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INCORPORATION OF NOVEL DIPHOSPHINES INTO POLYMER STRUCTURE FOR LIGHT ABSORPTION AND EMISSION APPLICATIONS

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INCORPORATION OF NOVEL DIPHOSPHINES INTO POLYMER STRUCTURE FOR LIGHT ABSORPTION AND EMISSION APPLICATIONS

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Chemistry

by
Thora R. Maltais
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Accepted by:
Dr. Rhett C. Smith, Committee Chair
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Dr. Andrew G. Tennyson
ABSTRACT

In today’s society, there is a constant need for the development and production of new and improved technology, especially in the development of light emitting diodes for screens in electronic devices, and photovoltaic cells as sources for alternative energy. New insights for the development of such technology can be elucidated through the incorporation of chromophoric diphosphines into phosphonium and platinum(II) polymer frameworks. From diphosphine incorporation, it will be shown that polymer properties can be enhanced for such applications by invoking phosphorescence, and providing a modular platform for generating multilayer polymer films that provide intriguing energy transfer capabilities in the visible spectrum. All of these attributes are highly desired qualities for better understanding how to control desired properties in polymer design and synthesis.
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SECTION 1: SYNTHESIS AND CHARACTERIZATION OF FLUORENE-BASED DIPHOSPHINE PLATINUM(II) METALLOPOLYMERS
Chapter 1: History and Metallopolymer Design Rational

In the early stages of polymer chemistry development, polymers typically contained C, H, N, O, S, Cl, Br, and, on occasion, P in their composition. However, the past 100 years have greatly changed this trend, and today polymers have been prepared with a wide variety of elements present throughout their structures.\(^1\) This diversity of polymer composition began with the work of Rochow’s preparation of polysiloxanes in the 1940s.\(^2,3\) After Rochow’s work, efforts intensified, and between the 1940s and 1960s a number of metals were incorporated into the repeating units of polymers by coordination.\(^4-6\) However, the synthesis of these metal coordinated polymers did not come easy, as insolubility, low molecular weights, and tendency towards uncharacterizable materials threatened progress.

In addition to coordination polymers, organometallic polymers, or polymers with a metal-carbon bond, were also pursued.\(^1\) The field of organometallic polymers took after the discovery of ferrocene by Kealy and Paulson in 1951.\(^1,7\) By 1955, the first polymerization of an organometallic compound was reported by Arimoto and Haven by subjecting vinyl ferrocene to homopolymerization in the presence of radical initiators (Figure 1.1.1).\(^8,9\)

**Figure 1.1.1:** Reaction scheme for the first reported polymerization of an organometallic compound using vinyl ferrocene.\(^1,7\)
Since this groundbreaking work in 1955, interest in organometallic polymers has only increased, due to their potential applications in organic light emitting diodes (OLED) and photovoltaic devices. In today’s society, OLEDs are in very high demand, as they can provide excellent color and image resolution for electronic device screens, improve durability, reduce production costs, lower energy consumption, lower thermal emission, and can be employed in thinner, smaller devices to meet consumer desire. As such, it has become increasingly important to continue research to improve OLEDs to meet the consumer demand for the latest technology.\textsuperscript{10}

In, OLEDs, an electric field is applied to a thin layer of emissive material between two electrodes (Figure 1.1.2). Upon application of this electric field, the emissive material is reduced at the cathode and is oxidized at the anode to create electron and hole carriers, respectively, which will migrate towards the opposite electrode under the influence of the applied electric field. This is due to two charge carriers being created within the film, one of a negative charge from reduction, and one of a positive charge from oxidation. When two such charge carriers meet, they will combine to produce one molecule in an excited state and one molecule in a ground state. Upon relaxation of the excited state, light emission can be observed (Figure 1.1.2).\textsuperscript{11-13}
The excited states produced from charge recombination in an electric field result in the direct formation of singlet and triplet excited states, also known as excitons. Singlet states occur when the excited electron is spin paired with the ground state electron, and triplet states when electrons in the excited electron have the same spin as the electrons in the ground state (Figure 1.1.2). In the process of fluorescence, an excitation from the singlet ground state to the singlet-excited state is followed by relaxation back to the ground state. During this process the electrons always remain spin paired. Relaxation from the excited state is what causes light emission; some of the energy that promoted the electron from the ground state is released as light. Light emission, or luminescence, from these two states can best be understood by considering a general Jablonski diagram (Figure 1.1.3).
Phosphorescence occurs when the electron in the excited singlet state undergoes intersystem crossing to access the triplet-excited state. During intersystem crossing, the spin of the electron is flipped so that it is the same spin as the electron remaining in the ground singlet state. Intersystem crossing not only serves to invoke the triplet state in emissive materials, but it can also double as a non-radiative decay mechanism by which energy is lost to the surroundings rather than being emitted as light. Other mechanisms of non-radiative mechanisms for energy loss include as heat from vibrational motions, dynamic collisional quenching, and through near-field dipole-dipole energy interactions (resonance energy transfer). \(^\text{14}\)

Assuming all energy is not lost through non-radiative decay mechanisms, the triplet excited states experience relaxation of energy from the excited state. Upon relaxation to the ground singlet state, the spin of the electron changes again,
reestablising the spin pairing of the electrons. If this relaxation is accompanied by light emission, as energy can still be lost through non-radiative decay mechanisms, this is known as phosphorescence. Prior to either fluorescent or phosphorescent relaxation, the excited states can also be subjected to internal conversions, which are nonradiative transfers to lower vibrational energy states with the prospective excited states (Figure 1.1.3).¹⁴

