentrations lower than 0.01 M. Figure 2.26b clearly illustrates deviations at concentrations an order of magnitude lower than 0.01 M that are not a result of limitations of Beer’s law. This nonconformity is attributed to the oligomerization of the chromophore in more concentrated solutions described by the process: \( n[ \text{dye} ] \rightleftharpoons [ \text{dye} ]_n \), with the equilibrium constant \( K_{1n} = c_n / c_1^n \), where \( c_1 \) and \( c_n \) represent the monomer and \( n \)-oligomer concentrations respectively. From the equilibrium equation and Beer’s law the following equation is derived:\( ^24 \)

\[
c_0A^{-1/n} = \frac{\left( n/(\varepsilon_n b) \right) A^{(n-1)/n} + (K_{1n} \varepsilon_n b)^{-1/n}}{\varepsilon_n b}
\]

where \( c_0 \) is the original concentration of the dye and \( b \) is the light path length from Beer’s law (1 cm). Figure 2.26c is a satisfactory fit (\( R^2 = 0.9779 \)) of \( c_0A^{-1/2} \) versus \( A^{1/2} \) given that \( n=2 \) in the above equation suggesting that the new absorption feature seen around \( \lambda=640 \) nm is the result of dimerization of the chromophore. From the equation of the linear regression, \( \varepsilon_2 \) and \( K_{12} \) are calculated to be 112 L mol\(^{-1}\)cm\(^{-1}\) and 1690 M\(^{-1}\) respectively. Figure 2.26d treats the data in the same manner with the exception that \( n=3 \), representing the trimer so the plot is \( c_0A^{-1/3} \) versus \( A^{2/3} \). The fit of the linear regression is also satisfactory (\( R^2 = 0.9838 \)) for \( n=3 \) suggesting the low energy band is the result of a trimer forming in solution. Both the formation of dimers and trimers are reasonable propositions. Trimers of square-planar tetracyanoplatinate(II) have been observed in aqueous solutions lending credibility to this conclusion.\( ^25 \)

The low extinction coefficient of the oligomer makes it difficult to have complete confidence in either assignment.


so the data taken as a whole should be viewed as qualitative proof that association does occur in solution, but not a quantitative assessment of the nature of association leading to the new energy absorption feature. It is very likely that one or more oligomer bands are hidden under the strong monomer peak and the red shifted edge is from a higher order oligomer.

2.4 Crystallographic Studies

The examination of crystallographic data reveals a propensity for head to tail stacking pattern where the molecule is rotated 180° around the axis perpendicular to the molecular plane in a repeating pattern. This dimer or dimer-like orientation places the (p/d) orbital of a dithiolate in close proximity to $\pi^*$–orbital of the diimine on an adjacent molecule. A common feature of all the following dimeric structures is an interplanar distance of less than 3.4 Å in this spatial region, a distance known to allow intermolecular electronic charge transfers.

2.4.1 Benzene-1,2-dithiolate(2,2'-bipyridine)platinum(II) -- Pt(bpy)bdt

Previously studied by Eisenberg, Connick, et al., for the properties of the oxidation products, the following crystal was grown in a dichloromethane/acetone solvent system and the structure was solved with a greater degree of accuracy than in previous studies ($R_1=0.0202$ vs 0.033).

---

Figure 2.26: (a) Absorption spectra for Pt(disopcb)qdt in CH$_2$Cl$_2$ solution (b) Extinction coefficient as a function of wavelength and concentration (c) Plot of $C_0A^{-1/2}$ vs. $A^{1/2}$ and (d) Plot of $C_0A^{-1/3}$ vs. $A^{2/3}$ for $\lambda$=640, the suspected band maxima for the oligomer.
Figure 2.27: Crystal packing arrangement of Pt(bpy)bdt, a slipped stacking association of π-interactions (represented by the blue lines). Hydrogens have been omitted for the sake of clarity.

The unit cell contains four individual molecules was determined to be of the P12/c space group. The individual residents of the unit cell formed close range interactions with a corresponding molecule in neighboring cells to produce intermolecular distances of 3.17 Å. This is within the range known to allow charge-transfer in these materials. The orientation of the molecules is uniform with a large offset on the stack to allow the dithiolate to be directly above the diimine. Assuming that the low energy charge transfer is primarily ligand based, there is hope to exploit this feature to incorporate more economically feasible metals in the future if it can be shown that the central metal atom only takes a minor role in the transition. Figure 2.27 illustrates this proximity of the overlap in the crystal structure. Four such unique stacks originate from the four distinct molecules of the unit cell.
Table 2.2: Crystallographic data and selected bond lengths (Å) and angles (°) for Pt(bpy)bdt using the atom labeling scheme in Figure 2.28

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<td>M_r</td>
<td>491.49</td>
<td>Z</td>
</tr>
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<td>D_calk (Mg/m³)</td>
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<td>μ(Mo)</td>
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<td>F (000) (e)</td>
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Figure 2.28: Atom labeling scheme of Pt(bpy)bdt
2.4.2. Quinoxilene-3,4-dithiolate(4,4'-tert-butyl -2,2'-bipyridine)platinum(II) -- Pt(dbppy)qdt

The compound Pt(dbppy)qdt formed a single crystal from a concentrated solution of dichloromethane diffusing into dry hexanes layered on top. The slow evaporation of this solvent mixture produced crystals suitable for analysis with regularity. The compound was solved without disorder in the P12/c space group with a large unit cell containing four dimeric units of the molecule (Figure 2.29). The planar distance separating the participants of the dimer was calculated to be 3.454 Å and the Pt-Pt distance was 3.749 Å with a head to tail orientation of the molecules in the dimer with a offset of 22.88° of the platinum atoms.

Figure 2.29: Dimer of Pt(dbppy)qdt in the unit cell showing a volte-face head to tail orientation between the partners within the dimer. Close intermolecular and Pt-Pt distances are represented by the green lines. Hydrogens have been omitted for the sake of clarity.
Figure 2.30: The atom labeling scheme for Pt(dbbpy)qdt

Table 2.3: Crystallographic data and selected bond lengths (Å) and angles (°) for Pt(dbbpy)qdt using the atom labeling scheme in Figure 2.30

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2.4.3 Dichloro(4,4'-diisopropoxyester-2,2'-bipyridine)platinum(II) Dichloromethane Solvate Pt(disopcb)Cl$_2$•1.5CH$_2$Cl$_2$

Crystals suitable for X-ray diffraction for the compound Pt(disopcb)Cl$_2$ were collected from the slow evaporation of dichloromethane. The structure was solved to be of the P-1 space group and contained one solvent molecule per two platinum chromophores. The unit cell contained two dimeric units with a continuous head to tail orientation (Figure 2.31). The planar distance between molecules in dimeric units and between adjacent dimeric units was found to be 3.35 Å. Only the offset between platinum atoms alternated from and 16.94° and 12.47° as the metal-metal distance changed from 3.502 Å in the dimer to 3.431 Å between dimers.

Figure 2.31: The volte-face head-to-tail orientation of the two molecules of the dimer in the Pt(disopcb)Cl$_2$ • 1.5 CH$_2$Cl$_2$ unit cell. Solvent molecules and hydrogens have been omitted for the sake of clarity.
Figure 2.32: Atom labeling scheme for Pt(disopcb)Cl₂ • 1.5 CH₂Cl₂

Table 2.4: Crystallographic data and selected bond lengths (Å) and angles (°) for Pt(disopcb)Cl₂ • 1.5 CH₂Cl₂ using the atom labeling scheme in Figure 2.32

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<td>Goodness-of-fit on F</td>
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<td>Cl(2) - Pt(1) - Cl(1)</td>
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2.4.4 Dichloro(4,4'-diisopropyloxyester-2,2'-bipyridine)platinum(II) -- Pt(disopcb)Cl₂

An alternate packing structure was found for Pt(disopcb)Cl₂ sans solvent was also discovered from the slow evaporation of an ethanol/hexanes layered solvent system using a concentrated solution of the platinum dye in ethanol. The space group was determined to be P-1, but the stacking is non-continuous unlike the solvent containing crystals (Figure 2.33). The four molecules contained in the unit cell are in herringbone arrangement. There is a close interaction between molecules in adjacent cells that have the familiar head to tail orientation with a planar distance of 3.350 Å and a platinum-platinum distance of 5.186 Å giving an offset of 49.76° in the metal atoms (Figure 2.34).

Figure 2.33: Close association C-Cl (represented by the dashed line) of two molecules of Pt(disopcb)Cl₂ with a contact distance of 3.365 Å which is less than the sum of their van der Waals radii. Hydrogens and solvent molecules have been omitted for the sake of clarity.
Figure 2.34: Planar distance between two associated molecules of Pt(disopcb)Cl$_2$ of 3.350 Å (represented by the vertical dashed line) and the offset Pt-Pt distance of 5.186 Å of two volte-face Pt(disopcb)Cl$_2$ molecules. Hydrogens and solvent molecules have been omitted for the sake of clarity.

Figure 2.35: Atom labeling scheme for Pt(disopcb)Cl$_2$. 
Table 2.5: Crystallographic data and selected bond lengths (Å) and angles (°) for Pt(disopcb)Cl₂ using the atom labeling scheme in Figure 2.35

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2.4.5 Dichloro(4,4'-dimethoxyester-2,2'-bipyridine)platinum(II) Dichloromethane Solvate Pt(dmecb)Cl₂●CH₂Cl₂

The compound Pt(dmecb)Cl₂ was crystallized in a concentrated solution of dichloromethane layered with and diffused into hexanes. The solvent system was allowed to slowly evaporate to give orange-red crystals that became red as solvent was stripped off under vacuum and destroyed the crystal. With one dichloromethane solvent molecule per platinum chromophores the compound crystallized in Pcba space group with the unit cell containing four...
dimeric units with a metal-metal distance of 3.470 Å and a planar distance of 3.375 Å giving an offset of 13.43° between platinum centers (Figure 2.36).

Figure 2.36: Two volte-face molecules of Pt(dmecb)Cl₂ with a planar distance of 3.375 Å and a Pt—Pt distance of 3.470 Å (represented as dashed lines). Hydrogen atoms have been omitted for the sake of clarity.

Figure 2.37: Atom labeling scheme for Pt(dmecb)Cl₂ • CH₂Cl₂.
Table 2.6: Crystallographic data and selected bond lengths (Å) and angles (°) for Pt(dmecb)Cl₂ • CH₂Cl₂ using the atom labeling scheme in Figure 2.37

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2.4.6 Dichloro(4,4'-dimethyl-2,2'-bipyridine)platinum(II) -- Pt(dmbpy)Cl₂

The Pt(dmbpy)Cl₂ was collected as a pale yellow crystal from the slow evaporation of a concentrated solution in dichloromethane and ethanol. The structure was determined to be of the P2₁/n space group with a unit cell that contained one dimeric unit of the chromophore and two molecules that formed dimers with partners in the adjacent cells. The dimers oriented head-to-tail volte-face and continued this stacking pattern throughout the crystal forming one-dimensional chains with alternating planar distances between chromophores of 3.328 and 3.317
Å and platinum-platinum distances of 5.695 and 6.796 Å (Figure 2.38). These offsets alternate from 54.24° and 60.79°.

Figure 2.38: Alternating planar distances between dimeric Pt(dmbpy)Cl₂ and the neighboring dimer of 3.328 and 3.317 Å represented by dashed lines. Hydrogen atoms have been omitted for the sake of clarity.

Figure 2.39: Atom labeling scheme for Pt(dmbpy)Cl₂
Table 2.7: Crystallographic data and selected bond lengths (Å) and angles (°) for Pt(dmbpy)Cl₂ using the atom labeling scheme in Figure 2.39

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2.4.7 Benzene-1,2-dithiolate(4,4'-dimethoxyester-2,2'-bipyridine)platinum(II)--Pt(dmecb)bdt

The compound Pt(dmecb)bdt was crystallized from a concentrated solution of dichloromethane layered with hexanes. After the concentrated solution diffused into the hexanes the solvent system was allowed to slowly evaporate in the dark. Dark and spooky forest green crystals formed as thin needles, analyzed immediately and found to be in the space group C2/c. The large unit cell contained eight separate molecules that formed stacks of dimers with adjacent cells (Figure 2.40). The head-to-tail orientation was again observed with alternating
planar distances of 3.433 and 3.407 Å and platinum-platinum distances alternating 5.049 and 3.541 Å giving offsets of 47.16° and 15.81°.

Figure 2.40: Stacking of Pt(dmecb)bdt showing head-to-tail volte-face dimeric orientation with alternating planar distances of 3.433 and 3.407 Å. A Pt—Pt distance of 3.541 Å is measured between overlain molecules and 5.049 Å for offset molecules. Hydrogen atoms have been omitted for the sake of clarity.

Figure 2.41: Atom labeling scheme for Pt(dmecb)bdt
Table 2.8: Crystallographic data and selected bond lengths (Å) and angles (°) for Pt(dmecb)bdt using the atom labeling scheme in Figure 2.41

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<td>M_r</td>
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<td>D_calc (Mg/m³) 2.074</td>
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<td>μ(Mo)(mm⁻¹) 7.458</td>
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<td>c (Å)</td>
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<td>T /K 100(2)</td>
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<td>β(°) 128.0040(10)</td>
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<td>γ (°)</td>
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<td>ρ_fin (max/min) eÅ⁻³ 0.896, -0.636</td>
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<td>C(16)-S(2)-Pt(1) 104.54(9)</td>
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2.4.8 Benzene-1,2-dithiolate(4,4'-diheptoxyester-2,2'-bipyridine)platinum(II)--Pt(dhepcb)bdt

The compound Pt(dmecb)bdt was crystallized from a solution of dimethysulfoxide. The solvent system was allowed to slowly evaporate in the dark. Deep purple crystals formed as thin needles in small amounts among an abundance of amorphous powder. This crystallization must absolutely not be disturbed and never occurred using concentrations above 10⁻⁴ M. The difficulty and low abundance of the crystal formation is attributed to the disorder and free rotation of the long alkyl chains of the ester group. The crystallization of such groups can be compared to stacking cooked spaghetti noodles. The space group was determined to be P-1 and the unit cell
contained two molecules that formed stacks of dimers with adjacent cells (Figure 2.42). The head-to-tail orientation was again observed with alternating planar distances of 3.179 and 3.194 Å and platinum-platinum distances alternating 5.652 and 5.870 Å giving offsets of 55.77° and 57.04°.

Figure 2.42: The stacking pattern of Pt(dhepcb)bdt with alternating planar distances of 3.179 and 3.194 Å. The zig-zag positioning of the platinum atoms produces large alternating Pt—Pt distances of 5.652 and 5.870 Å. Hydrogen atoms have been omitted for the sake of clarity.

Figure 2.43: The atom labeling scheme of Pt(dhepcb)bdt
Table 2.9: Crystallographic data and selected bond lengths (Å) and angles (°) for Pt(dhepcb)bdt using the atom labeling scheme in Figure 2.43

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<th>Crystal Data</th>
<th>Pt(dhepcb)bdt</th>
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<td>S(1)-Pt(1)-S(2)</td>
<td>89.37(5)</td>
<td>N(1)-C(1)-C(14)</td>
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</table>

2.5 Conclusions and Future Work

The proclivity of Pt(diimine)dithiolate compounds to form extended one-dimensional stacks red shifts the absorption of visible light this type of chromophore, by way of intermolecular charge transfer, in the solid state and concentrated solutions. This conclusion is based on crystallographic observations that the intermolecular interactions are governed by head-to-tail offset or anti-parallel stacking between the dithiolate moieties of one unit and the diimine moieties of adjacent units, as opposed to symmetrical stacking forces such as Pt-Pt or parallel π-π interactions. Thus, the red shifts in the absorption bands in the solid state or concentrated
solutions vs. dilute solutions are attributed to such intermolecular charge transfer interactions. Occurring at a lower energy than the primary charge transfer from the Pt(d$_z$)/S(p) mixed orbital to the $\pi^*$ of the diimine, this intermolecular electron mobility gives the solid state semiconducting properties. The crystallographic evidence supports the conclusion that one-dimensional stacks are forming with small intermolecular distances. Less than 4 Å in all reported structures, a distance accepted to permit intermolecular interactions was also implied to occur in concentrated solutions by emergent low energy absorption. Finally, this study also has allowed the distinction between the aforementioned Pt(d$_z$)/S(p) mixed orbital to the $\pi^*$ of the diimine assignment that is now widely accepted from situations where the assignment needs to be “split” such that both metal-to-ligand charge transfer (MLCT) and dithiolate to diimine charge transfer (LL’CT) when the dithiolate is a weaker donor with electron-withdrawing moieties in its chemical structure.

Pt(diimine)dithiolate semiconducting properties make this class of chromophores interesting to study for the use in OPV applications. Both the charge transfer and absorption extension emanating from the closely packed solid state are a boon to solar harvesting applications. Future studies should be focused on a reliable method to process a thin film on a transparent metal oxide semiconductor for use in devices. Attempts have been made on ITO and FTO substrates using a variety of methods that will be discussed in another chapter, but a consistently successful deposition method for the neat film is still under investigation.

The modification of the diimine ligand by the addition of two ester groups to produce a highly soluble metallorganic chromophore should not be limited to one application. Of the aromatic ring containing ditholates, the HOMO of the targeted charge transfer lay on the sulfur
and platinum atoms at one side of the ring. The opposing side of the ring serves to provide or remove electron density to the mixed orbitals. If this side were replaced with another pair of thiolate groups in the appropriate step, an additional Pt(diimine) unit could be attached rendering another Pt(S) orbital and diimine (π*). Whether this type of arrangement would produce two isolated or one integrated system is of interest as increasing the solubility of the compounds could introduce liquid crystal effects that can be further tuned. An addition to promoting solubility of the molecule, by virtue of adding the second functionalized diimine, the possible variations on the theme (diimine)Pt(bis-dithiolate)Pt(diimine) increases. The functionality of the binuclear could be tuned at both ends to optimize the properties needed for the application.
CHAPTER 3

SPECTROSCOPIC, MAGNETIC, AND CRYSTALLOGRAPHIC STUDIES OF

PLATINUM(DIIMINE)DITHIOLATE ELECTRON DONORS WITH

Π-CONJUGATED ORGANIC ACCEPTORS

3.1 Introduction

The idea of decreasing proximity producing a reduction of energy needed for electronic transfer between neighboring molecular structures should be understood fairly intuitively. The energy needed for a charge, either electron or hole, to transfer from one carrier to the next decreases as the physical distance decreases. Analogous to the energy needed for a baseball to be thrown from the outfield to home plate decrease as the distance between players decrease. As shown in past chapters, the neighboring species involved in charge transfer (CT) were of similar or identical molecules where the origin of the charge transfer is of the π-orbital of dithiolate character and the terminal end of the CT was suspected to be the π*-orbital of the diimine. The focus of this chapter is a probing of interactions between alternating molecules of differing types. Specifically, the organometallic platinum(diimine)(dithiolate) and planar organic molecules typified by highly conjugated centers bordered by electron withdrawing substituents are of interest here. This type of organic material has shown to form super conducting states dependent on the segregated columnar packing arrangement. The assembly of many organometallic charge transfer complexes with organic electron acceptors has been studied both

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as segregated stacks\textsuperscript{28}, which produce superconducting materials, and integrated stacks,\textsuperscript{29} producing semiconducting binary materials.

While the platinum(diimine)dithiolate compound is considered a charge transfer complex alone due to its ambipolar nature, this attribute can further be exploited and tuned by integration with the electron accepting organic molecule.\textsuperscript{30} A summary of the two complementary donor and acceptor electronic properties follows. The platinum compound contains a diffuse electron occupied orbital centered on the metal atom and the sulfur atoms of the dithiolate moiety; lending this molecular orbital a propensity for the donation of electrons into unfilled orbitals. The planar organic molecules, highly conjugated in the center but as a result of electron withdrawing functional groups on the extremities, possess low-lying empty $\pi^*$-orbitals fain to accept electrons from transition metal complexes.\textsuperscript{31} The complementary nature of these electronic potentials compels the two compounds often to self-assemble in solution and form integrated stacks as solids. Such an assembly promotes low energy electronic transfers, much lower than either compound exhibits in isolation or dilute solution. In the solid state, integrated stacks form; allowing these binary materials semiconducting properties suitable for photovoltaic applications. Organometallic compounds containing organic ligands have gained much interest as sensitizers in photovoltaic cells on wide band gap semiconductors, specifically colloidal TiO$_2$.


Ruthenium (II) being the most prodigious of these, followed distantly by Pt(II), has widened the field of available electron donors available to materials scientists for pairings with acceptors in organic thin film photovoltaics. Several Pt(II) compounds are studied as representative of this class of chromophore and their aggregation, absorption, and electronic characteristics reported.

3.2. Experimental Section

3.2.1 Synthetic Details

3.2.1.1 Synthesis of 4,4’-dicarboxy-2,2’-bipyridine (dcbpy)

4,4’-Dimethyl-2,2’-bipyridine was added to concentrated sulfuric acid and stirred until the organic molecule was completely solvated. Potassium dichromate was ground to a fine powder added in small amounts with deionized water while the solution stirred in an ice/water bath to maintain a temperature of 70-80°C. The dark green solution was stirred for three hours then poured over ice and filtered. The pale yellow-green chalky solid was washed with water and dried under vacuum. The product was refluxed for 4 hours in concentrated nitric acid. This solution was cooled to room temperature and diluted with ice. The pale yellow solution was allowed to sit in a refrigerator at 5°C for one hour. A fine white powder was collected by filtration and washed with water and then acetone then diethyl ether. The solid was dried under vacuum.

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Further purification by recrystallization in pyridine yielded colorless crystalline flakes that were used in subsequent synthetic procedures.

3.2.1.2  Synthesis of 4,4'-dimethoxy-2,2'-bipyridine (dmecb) and Other Ester-substituted Bipyridine Ligands

4,4'-Dicarboxy-2,2'-bipyridine was dissolved in 20 mL of thionyl chloride and refluxed in an inert atmosphere for 2 hours. The volume of the yellow solution was reduced to dryness under gentle heating (50°C) and vacuum. The matte yellow solid was dried using these conditions for 24 hours.

A toluene-methanol solution was prepared in a separate flask containing an argon environment using degassed and dried solvent. This solution was cannulated into the flask containing the acyl chloride under vacuum. An inert atmosphere was reintroduced to the reaction flask and the mixture was refluxed for five hours then cooled to room temperature. The faint pink solution was added to 30mL of chloroform and washed with a saturated solution of sodium bicarbonate. The organic layer was then washed with a saturated solution of sodium chloride, dried with sodium sulfate, and filtered. The solution volume was evaporated using only reduced pressure at room temperature. The white powder was then recrystallized in pyridine and methanol for use in subsequent synthetic procedures.

3.2.1.3  Synthesis of Dichloro(4,4'-dimethoxyester-2,2'-bipyridine)platinum(II) and Other Platinum Diimine Dichlorides

K₂PtCl₄ was dissolved in deionized water and heated to 60°C and dmecb (an equimolar amount) was dissolved in acetone at 60°C. The two solutions were mixed and refluxed for 8 hrs at 60-70°C. The yellow-orange water insoluble product was collected on a filter and washed with diethyl ether then hexanes to remove unreacted ligand. The product was then dissolved in dry
and degassed dichloromethane and any insoluble material was removed by filtration. The solution was deep red to pale yellow depending on the concentration of the solution from high to low, respectively. A yellow-red compound was collected from the slow evaporation of dichloromethane.

3.2.1.4 Synthesis of Benzene-1,2-dithiolate(4,4'-dimethoxyester-2,2'-bipyridine)Platinum(II) and Other Platinum Diimine Dithiolates

Pt(dmecb)Cl₂ was dissolved in dry degassed dichloromethane under argon. 1,2-benzenedithiol was added to an amount of absolute ethanol to achieve a (1:1) ethanol:CH₂Cl₂ solution. KHCO₃ stirred in suspension, then the solution cannulated into the platinum diimine solution. A dark product formed almost immediately and the solution stirred under argon overnight. The solution volume was reduced and the addition of excess hexanes produced a dark precipitate. This was filtered under an inert atmosphere and washed with hexanes, diethyl ether and dried under vacuum for 24 hours. The compound was purified by filtration over a bed of activated alumina and eluted with dichloromethane. The eluted product was collected by evaporation of the solvent under reduced pressure and addition of excess hexanes. The product was washed and dried again by the procedure mentioned above.

3.2.1.5 Synthesis of 2,4,7-trinitro-9-fluorenone(TRNF) and 2,4,5,7-Tetranitrofluorenone(TENF)

These electron accepting materials were synthesized by published procedures and purified by chromatography.³⁴

3.2.2 Instrumentation

Electronic absorption measurements were collected on a PerkinElmer® Lambda™ 900

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double beam UV-Vis-NIR spectrophotometer. Solution samples were prepared in volumetric glassware using dry degassed solvents and then transferred to one millimeter, one centimeter or ten centimeter Supersil quartz cuvettes for electronic absorption characterization. The solid reflectance data were collected using the LabSphere integrating sphere accessory to the Lambda 900 spectrophotometer.

Infrared spectra for all compounds were recorded on a Nicolet 740 FT-IR spectrophotometer. Background pellet consists of 0.2000 g of FT-IR grade KBr (Fluka) and the sample pellet consists of approximately 1-2% sample, ground with KBr to equal 0.20 g.

Proton NMR was used to verify the purity of compounds in this study on a Varian VNMRS 500 MHz or 400 MHz spectrometer. Between 5-20 mg of compounds was dissolved in CDCl₃ or d⁶-DMSO depending on the best solubility or availability of the solvent and collected at least 265 scans and 1.0s relaxation delay in 5 mm NMR tubes (Wilmad). The spectra were referenced to the solvent peak (7.26 ppm for CDCl₃ or 2.50 ppm for d⁶-DMSO) without TMS. 2D ¹H NOESY (Nuclear Overhauser Effect Spectroscopy) spectra were acquired with 0.7 s mixing time, 1.0 s relaxation delay and 128 second dimension increments with 128 scans in each increment. The spectra were referenced to the solvent peaks for CDCl₃ (7.26 ppm).

3.3 Results and Observations

3.3.1 Pt(II) Donors with Nitrofluorenones

The following platinium chromophores where mixed in an 2:1 (D:A) molar combination to produce the following solid-state diffuse reflectance spectra and compared with the dilute solution data for the respective donor: Pt(dbbpy)tdt, Pt(dhepcb)bdt, Pt(disopcb)bdt, and Pt(dmecb)bdt. The comparison to both the solution and solid absorption spectra allows
discernment of the donor-acceptor charge transfer absorptions from those resulting from platinophilic intermolecular charge transfers and intra-molecular ligand-to-ligand charge transfers (LL’CT) and mixed-metal-ligand-to-ligand charge transfer (MMLLCT).

In addition to the apparently important absorption studies probed here, the magnetic properties of the binary adduct are reported. The magnetic susceptibility of the donor-acceptor complexes are an insight to the partial oxidation of the platinum donor as the photoexcited electron is transferred to the acceptor. All donor and acceptor molecules in this study are diamagnetic and predictably have no magnetic moment. The occurrence of magnetic moments in the binary adducts implicates the charge transfer between the donor and acceptor.

Nuclear magnetic resonance studies in concentrated solutions are also employed along with titration studies when self-assembly is suspected to occur in concentrated solutions. Often 2-D NOESY spectra reveal coupling between the protons of adjacent donor and acceptor molecules in solution. The intensity of this coupling is thought to increase as intermolecular distances decrease.

3.3.1.1 With 2,7-dinitro-9-fluorenone (DNF)

Combination of 2,7-dinitro-9-fluorenone with the representative platinum chromophores resulted in a blue shift in the overall absorption edge of the solid adduct compared to the donor compound alone (Figure 3.1). With one exception, Pt(dhepcb)bdt, where a small and perhaps insubstantial increase of the lowest energy absorptions suggest that some charge transfer of the binary complex is occurring close to the same energies as the intermolecular platinum-platinum absorption in the solid state (Figure 3.1a).
Figure 3.1: (a) UV/Vis absorption spectra for a dilute solution (~10^{-5} M) of Pt(dhepcb)bdt in CH₂Cl₂ compared with its solid diffuse reflectance and the solid diffuse reflectance of the Pt(dhepcb)bdt/DNF adduct (b) UV/Vis absorption spectra for a dilute solution (~10^{-5} M) of Pt(dmecb)bdt in CH₂Cl₂ compared with its solid diffuse reflectance and the solid diffuse reflectance of the Pt(dmecb)bdt/DNF adduct (c) UV/Vis absorption spectra for a dilute solution (~10^{-5} M) of Pt(disopcb)bdt in CH₂Cl₂ compared with its solid diffuse reflectance and the solid diffuse reflectance of the Pt(disopcb)bdt/DNF adduct

Other adducts formed with the DNF acceptor retard the intermolecular charge transfer between the HOMO of Pt(d)/π(S) and the LUMO π*(diimine) of neighboring chromophores. Also in the case of Pt(disopcb)bdt, there is significant loss of intensity in the intramolecular photoinduced
transfer as implied by the blue shift in absorption maxima from the dilute solution spectra. It can be assumed that DNF is capable and to some extent does form binary complexes with these platinum electron donating chromophores, but the electron accepting character of DNF is weaker than that of the platinum donors accepting character for itself. That is $\Delta E[HOMO(Pt(d)/\pi(S)) \rightarrow LUMO(\pi^*(\text{diimine}))] < \Delta E[HOMO(Pt(d)/\pi(S)) \rightarrow LUMO(\pi^*(\text{DNF}))].$

3.3.1.2 With 2,4,7-trinitro-9-fluorenone (TRNF)

Combination of 2,4,7-trinitro-9-fluorenone produced mixed results when compared to the solid absorption of the platinum donor alone. The trend that was observed from following spectra suggests increasing the steric bulk of the substituents attached to the diimine promote the emergence of a charge transfer band around 900 nm (Figure 3.2). In the compounds Pt(dbppy)tdt and Pt(dhepcb)bdt where the substituents are the donating tert-butyl and the weakly withdrawing heptanoic-ester respectively, there is a red shift in the absorption edge(Figure 3.2a,b). The steric bulk of the tert-butyl group on Pt(dbppy)tdt lies close to the donor-acceptor complex, thus accentuating the shoulder in the near IR region. The bulk of the heptanoic ester is more spread along the alkyl chain compared to tert-butyl, thus smoothing the appearance of the donor-acceptor charge transfer band. As steric bulk of the diimine substituents decrease this charge transfer dissipates and eventually the lack of size in these groups contributes to a detrimental effect on the main intermolecular charge transfer of the solid platinum compound alone(Figure 3.2c,d). The appearance of this near infrared absorption band suggests the electron accepting character of TRNF is superior to DNF. When compared to the intermolecular charge transfer of the platinum donor alone, the LUMO of the nitrofluorenone in the Pt $\rightarrow$ TRNF absorption is lower in energy with the limit being around 850 nm.
Figure 3.2: (a) UV/Vis absorption spectra for a dilute solution (~10^{-5} M) of Pt(dbbpy)tdt in CH_{2}Cl_{2} compared with its solid diffuse reflectance and the solid diffuse reflectance of the Pt(dbbpy)tdt/TRNF adduct (b) UV/Vis absorption spectra for a dilute solution (~10^{-5} M) of Pt(dhepcb)bdt in CH_{2}Cl_{2} compared with its solid diffuse reflectance and the solid diffuse reflectance of the Pt(dhepcb)bdt/TRNF adduct (c) UV/Vis absorption spectra for a dilute solution (~10^{-5} M) of Pt(dmecb)bdt in CH_{2}Cl_{2} compared with its solid diffuse reflectance and the solid diffuse reflectance of the Pt(dmecb)bdt/TRNF adduct (d) UV/Vis absorption spectra for a dilute solution (~10^{-5} M) of Pt(disopcb)bdt in CH_{2}Cl_{2} compared with its solid diffuse reflectance and the solid diffuse reflectance of the Pt(disopcb)bdt/TRNF adduct
That is, \( \Delta E[\text{HOMO}_{\text{Pt}(d)/\pi} \rightarrow \text{LUMO}_{\pi^*\text{(TRNF)}}] = \sim850 \text{ nm} \). Beyond this limit, the inclusion of TRNF has a detrimental effect on the latent intermolecular charge transfer of the solid state platinum donor.

![X-ray crystal structure of Pt(dbbpy)(tdt)/TRNF illustrating the one-dimensional stacking motif and interactions between the donor and acceptor molecules. Hydrogen atoms have been omitted for the sake of clarity.](image)

Figure 3.3 shows a Pt-trinitrofluorenone (TRNF) distance of 3.405 Å alternating with 3.436 Å in the neighboring dimer. This is well within the range for \( \pi \)-interactions between the Pt(d)/S(p) hybrid orbital and the \( \pi \) system of the aromatic fluorenone core. The metal to organic distance was taken because the two planes cast from the molecules are slightly askew and are not parallel. These distances are similar to what has been found in dimers of the Pt complexes alone (\( \sim3.45 \)

Å) but the red shifted absorption can be attributed to the electron affinity of the nitrofluorenone.\textsuperscript{36}

Figure 3.4: X-ray crystal structure of Pt(dbbpy)(tdt)/TRNF illustrating slipped stacking caused by steric repulsions between the tert-butyl groups of the diimine ligand of the donor and the nitro heavy side of the acceptor. Hydrogens have been omitted for the sake of clarity.

In figure 3.4, the Pt dye is shown slipped from the center of the organic TRNF toward the side of the acceptor with less steric bulk so as not to interact with the t-butyl substituents on the diimine. The trend shown in figure 3.2 with the bulkier substituents on the 4,4' carbons of the bipyridine rings interacting favorably to produce strong donor-acceptor charge transfers in the near IR region may be the result of this slipped stacking orientation caused by steric repulsions between the two molecules of the dimer. This “slipped-stacking” was discovered to be a common motif when Pt(dbbpy)tdt was combined with other nitrofluorenones that produced strong near IR DACT absorptions.\textsuperscript{37}

Magnetic susceptibility studies also provide evidence of partial oxidation of the donor and


\textsuperscript{37} Browning, C.; Hudson, J.M.; Reinheimer, E.W.; Kuo, F.-L.; McDougald, R.N. Rabaa, H.; Pan, H.; Shepherd, N.; Basca, J.; Wang, X.; Dunbar, K.D.; Shepherd, N.D.; Omary, M.A. \textit{submitted}
partial reduction of the acceptor through the DACT. Magnetic moments of 1.07 and 1.05 Bohr magnetons were measured in the Pt(dbppy)tdt/TRNF and Pt(dhepcb)bdt/TRNF adducts respectively due to the charge transfer resulting in formally unpaired electrons rather than paramagnetism.

The $^1$H NMR spectrum for the aromatic region of a saturated solution ($\sim 10^{-2}$ M total) of a 1:1 molar ratio of Pt(dbppy)tdt and TRNF is depicted in Figure 3.5 and compared with the stock solutions the mixture was prepared from. The aromatic protons should be the most sensitive to small changes in the electronic environment due to intermolecular charge transfer in solution. The data reveal a significant alteration of the electronic environment as all the aromatic peaks are shifted up-field relative to the free components. As well, there seems to be significant peak broadening indicating unpaired electrons, which supports the contention that the DACT process occurs in solution as well as the solid state. These data represent rare structural evidence of D:A intermolecular interactions involving closed-shell metal complexes in solution, a situation first reported by Burini et al. for trinuclear d$^{10}$ complexes.$^{38}$

Two-dimensional homonuclear proton nuclear overhauser effect spectroscopy (NOESY) NMR spectra were collected for the Pt(dbppy)tdt/TRNF solution presented in Figure 3.6. These spectra reveal coupling between the aromatic protons of the dithiolate moiety of the platinum donor molecule at 7.47 ppm and the aromatic proton at the 3-positon on the nitrofluorenone acceptor at 8.92 ppm (Figure 3.6). This coupling correlates with the stacking orientation found in the solid crystal state (Figures 3.3, 3.4).

Figure 3.5: $^1$H NMR spectra for TRNF (acceptor, bottom), Pt(dbppy)(tdt) (donor, middle), and the mixture of the two in CDCl$_3$ (top)

Figure 3.6: 2D $^1$H-NOESY NMR spectra for a 0.01 M Pt(dbppy)tdt/TRNF solution in CDCl$_3$. The 1D spectra parallel to the axis are from the same solution.
The absorption spectra for a mole fraction variation of Pt(dbbpy)(tdt) with TRNF are presented as Figure 3.7. The growth of a new absorption feature in the 825 nm region becomes more intense with increasing concentration of TRNF and is very strong in the reflectance spectrum of the solids. The solution absorption features at 800 and 825 nm were fit using the method of Benesi and Hildebrand (Figure 3.7b,d).\textsuperscript{39} Job plots are also shown to illustrate the dominance of the 1:1 association ratio (Figure 3.7c,e). The equilibrium constant is approximately 90 M\textsuperscript{-1} for D+A $\rightleftharpoons$ DA and the extinction coefficient is 521 and 564 M\textsuperscript{-1} cm\textsuperscript{-1} at 800 and 825 nm, respectively. TRNF is a slightly stronger acceptor compared to DNF but weaker than TENF. The new band at 825 nm is attributed to the DACT of the complex Pt(dbbpy)(tdt)/TRNF in solution.

3.3.1.3 With 2,4,5,7-tetranitro-9-fluorenone (TENF)

The complexation of 2,4,5,7-tetranitro-9-fluorenone with the selected platinum donors follows the same trend as TRNF in that there is a predilection for red shifted absorption edges as electron withdrawing strength of substituents on the diimine ligand decreases. Moreover, the addition of another nitro group to the nitrofluorenone establishes the trend of increasing electron affinity of the nitrofluorenone as more nitro groups are added to alternating carbons around the flank of the aromatic core (Figure 3.8). Only in the adduct employing the most electron withdrawing diimine moiety, Pt(dmecb)bdt, does the adduct exhibit a blue shifted absorption maxima. The development of the near infrared charge transfer band around 1000 nm occurs in all adducts in the solid state, but only to a minor amount in the donor mentioned above.

Figure 3.7: (a) Absorption spectra showing DACT band growth during the titration experiment for [Pt(dbbpy)(tdt)] and [TRNF] in CH2Cl2 using a 10-cm cuvette at room temperature. [Pt(dbbpy)tdt] = 5x10^{-4} (b) Benesi-Hildebrand plot of the spectral changes at 800 nm. (c) Job plot for the spectral changes at 800 nm. [Pt(dbbpy)tdt + TRNF]= 5x10^{-4} (d) Benesi-Hildebrand plot of the spectral changes at 825 nm. (e) Job plot for the spectral changes at 825 nm. [Pt(dbbpy)tdt + TRNF] = 5x10^{-4}
Taken at face value, the Pt(dmecb)bdt complexes lack of favorable increases in near IR DACT (Figures 3.1b, 3.2c, 3.8c) and the physical position of the dithiolate HOMO above the conjugated electron poor center of the acceptor, I suspect there is competition between DACT and the intrinsic charge transfer of the donor. The electron withdrawing power of the dimethoxyesterbipyridyl moiety to stabilize the LUMO may be too strong to allow considerable intermolecular charge transfer to the organic acceptor that is observed in dyes with less significant electron withdrawing character.

Evidence of partial oxidation of the donor and partial reduction of the acceptor through the DACT was measured with magnetic susceptibility measurements. Magnetic moments of 1.21, 1.11, 0.67, and 0.99 Bohr magnetons were measured in the Pt(dbbpy)tdt/TENF, Pt(dhepcb)bdt/TENF, Pt(dmecb)bdt/TENF, and Pt(disopcb)bdt/TENF adducts respectively due to the charge transfer resulting in formally unpaired electrons rather than paramagnetism. The Pt(dmecb)bdt/TENF adduct which shows no DACT absorption in Figure 3.8c also was measured to be least affected by the magnetic field implying a lack of unpaired electrons due to little if no oxidation of the donor or reduction of the acceptor.

3.3.2 Pt(II) Donors with Rylene-diimide Derivatives

Perylene-diimide (PDI) is a highly conjugated planar organic molecule of an intense red color and the same is true with the derivatives used in this study. Theoretical models using density functionals have explored the tuning of this class of molecule at both the nitrogen of the imide groups and within the hydrocarbon core.40

Figure 3.8: (a) UV/Vis absorption spectra for a dilute solution (~10^{-5} M) of Pt(dbbpy)tdt in CH_{2}Cl_{2} compared with its solid diffuse reflectance and the solid diffuse reflectance of the Pt(dbbpy)tdt/TENF adduct (b) UV/Vis absorption spectra for a dilute solution (~10^{-5} M) of Pt(dhepcb)bdt in CH_{2}Cl_{2} compared with its solid diffuse reflectance and the solid diffuse reflectance of the Pt(dhepcb)bdt/TENF adduct (c) UV/Vis absorption spectra for a dilute solution (~10^{-5} M) of Pt(dmecb)bdt in CH_{2}Cl_{2} compared with its solid diffuse reflectance and the solid diffuse reflectance of the Pt(dmecb)bdt/TENF adduct (d) UV/Vis absorption spectra for a dilute solution (~10^{-5} M) of Pt(disopcb)bdt in CH_{2}Cl_{2} compared with its solid diffuse reflectance and the solid diffuse reflectance of the Pt(disopcb)bdt/TENF adduct
Modifications to the PDI base are shown to have two effects depending on the location. Substituents added to the hydrocarbon core at 1, 6, 7, and 12 positions will affect the optical and electronic properties. Substituents added to the imide nitrogen have little effect on these properties at the molecular level but affect the solubility and aggregation.\textsuperscript{41} Such derivatives of this class have highly favorable characteristics for use as n-type semiconductors in thin-film organic photovoltaics due to their air, thermal, chemical and weather stability and strong electron accepting susceptibility.\textsuperscript{42}

3.3.2.1 With PDI8-CN2 (A Perylene-diimide Derivative)

Complexation with the perylene-diimine (PDI) derivative, N,N'-bis(n-octyl)-1,7-dicyanoperylene-3,4:9,10-bis-(dicarboximide) (PDI8-CN2), in all cases modifies the absorption spectra of the adduct as compared to the solid-state absorption of the donor alone. First and most apparently is the manifestation of may be several new charge transfer bands in the near infrared region. In the spectra for the acceptor with Pt(dbbpy)tdt at least two new peaks can be discerned, one at around 810 nm and another near 1150 nm (Figure 3.9). While less apparent in other adducts of the platinum dyes and PDI8-CN2, the broad extension of the spectra into the NIR would suggest that more than one charge transfer is responsible for this egress. The second modification resulting from the formation of the binary adduct is the depression in intermolecular charge transfer resulting in a significant blue shift in this absorption. PDI8-CN2 is reported to have LUMO 4.3eV below vacuum which puts its reduction potential near that of TRNF. The first and shortest new absorption peak to arise upon complexation can be seen

\textsuperscript{41} Huang, C.; Barlow, S.; Marder, S. M. J. Org. Chem., 2011, 76, 2386

\textsuperscript{42} Wurthner, F. Chem. Commun. 2004, 14, 1564.
approximately in the same region of the long-wavelength visible and near IR energies as does the
only DACT for the corresponding dye with TRNF. The second peak clearly seen in figure 3.9a
should be attributed to a second reduction to a LUMO+1 on the PDI8-CN2. This peak is not as
clearly seen in the other adduct spectra, but extrapolation of this trend may explain the
difference in behavior when the dimethoxyester and diisopropoxyester dyes complex with PDI8-
CN2 verses TRNF (Figures 3.9c and 3.9d vs. 3.2c and 3.2d). Another difference notable is that
these new charge transfers do not seem to be additive to the overall integration of the spectra
as seen in TRNF, but roughly distributive. The major CT band associated with the donors in both
the solid and dilute solution decrease upon association with PDI8-CN2 implying there is a
competitive effect for reduction between the diimine ligand and the organic acceptor. While a
decrease in absorption generally would be seen as disadvantageous to the goals of this project
to absorb light with high extinction coefficient materials, the presence of an acceptor easily
reduced lengthen the lifetime of a device by protecting the chromophore from photooxidation.

3.3.2.2 With P(NDI2OD-T2) (A Naphthalene-diimide Derivative)

The naphthalene-diimide (NDI) derivative, poly{[N,N’bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5’-(2,2’-bithiophene)}, P(NDI2OD-T2) contains an
electron poor naphthalene-diimide core and contains a highly conjugated dithiophene polymeric
backbone.43 With an optical band gap of about 1.45 eV, corresponding to a absorption cutoff
around 855nm, and a LUMO reported to as approximately 4.0 eV below vacuum,44 this n-type

material exhibits one of the best reduction potentials for a polymer material developed in recent years.

Figure 3.9: (a) UV/Vis absorption spectra for a dilute solution (~10^-5 M) of Pt(dbbpy)tdt in CH2Cl2 compared with its solid diffuse reflectance and the solid diffuse reflectance of the Pt(dbbpy)tdt/PDI8-CN2 adduct and the PDI8-CN2 solid alone (b) Solid diffuse reflectance of Pt(dhepcb)bdt , the Pt(dhepcb)bdt/PDI8-CN2 adduct, and PDI8-CN2 solid alone (c) UV/Vis absorption spectra for a dilute solution (~10^-5 M) of Pt(dmecb)bdt in CH2Cl2 compared with its solid diffuse reflectance, the solid diffuse reflectance of the Pt(dmecb)bdt/PDI8-CN2 adduct,
and PDI8-CN2 solid alone (d) Solid diffuse reflectance of Pt(disopcb)bdt, the Pt(disopcb)bdt/PDI8-CN2 adduct, and PDI8-CN2 solid alone

Combined with its virtually complete absorption of the visible region, the marriage of this promising electron carrier with the “dark absorbers” was a hopefully to have ambitious but ultimately disappointing. In none of the mixtures formed did I observe the emergence of new charge transfer bands (Figure 3.10). The NDI derivative with the platinum dyes behaves much like the DNF here. The P(NDI2OD-T2) and DNF with their similar reduction potentials, both approximately 4.0 eV, neither is strongly electron deficient enough at their cores to compete with the intramolecular charge transfer inherent in the platinum dye. This disappointment illustrates that as tempting as low-energy absorptions of the acceptor may be, the position of the LUMO in the acceptor is of greater importance.

3.4 Toward a Donor-Acceptor Device

The following is a discussion on how the materials in this study and those with similar electrochemical properties should be paired to build a photovoltaic device capable of exothermic electron transfer. This section focuses on the arrangement and overlap of energy levels and does not cover other topics relevant and certainty important to the working of a photovoltaic cell, such as but not limited to, carrier mobility, lifetime of the excited state in the chromophore, photooxidation, diffusion length, and current leakage. For consistency, energy levels presented here will be based on comparison to the vacuum level, or that of a free electron, rather than to the reference electrode used to actually measure the values that the energy levels can be calculated from.
Figure 3.10: (a) UV/Vis absorption spectra for a dilute solution (~$10^{-5}$ M) of Pt(dbbpy)tdt in CH$_2$Cl$_2$ compared with its solid diffuse reflectance and the solid diffuse reflectance of the Pt(dbbpy)tdt/P(NDI2OD-T2) adduct and the P(NDI2OD-T2) solid alone (b) Solid diffuse reflectance of Pt(dhepcb)bdt , the Pt(dhepcb)bdt/ P(NDI2OD-T2) adduct, and P(NDI2OD-T2) solid alone (c) UV/Vis absorption spectra for a dilute solution (~$10^{-5}$ M) of Pt(dmecb)bdt in CH$_2$Cl$_2$ compared with its solid diffuse reflectance, the solid diffuse reflectance of the Pt(dmecb)bdt/ P(NDI2OD-T2) adduct, and P(NDI2OD-T2) solid alone (d) Solid diffuse reflectance of Pt(disopcb)bdt , the Pt(disopcb)bdt/ P(NDI2OD-T2) adduct, and P(NDI2OD-T2) solid alone.

The two important quantities for the electron and hole transport materials in an organic photovoltaic (OPV) cell in which this discussion is based upon are the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the
electronically excited molecule. The energy of the HOMO can be estimated from the ionization potential (IP), defined as the amount of energy released when an electron is removed from a neutral molecule to produce a cation. The IP be measured in solution through cyclic voltammetry using a reference electrode, although here the complications of the various possible references are ignored and all energies are discussed on an absolute scale. The energy level of the LUMO in the excited molecule can be estimated from the addition of the energy gap ($E_g$) measured by absorption and/or emission spectroscopy from the HOMO energy. (Figure 3.11)

![Energy Levels Diagram](image)

**Figure 3.11: Illustration of energy levels in relation to the energy of a free electron**

The relative levels of these energies for the donor and acceptor needs to be as follows. The ionization energy of the donor should be less than that of the acceptor and the electron affinity of the acceptor needs to be greater than that of the donor. By definition, the donor must be the partner of the donor-acceptor pair that most easily gives up an electron and the acceptor, the most likely to receive an electron. Therefore, the HOMO(donor) < HOMO(acceptor) and LUMO (acceptor) > LUMO (donor). (Figure 3.12)
A second consideration regarding energy levels is the work function of the electrodes that facilitate the transport electrons in and out of the photovoltaic cell. OPV cells require at least one electrode that has a sufficiently low enough work function to either collect or inject electrons into the cell. Alkaline-earth metals, such as Mg and Ca, can be used or metals coated with alkali metals, such as Li or Cs. Of course one electrode, typically the anode, needs to be transparent to light to allow photons to reach the absorbing layer. Generally this is a indium-tin oxide (ITO) coated glass substrate which leaves only the material of the cathode with much variation for its work function energy work function. The work function of ITO can be manipulated by functionalization or with coatings applied between the active layer and the anode, but is beyond the scope of this discussion.
The discussion so far has been focused on the qualitative treatment of relative energy levels in the donor-acceptor pair. However, for a photovoltaic to be useful there is the concern that the maximum voltage is of the magnitude to be relevant to the needs of. To maximize voltage from available energy gained when a photon is absorbed by the donor, there needs to be sufficient orbital overlap between the donor and acceptor. The maximum, or open-circuit voltage, is directly proportional to the difference between the HOMO of the donor and the LUMO of the acceptor. Since any difference in the LUMO levels of donor and acceptor is lost from the initial photon energy absorption, it is favorable for the LUMO of the acceptor to be slightly below the LUMO of the donor to convert the maximum amount of light energy into current. However the LUMO of the acceptor cannot be so close in energy to the donor that charge transfer is not spurred to take place before the excited electron donor relaxes to its ground state.

Table 3.1 lists various donor and acceptor materials for examples of HOMO and LUMO levels. From this table, appropriate acceptors can be paired with the square-planar platinum chromophores that have been the main focus of this dissertation.
<table>
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<th>Acceptor Material</th>
<th>LUMO (V)</th>
<th>$E_{\text{Gap}}$ (V)</th>
<th>Donor Material</th>
<th>LUMO (V)</th>
<th>HOMO (V)</th>
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4.1 Introduction

The passage from a potential technology to viable application for wide spread usage is unclear for many great ideas until a spark of light released by an aperture of success in a looming cave of uncertainty. The dawn of success of the Dye-Sensitized Solar Cell (DSSC) technology that saw that technology grow in 1991 to stand aside the heroes of photovoltaics was in the treatment of the dye as a thin film. The potential of DSSC had lain hidden since 1968,\(^45\) studied but unexploited until rising in 1993 through the present\(^46\) to the pinnacle of its class reported by Gratzel\(^47\) as \(\text{cis-bis(dithiocyanato)}-\text{N,N-bis(2,2'}\text{-bipyridyl-4,4'}\text{-dicarboxylate)}-\text{Ruthenium(II)}\) commonly known by the more phonetically palatable name “N3”. Variations and convolutions of the “N3” dye are ubiquitous in the literature of DSSCs.\(^48\) In spite of the branching arboreal growth of adaptation on Gratzel’s theme, the evolution of a progeny that could outperform the

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original in the arena of efficiency never materialized. For two decades ruthenium based dyes have been the shade and shine of organometallic photovoltaics until several research groups (e.g., Sugihara, Durrant, and Omary)\(^49\) were inspired by the rich spectroscopic properties of platinum(diimine)(dithiolate) complexes as reported most notably by the Eisenberg group.\(^50\) The tuning and absorption has been discussed at length in preceding chapters of this document. Similarities do exist among group 10 transition metals in regard to their chemistry to form analogous (diimine)dithiolate square planar complexes. However, the focus herein will be upon Pt(II) complexes because of their superior stability. The Ni(II) complexes have somewhat similar spectroscopic and electrochemical properties to Pt(II) analogues but are synthetically troubling, whereas Pd(II) congeners have been shown to be sub-standard in terms of both spectroelectrochemical properties and DSSC performance.\(^51\)

In this chapter, focus will be upon screening Pt(diimine)(dithiolate) complexes for solid-state organic photovoltaic devices (OPVs), which have yet to be investigated for this class of materials. The approach will entail fabrication of thin films, both by thermal evaporation of pure solid powders and by solution casting via spin coating from saturated solutions, characterization


of the resulting thin films spectroscopically, and finally evaluating their photoconductivity and proof-of-concept OPV devices.

4.2 Experimental Section

4.2.1 Device Fabrication

The device work in this chapter employed the help of several laboratories, each using slightly different methods and equipment for the deposition. These include the Sheppard group (University of North Texas Department of Materials Science and Engineering), the Youngblood group (University of North Texas Department of Chemistry), the Forrest group at the University of Michigan, and the So group at the University of Florida. Thermal evaporation attempts have succeeded during material purification by sublimation by the author in the Omary laboratory as well as for the proof-of-concept photoconductivity measurements of thin films in the Shepherd laboratory (Figure 4.1a), the latter adopting deposition conditions published earlier for a phosphorescent Pt(II) complex utilized in OLED devices.\textsuperscript{52} However, similar thermal evaporation attempts have failed with the in-house equipment in both the So and Forrest laboratories citing the very low vapor pressure of the material and its relatively poor thermal stability compared to other more conventional organic electronics materials typically sublimed into thin films by these groups. Therefore, the description in the remainder of this section describes the method of solution casting via spin coating done in collaboration with the Youngblood group (Figure 4.1d).

For spin-coated thin film studies in this chapter fabricated in the lab of the Youngblood group (Figure 4.1d), solar cell slides were prepared from 1 cm\textsuperscript{2} cut Fluorine Tin Oxide (FTO) tiles.

A non-conductive band was etched using Zn powder and 4M HCl. A band cut out of a chemically resistant tape used as a resist to mask the conductive layer of FTO and the acid was added drop wise to the powdered Zinc that filled the cut out area. The tape was peeled away and cleaned with deionized water, acetone, and absolute ethanol facilitated by a sonicator in series. The cleaned slides were then dried in a vacuum oven.

A layer of poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonate) (PEDOT:PSS) was deposited by spin coating 0.4mL filtered solution of PEDOT:PSS to deionized water (16:1 ratio by volume). The volume used in this study was adequate to cover a 1 cm² slide by gently pulling the edges of the dropped solution to cover the slide. The slide was rotated under a nitrogen stream at 300rpm for 3 minutes. At the end of the spinning a dark translucent layer was visible and from previous calibrations using this method assumed to be 70 nm. The nonconductive band was cleaned with deionized water and annealed at 110°C under vacuum for two hours to remove lingering water molecules. Solutions of the photoactive layer (P3HT/PCBM/Pt[diimine]dithiolate) were prepared in chlorobenzene and sonicated for 15 minutes to insure maximum solubility. The solutions were filtered and deposited by spin coating. 0.3mL of the filtered solutions was sufficient to cover the active area of the slide. The nonconductive band was cleaned with chlorobenzene, and directly annealed in at 120°C for fifteen minutes.

A 50 nm aluminum electrode was deposited from a thermally evaporated source. In some cases a protective glass cover slide was placed over the non-transparent electrode for protection. In the case that slides had surface area too small to place the protective glass over the opaque electrode, IPCE and I-V measurements were conducted directly after removal from the glove box where the deposition occurred. Typically any analysis of this type would be executed within
hours after the final device was complete, but special care was taken for these more vulnerable exposed cells to minimize oxidation and wear on the thin electrode. Such oxidation produces a less conductive contact leading to reduced photoelectric response and eventual failure of the cell from short circuit behavior.

![Figure 4.1: (a) Shepherd Lab Cell (b) So Lab P3HT Cell (c) So Lab MDMO-PPV Cell (d) Youngblood Lab Cell](image)

4.2.2 Synthetic Details

4.2.2.1 Synthesis of 1-(3-(Methoxycarbonyl)propyl)-1-phenyl[6,6]-C61 (PC60BM)

4-benzoylbutyric acid and p-toluenesulfonyl hydrazide were purchased from Sigma-Aldrich and used without any further procedures. [60]fullerene (C60) was acquired from the Youngblood lab and used without any further purification.

4.2.2.2 Synthesis of Methyl 4-benzoylbutrate

1.49 grams of 4-benzoylbutyric acid was suspended in ~10mL dry MeOH (0°C). 0.65 mL of acetyl chloride was added dropwise, stirred, and allowed to come to RT. Reaction mixture was reduced to half volume and diluted with 75 mL of CH₂Cl₂. The organic layer was washed with
NaHCO₃, brine, and dried with MgSO₄. 1.4 g was collected Methyl 4-benzyloxybutrate as a tan clear liquid. (IR: ester C=O 1730 cm⁻¹, C-O 1210 cm⁻¹)

4.2.2.3 Synthesis of Methyl 4-benzyloxybutrate p-tosylhydrazone

1.12 g (5.4 mmol) of Methyl 4-benzyloxybutrate, 1.16 g (6.2 mmol) of p-toluenesulfonyl hydrazide, and 5 mL of dry MeOH where refluxed for 5 hours and allowed to come to room temperature. The reaction vessel was cooled to -15°C in a dry ice/ethylene glycol bath and then filtered and rinsed with dry MeOH in a schlenk flask. The white powder was dried under vacuum over the weekend. 1.44 g of dried methyl 4-benzyloxybutrate p-tosylhydrazone (FW378) was collected after drying under vacuum over the weekend (70% yield)

4.2.2.4 Synthesis of PCBM

1.00 g of Methyl 4-benzyloxybutrate-tosylhydrazone was stirred at 80°C with NaOMe for 15 minutes in 20 mL dry pyridine. 0.961 g of C₆₀ was dissolved in 75 mL 1,2-dichlorobenzene and added to the heated solution and refluxed at 70°C for 48 hours. The reaction progress was monitored by High-Performace Liquid Chromatography (HPLC) every 12 hours until a satisfactory yield could be estimated. The volume of the reaction was reduced to 30 mL and loaded onto silica that had been pre-eluted with 200 mL of chlorobenzene. Separation of C₆₀ from the PCBM precursor ((6)-1-(3-(methoxycarbonyl)propyl)-(5)-1-phenyl[5,6]-C₆₁) was achieved with elution with 300 mL of chlorobenzene and switching to toluene to collect the final fractions. The PCBM precursor was refluxed in 1,2-dichlorobenzene for 5 hours then the volume was reduced to 5 mL and split between two centrifuge tubes containing 40 mL of dry methanol. A brown precipitate formed and the tubes were centrifuged. The clear supernate was removed and the brown precipitate was mixed again with 40 mL of dry methanol, sonicated for three minutes, and
centrifuged. The methanol wash, sonication, and centrifuge procedure was repeated three times before the brown solid was collected by gravity filtration and dried overnight under vacuum at 50°C.

4.3 Results and Observations

This chapter contains data on thin films and OPV devices shown in Figure 4.1. Figure 4.2 illustrates the molecular structure for the materials used for these devices.

Figure 4.2: Chemical structures of materials used in this study
Polymer blends with the P3HT acting as the donor and PCBM fullerenes acting as acceptor are one of the most widely studied couples in the literature of organic photovoltaic and were adopted as a good starting point for the investigation of platinum dyes effects on long wavelength/low energy absorptions in light harvesting devices. P3HT has an absorption edge of ~650 nm, thus leaving an optimal window for the platinum dyes effects to be observed in the longer wavelengths of the visible spectrum (>650 nm). P3HT forms an amorphous matrix of microcrystalline domains with \( \pi \)-stacking thiophene units along the polymer chains and interlocking alkyl side groups. The spectra of pure P3HT films have three main features, two high energy absorptions due to \( \pi-\pi^* \) interactions in the thiophene moiety and a long wavelength shoulder arising from the interlocking alkyl groups.\(^{53}\) The most intense absorptions of the P3HT film are greatly diminished by increasing the concentration of PCBM in the film as the polymer chains become more disordered from the inclusion of the fullerene.\(^{54}\)

MDMO-PPV is a well characterized \( \pi \)-conjugated polymer of the MEV-PPV class and has been used through the literature as an electron donating substituent of organic polymer:PCBM bulk heterojunction blends. Having an ionization potential of 5.33 eV and electron affinity of 2.97 eV, the absorption cut-off in the visible range occurs at shorter wavelengths than 600 nm allowing the profile of the platinum dyes to be observed at lower energies.\(^{55}\)


The poor solubility of C$_{60}$ and C$_{70}$ in most organic solvents limits their use as the electron acceptor in thin film devices. The unmodified fullerenes tendency to crystallize during film formation is a detriment to high concentration blends of these materials. It has been repeatedly shown that inclusion of fullerene derivative in polymer photovoltaic devices increase the efficiency compared to the polymer alone.$^{56}$ The presence of these compounds in this research provides a baseline comparison to move away from to compare the effects of the platinum dyes on the overall device performance.

The ionomeric copolymer PEDOT:PSS was selected to be included for its well-documented conductivity boosting property due to its ability to planarize the oxide surface thus preventing short circuits and act as a hole transport layer. The use of PEDOT:PSS in cells containing fullerenes increases the open-current voltage leading to significant improvement in efficiency.$^{57}$ Conveniently water soluble, PEDOT:PSS is easily deposited through solution casting methods and annealed with mild heat in no special environmental conditions and has excellent transparency in the visible range.$^{58}$

The metal-organic compounds Pt(dmecb)bdt and Pt(dhepcb)bdt have been discussed in Chapter 2 of this dissertation and readers are referred to that chapter for their synthesis, structural, electronic and photophysical properties.


4.3.1 Pt(dmecb)bdt as a Single Layer Schottky Diode

After encouraging results from the spectroscopic studies of the chromophores coordinated with ester adorned bipyridine ligands, the following question was posed: If close stacking of the square-planar molecules occurred in solution and amorphous powder samples, would the same properties carry over to thin films of less than 200 nanometers. The ester containing compound of the lowest molecular weight, Pt(dmecb)bdt (FW 607.57), was selected to represent attempts as it showed by thermogravametric analysis to have a good thermal stability over a wide range of temperatures (Figure 4.3). The gradual decline in weight percent of the original mass over the temperatures 200-300°C provides evidence of sublimation of the material before decomposition of the organic ligands. This suggests Pt(dmecb)bdt would be the easiest to sublime and self-organize compared to the esters containing branched or long chain aliphatic moieties due to their increased molecular mass.

Figure 4.3: Thermogravametric analysis of Pt(dmecb)bdt in an inert atmosphere
Figure 4.4: (a) Current vs. voltage plot of the Shepherd Lab Cell (b) Current vs. wavelength of the Shepherd Lab Cell (c) Diffuse reflectance of Pt(dmecb)bdt and transmission of a drop-cast film of Pt(dmecb)bdt from a saturated dichloromethane solution

The first successful attempts in Dr. Sheppard’s lab are summarized in figure 4.4. After some refinement of the procedure a 200 nm film was deposited on ITO as a single layer. The
data shows at both long (880 nm) and short (260 nm) wavelengths that the current increases as
the potential voltage increases. Also when the potential is fixed, the current remains relatively
stable regardless of the wavelength of light irradiating the cell. A promising result for this type
of device expected to still act as a “black absorber” in the thin film architecture and deliver a
current at both ends of its action spectrum. The current tested over the visible spectrum
matches remarkably well with the diffuse reflectance of the material in Figure 4.2c despite
showing a decrease in absorbance around 520 nm as a thin film. This deviation between film
absorbance and current is probably due to a leveling effect of charge separation in which
increased absorption has a limited effect on current at wavelengths greater than 550 nm. At
these energies corresponding to longer wavelengths, the IPCE is reduced compared to the valley
centered around 520 nm.

4.3.2 Pt(dmecb)bdt in a MDMO-PPV/PCBM Matrix

Further depositions were done at the University of Florida in Dr. Frankie So’s laboratory
using the methoxyester bipyridine chromophores. Thermal deposition of the Pt(dmecb)bdt was
reported to be a failure by the So group. Pt(dmecb)bdt is still a good candidate for solution
processing and was mixed and deposited with a mixture of MDMO-PPV, and modified fullerene,
PC70BM. Ratios by weight were 1:4:0.4 [MDMO-PPV:PC70BM:Pt(dmecb)bdt] with the platinum
compound acting as a dilute sensitizer in the polymer/fullerene blend. The deposited film was
placed over an annealed layer of PEDOT:PSS on ITO. The current-voltage and IPCE results are
presented in Figure 4.5.
The effective cell area for these experiments was 1 mm$^2$, an advantage when testing these properties because the compact cell size compared to subsequent studies conducted as a collaborative effort between the Youngblood and Omary groups with a cell surface area of 1.1 cm$^2$. The surface area is directly proportional of the quantity and magnitude of any imperfections or aberrations resulting from the process. The short circuit voltage ($J_{SC}$) was determined to be 2.08 mA/cm$^2$ and the open current voltage ($V_{OC}$) was 0.61 V. From this the fill factor for the cells made were 34% and the efficiency 0.43%. Unfortunately, the stacking of platinum chromophores that contribute to the low-energy absorptions is not preserved in the
polymer/fullerene matrix and efficient charge separation declines rapidly at wavelengths longer than 550nm.

4.3.3 Pt(dmeceb)bdt in a P3HT/PCBM matrix

Further solution depositions were done at the University of Florida in Dr. Frankie So’s laboratory using the methoxyester bipyridine chromophores with a mixture of the widely studied thiophene, P3HT, and modified fullerene, PC70BM. Ratios by weight were 10:10:2 with the platinum compound acting as a dilute sensitizer in the polymer/fullerene blend. The deposited film was placed over an annealed layer of PEDOT:PSS on ITO. The current-voltage and IPCE results are presented in Figure 4.6.

![Image](image_url)

Figure 4.6: (a) Current vs. voltage of So Lab P3HT Cell. (b) Internal Photon to Current Efficency (IPCE) vs wavelength over the visible spectrum for the So Lab P3HT Cell (shown)

The effective cell area for these experiments was 1 mm², an advantage when testing these properties because the compact cell size compared to subsequent studies (1.1 cm²). The surface area is directly proportional of the quantity and magnitude of any imperfections or aberrations resulting from the process. The short circuit voltage ($J_{SC}$) was determined to be 8.36 mA/cm² and the open current voltage ($V_{OC}$) was 0.63 V. From this the fill factor for the cells made were 29.50% and the efficiency 1.55%. Unfortunately, the stacking of platinum chromophores that contribute
to the low energy absorptions is not preserved in the thiophene polymer matrix and efficient charge separation declines rapidly at wavelengths longer than 550 nm. However unlike the So lab MDMO-PPV cell, the So Lab P3HT cell retains an interesting absorption feature around 690 nm attributed to the sensitization due to the platinum dye.

4.4.4 Pt(dhepcb)bdt in P3HT/PCBM Polymer Matrix

In attempts made to improve quantum efficiency at long wavelength using equipment available at University of North Texas Department of Chemistry, the concentration of chromophore was increased and the bulky fullerene reduced slightly. The reasoning behind this strategy was to allow the square-planer platinum compounds to come in closer contact with each other thus promoting greater absorbance at long visible wavelengths while embedded in the P3HT polymer. The spin-coating procedure was challenging to consistently achieve reproducible results due to the lack of “clean room” type environmental conditions, but an overall trend was observed and illustrated in the figures 4.7-4.9. While the overall IPCE of the cell dropped over the ultraviolet and visible wavelength, there is a marked increase in the long wavelength absorption around 700 nm compared to the main peaks. This is attributed to the platinum dye activity in this region.

The measurements were done once directly from the glove box after the electrode was deposited and cover slide affixed (blue) and 12 hours later after a silver contact was applied to facilitate the connection to analytical instruments. This silver application is not expected to change the internal properties of the device and only to increase the surface area for the clamps of the instrumentation to make contact. Indeed the increase in efficiency is proportionate over the measured spectra.
Figure 4.7: (a) Quantum efficiency of the P3HT:PC60BM:Pt(dhepcb)bdt of mass ratio (10:8:2) using bare (blue) and Ag-coated contacts (red) (b) Quantum efficiency of the P3HT:PC60BM:Pt(dhepcb)bdt of mass ratio (10:8:6) using bare (blue) and Ag-coated contacts (red)

The data shows an overall drop in efficiency for the higher concentrations of chromophores, but noticeable increase at the longer wavelengths that were the targets of this study. The overall drop in efficiency in the ultraviolet and short wavelength visible spectrum is suspected to be the result of the darkening of the active layer. Such darkening that hinders the deep permeation of
radiant light into the cell is observed from comparison in Figure 4.8 of the diffuse reflectance and the above action spectra.

Figure 4.8: Quantum efficiency of the P3HT:PC60BM:Pt(dhepcb)bdt of mass ratio (10:8:2) and transmission of the cell (b) Quantum efficiency of the P3HT:PC60BM:Pt(dhepcb)bdt of mass ratio (10:8:6) and transmission of the cell
The quantum efficiency of the cell shadows the transmission through the film within a few nanometers, with the former having a slightly greater range at the longer and shorter wavelengths.

The reduction of the internal quantum yield in the more chromophores laden cell compared to the control cell is typical of the reduction due to reflection within the cell and low diffusion lengths. Clearly the improvement near the band gap shows much improvement; however it is uncertain whether this tradeoff is a lucrative light harvesting strategy.

The platinum dye enhanced cells had fill factors of 23% and 39% and efficiencies of 0.2% and 0.4% respectively. The near doubling of fill factor in the cell of higher chromophores concentration is a promising result but does not appear to magnificently improve the efficiency. The reduction of efficiency when comparing the control cell to the analogous cell fabricated in Dr. So’s lab is attributed to several causes beyond my control at this time. First as mentioned before, there are environmental factors that influence the integrity of the film. First, the lack of a clean room increases the chance of contamination from dust or particles that weaken the integrity of the film produced in the Youngblood lab. In addition the size of the active area in the UNT study was 1.1 cm² compared to 1 mm² produced in the So lab. An over 100x increase in size proportionally increases defects that lead to recombination of charge and lower the number of charge carriers that reach the electrodes though the light active layer.

4.5 Conclusions

The performance of spin-coated photovoltaic cells improves with increasing additions of the platinum dye incorporated into the familiar P3HT:PCBM blend. Although small in magnitude, the potential for improvement is predicted from the exclusion of the typical electron acceptor
PCBM and a total replacement with the platinum dye. The separation of donor and acceptor channels is suspected to be perturbed by the inclusion of a third ambipolar molecule leading to poor charge separation. Further studies should be conducted reducing or excluding the fullerene acceptor and increasing the concentration of the sensitizing platinum dye. The close packing of the platinum chromophores within its channels of the bulk heterojunction device is expected to replace the conductive boosts provided by PCBM. The platinum dye Pt(dmecb)bdt holds promise as a potential chromophore that can be thermally deposited and has excellent consistency in current generated in the visible region. The ultra-soluble Pt(dhepcb)bdt proved to be capable of increasing the long wavelength absorptions of solution processed polymer films.
Figure 4.9: (a) Current density vs. Voltage of the P3HT:PC60BM:Pt(dhepcb)bdt of mass ratio (10:8:2) (b) Current density vs. Voltage of the P3HT:PC60BM:Pt(dhepcb)bdt of mass ratio (10:8:6)
CHAPTER 5

CONCLUSIONS AND FUTURE DIRECTIONS

The major thrust of this work was to develop chromophores that could be used for solar energy harvesting applications. Over twenty-five square-planar platinum complexes were studied to assess their suitability for this purpose. The known tuning mechanisms outlined by Eisenberg were consistent when applied to the new chromophores that were synthesized to optimize physical and electronic parameters for photovoltaic cell use. Electron withdrawing ester moieties on the diimine ligand would stabilize the lowest occupied molecular orbital (LUMO) participating in the photoexcitation and subsequently responsible for the charge transfer to a donor or electrode. This stabilization results in decreasing the band gap and increasing the boundary of absorption close to or into the near infrared region (NIR). In the solid state, these dyes often exhibit stacking patterns with close intermolecular distances that favor intermolecular charge transfers of lower energy than the lowest energy found in dilute solutions. Concentrated solutions and solids of these platinum dyes also tend to aggregate with nitrofluorenone and perylene-diimine organic acceptors that would sometimes produce even longer wavelength absorptions from donor-acceptor charge transfers (DACT). Finally, select dyes were incorporated into known systems used in organic photovoltaics (OPV) by spin coating and by vapor deposition as a neat film to show that these platinum dyes maintain their electronic properties as a film. This chapter concludes my original research with summaries of important findings and suggests directions for future research.
5.1 Concluding Remarks on Dye Design, Tuning, and Future Considerations

The chromophores studied in this dissertation that were ultimately used in a device and had long wavelength absorptions covering most of the visible spectrum in the solid state had all been modified to include an ester group at the 4,4’ positions. The high extinction coefficient and red shifted absorption was expected and desired due to the electron withdrawing effects of the ester groups of the diimine. The absorption tuning scheme proposed by Eisenberg and coworkers provided the strategy to achieve the electronic absorption profile required for the so-called “black absorbers”.\(^{59}\) From a materials and process standpoint though, the rational was to reduce the effort needed to create a thin film by vapor deposition, in the case of the methoxyesterbipyridine bearing dye, or improve the solubility of the complex to facilitate solution processing, as was the case with the heptanoxyesterbipyridine coordinated dye. However ester substituents are only one possible modification that would produce black absorbing dyes. The synthesis can be easily modified by introducing appropriate primary amines to produce amide substituents in the same manner alcohols were used to with acyl chlorides to produce esters. The result of this modification would change the electron withdrawing effects on the diimine LUMO. This may not only increase the absorption wavelength of the “charge-transfer-to-diimine” but also favorably affect the dyes solubility in protic solvents due to the amides ability to participate in hydrogen bonding.

Another future consideration that is consistent with the overall goals of this project would be to replace the central metal, platinum, with cheaper and more abundant group 10 metals such

as nickel or palladium. The lowest energy absorption of the dyes studied in this work has been assigned as a mixed-metal-ligand to ligand charge transfer and there is evidence of a closely related ligand-to-ligand charge transfer in some complexes. The influence of the platinum atom on the character of these transfers has yet to be determined and a systematic study of the role of the central metal atom may not only reveal something about the fundamental nature of this absorption but produce dyes for use in photovoltaics from a less expensive source. Analogous Ni(II) complexes should produce materials that fit the requirements for sensitizing photovoltaic cells providing strong absorptions in the visible region. However it should be noted that group 10 d8-metals are not a series of interchangeable parts, the role of the central atom does influence the aromaticity responsible for the ditropic driving force for the much desired low energy “charge-transfer-to-diimine”. Should this area of research be attempted, information about low frequency vibrational modes associated with bonds at the metal center would provide valuable information about energy redistribution through vibrational redistribution. While infrared and Raman spectroscopy are the most common methods to directly measure the energy of vibrational modes, infrared spectroscopy would be useless for studying vibrations around metal centers and Raman would be limited by its selection rules and its inability to access some vibrational modes. Inelastic neutron scattering (INS) could probe regions of as low as 16 cm⁻¹, an area inaccessible to even Raman measurements and has the added bonus of not having selection rules thus making all modes accessible for study. INS recently has been used to study vibrational

modes of transition metal hydrides and cis-platin.\textsuperscript{62} From low wavenumber measurements combined with density functional calculations, a great amount of fundamental research could be done about the role the metal center in the extended “pseudo-aromatic” NN-M-SS core of these metal(diimine)(dithiolate) dyes. Vibrational relaxation leads to lower efficiencies in both light-harvesting and –emitting devices as potential energy is lost through these vibrational decays. Optimization of this core would prove beneficial when designing materials to be used in such applications.

The explanation given from the foundation laying literature for the high extinction coefficient for what should be a symmetry forbidden transition is the diffuse orbitals of sulfur atoms in the dithiolate overlapping with the d-orbitals of the platinum to create an orbital hybridized d/p character. The use of selenium as a replacement for sulfur may present opportunities to modify the HOMO energy level. Using the rationale that the orbitals of selenium would be more diffuse than the sulfur, thus minimizing the role of the metal as a determining factor on the energy level, we could possibly reduce the central atom to simply a link between the HOMO of the diselenolene and the LUMO of the diimine. However, it would be expected that the diselenolene ligand would still be susceptible to photo-oxidation similar to what occurs in the dithiolate.\textsuperscript{63}


5.2 Concluding Remarks on Donor-Acceptor Adducts and Future Considerations

Chapter 3 explored the use of organic electron acceptors with an electron deficient core that associates with the platinum chromophores of chapter 2. This complementary arrangement in some cases depending on the accepting ability of the organic molecule produces new red shifted intermolecular charge transfers from donor to acceptor that appear in the near-infrared region. Nitrofluorenones were synthesized and mixed with platinum chromophores and the band gap was inferred from absorption spectroscopy. The narrowing of this electronic transfer in energy was also observed with some perylene-diimide acceptors but often the donor acceptor charge transfer that was produced had such a low extinction coefficient that it could not be seen in the absorption spectra. Perhaps these transitions if they do occur in solution could be probed through cyclic voltammetry or in the solid state through ultraviolet photoelectron spectroscopy. The geometry for the donor and acceptor suggests that close association should occur as it does in the nitrofluorenone adducts but it is either too week or the alkyl substituents perturb the stacking of the donors and acceptors along a regular axis.

An extension of this research is needed with other electron accepting organic molecules. The propensity for 2,4,5,7-tetranitrofluoren-9-one (TENF) to accept electrons from the square-planar platinum dyes due to its favorable electron affinity makes similar organic molecules attractive partners for the same potential interactions. Could one of the nitro- groups be substituted with an ester, nitrile, or carboxylic acid group which would also be electron withdrawing and facilitate charge injection into an electrode of a photovoltaic device? Electrochemical studies in solution have found several similar first reduction half-potentials that suggest these and other modifications may be worth investigation including use of 9-
fluorenyidenemalonitriles, dialkyl-tetranitrofluorenone-9,9'-dipropionates, benzylidene and benzophenone malonitriles, and terphthalylidemalonitriles. While p-type semiconductors appear to be abundant in the literature, n-type organic semiconductors with high charge mobility are rarer. One such acceptor that looks promising for donor acceptor adducts with square-planar platinum chromophores is the quinoidal terthiophene, 3'-4' dibutyl-5,5’’-bis(dicyanomethylene)-5,5’’-dihydro-2,2’;5’,2’’-terthiophene (DCMT) or some variation might be a candidate for and electron accepting material to be paired with square-planar chromophores with group 10 metals at their core. DCMT undergoes a reversible two-electron reduction at 4.57 V vs. vacuum and also stacks well through π-interactions with neighboring molecules. The presence of π-stacking interactions in organic semiconductor materials often increases mobility within the charge carrier and fast mobility of the charge keeps the unpaired electron from the reduction delocalized so that the exciton electron-hole pair does not recombine before arriving at the respective electrode. These properties and the presence of the nitrile groups that would facilitate charge injection into a wide band gap metal oxide semiconductor make DCMT an unexplored but attractive partner for the chromophores studied in chapter 3. While the literature is filled with the use of C_{60} and perylene derivatives as n-type materials, small oligothiophenes known for self-assembly making well-ordered films as p-type materials.

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semiconductors could be functionalized with electron withdrawing groups in order to stabilize their anionic forms and allow them to be efficiently transport negative charges.\textsuperscript{67}

In addition to the unexplored partnership between donor dyes and new organic acceptors, much still remains unknown about the nature of the donor-acceptor relationship. All the donor acceptor complexes were observed to have some degree of magnetic moment in the solid state and line broadening in nuclear magnetic resonance for concentrated solutions. This implies partial oxidation of the dye and partial reduction of the acceptor. More information about the nature of this behavior would be insightful when considering future attempts at photovoltaic devices. At this point, it cannot be determined if the transferred electron is shared between the donor and acceptor or is there complete charge separation. The conductivity of the solid, magnetic measurements from electron paramagnetic resonance (EPR) studies and the use of a superconducting quantum interference device (SQUID) to measure the small subtle magnetic fields produced by these donor-acceptor charge transfer complexes.

5.3 Concluding Remarks on Device Fabrication and Future Considerations

In Chapter 4, two platinum chromophores, 1,2-benzenethiol (4,4'-dimethyloxyester-2,2'-bipyridine)platinum(II) and 1,2-benzenethiol(4,4'-diheptoxyester-2,2'-bipyridine)platinum(II), were selected for study in photovoltaic devices for their high extinction coefficients, broad coverage of the visible region in the solid state, and a suspected facile process to incorporation into a device. The former designed to for its thermal stability and the latter for good solubility,

these chromophores in at least the successfully executed attempts at complete devices, provide a proof on concept that these materials can sensitize metal-oxide semiconductors for solar energy harvesting of long wavelength visible light. The dimethoxyester modified dye was determined to have good internal-photon-to-current efficiency (IPCE) independent of wavelength throughout the visible spectrum up to 700nm as a single layer device fabricated through vapor deposition. The diheptoxyester modified dye would hopefully become the solution processed analog here, but all attempts at spin-coating a layer thick enough to generate charge separation failed with losses of material on each attempt. This dye was eventually incorporated into the well-studied poly(3-hexythiophene-2,5-diyl):phenyl-C61-butyric acid methyl ester (P3HT:PC60BM) matrix at different concentrations to determine if at various doping levels an increase in absorption and IPCE could be seen at wavelengths longer than what is generally produced in the undoped cell. Measurement of the internal quantum efficiency established small increase in the action spectra of the doped cells but beyond proof of concept it is difficult to assert trends that would help optimize this system. Efficiency of cells is influenced by the quality of the film produced and the environmental conditions under which these solar cells were fabricated were difficult to control. If these cells could be produced again using a controlled clean environment, trends could be established about the effect of the dye molecule in the studied organic photoactive matrix.

Further work with these dyes is incorporation with various electron acceptors seen in Chapter 3 or possibly metal cations as either double layer or co-deposited devices. As availability to equipment improves, the advantage of using donor acceptor systems would enhance spectral coverage of light absorption and conductivity by reducing recombination of the charge carriers.
5.4 Other Future Considerations

One subject not covered at all in this dissertation, but possibly warrants study in respect to the platinum dyes herein, is the photogeneration of hydrogen from water. Solar energy conversion through photovoltaics is an attractive source of clean electricity for onsite applications, but due to seasonal and circadian fluctuations in light intensity it would be advantageous to store and transport collected solar energy. The generation of hydrogen gas from transition metal complexes has been studied, most notably Ru(bpy)$_3^{2+}$, and acidic platinum dyes have been reported to generate small amounts of H$_2$ when irradiated with visible light.\textsuperscript{68} These systems leave much room for improvement not only in efficiency but stability. The adoption of this project would be a major turn from the momentum of the current studies, but platinum and other group 10 metal chromophores used as sensitizers in hydrogen generation through water splitting is largely unexplored.

\textsuperscript{68} Zhang, J.; Du, P; Schneider, J.; Jarosz, P.; Eisenberg, R. J. Am. Chem. Soc. \textbf{2007}, \textit{129}, 7726.