In purely organic emissive materials, the statistical ratio of singlet to triplet states generated would be 1:3. Selection rules, however, forbid both intersystem crossing and phosphorescence because of the change of electron spin during intersystem crossing. Consequently, organic materials show little or no phosphorescence in solution at room temperature. In an OLED, however, the selection rules are not operative in the excitation process because, in this case, no electron spin change is required. The selection rules still apply to the OLED emission process, however, because in emission, spin flip is required. This means that, to a first approximation, only 25% of generated excited states are singlet and ~75% are triplets, and, thus, are negligible contributors to emission.¹¹

The efficiency of OLED devices can be significantly improved if emission from the triplet state could be invoked. This would increase the efficiency of the device beyond 25% by adding the phosphorescence emission to the fluorescence emission. This can be accomplished if spin-orbit coupling is made efficient by incorporating heavy metal atoms like platinum,¹⁵-²⁰ ruthenium,¹⁹,²¹ osmium,¹⁷,²² iridium,¹⁷,²³,²⁴ rhenium,¹⁷,¹⁹ and even lanthanides¹⁷,²⁵,²⁶ into the emissive material structure, all of which have been studied for emissive material applications.
Of these metals, platinum is one of the best metals to incorporate into the emissive material structure to invoke phosphorescence, as many of the other metals form octahedral or tetrahedral geometries with oxidation states of (II) and (III). The square planar geometry of platinum(II) is a unique feature, and has potential to increase efficiency in electronic devices.\textsuperscript{11} An explanation of why platinum(II) is one of the best metals to use will be explored here.

The first metal-based phosphorescent material to be investigated for OLEDs was platinum(II) octaethylporphyrin by doping it into a widely used electroluminescent emissive material, Tris(8-hydroxyquinolinato)aluminium (Figure 1.1.4).\textsuperscript{11}

\textbf{Figure 1.1.4:} The first metal-based phosphorescent material to be investigated (A) and the electroluminescent material doped with the metal containing species (B).\textsuperscript{11}

Doping with the platinum(II) complex led to an increase in efficiency from 4 to 23%. Even though triplet emission was achieved in this case, the efficiency was still rather low. This was caused by the long phosphorescence lifetime, which was ~80 µs in solution, such a long lifetime allowed significant triplet-triplet annihilation, especially at high electric current. Overall, this means that the triplet state was so long lived that it
lived long enough to encounter other triplet excitons to facilitate non-radiative energy loss (triplet-triplet annihilation). These observations suggest that, there is potential to use platinum(II) to enhance OLED devices, but that improvements need to be made to reduce the radiative lifetimes of the triplet state in order to make the investment of using such organometallic species worthwhile.\textsuperscript{11}

The efficiency of luminescent organometallic materials from the triplet-excited state, $\eta_r^T$, is favored by high radiative rate constants, $k_r^T$, and low non-radiative decay rate constant pathways, $\Sigma k_{nr}^T$:

$$\eta_r^T = \frac{k_r^T}{k_r^T + \Sigma k_{nr}^T}. \quad (1)$$  \textsuperscript{11}

When considering the triplet state, the quantum yield for the observed triplet luminescence, $\Phi_T^{\text{lum}}$, is dependent upon the ability to form the triplet state following light absorption. The quantum yield is further dependent upon the magnitude of the rate constant for intersystem crossing, $k_{\text{ISC}}$ (Eq. 2), where $k_r^S$ and $\Sigma k_{nr}^S$ are radiative and non-radiative decay rate constants for the singlet state:

$$\Phi_T^{\text{lum}} = \eta_r^T \cdot \frac{k_{\text{ISC}}}{k_r^S + \Sigma k_{nr}^S}. \quad (2)$$  \textsuperscript{11}

Access to the triplet state is enhanced by spin-orbit coupling, which is facilitated in systems containing heavier metal atoms in comparison to the lighter elements like carbon. Spin-orbit coupling is a mechanism, or perturbation, by which the singlet and triplet states can mix. The mixing of the two states allows the quantum mechanically forbidden triplet state to occur via intersystem crossing between the singlet and triplet states.\textsuperscript{27} The extent of mixing the singlet and the triplet states can be described in terms of a mixing coefficient, $\lambda$, by Equation 3:
\[ \lambda \sim V_{SO} / (E_S - E_T)^2 \]  \hspace{1cm} (3)^{27}

Where \( V_{SO} \) is a quantum mechanical matrix element that describes the interaction that flips the electron spin, and \( E_S - E_T \) is the energy difference between the singlet and triplet states. As such, the smaller the energy difference between the two states, the higher the probability of mixing the two states and promoting the triplet state, and the larger the \( \lambda \) quantity from the two excited states mixing.\(^{27}\)

How the electron actually flips its spin is best understood through considering that the spin-orbit coupling has relativistic origins. As the electron and nucleus move, they have influences on each other. For example, the spinning electron generates a magnetic field, because it is spinning and is a charged particle, which creates a magnetic dipole. In the same light, the nucleus generates its own magnetic field, as it also has charge and spin. The net effect of the interaction between the two generated magnetic fields applies a force or torque that can cause the electron to flip its spin direction.\(^{27}\)

In addition to these relativistic ideas to explain electron spin flips, there is also a dependence on the size of the atom known as the heavy atom effect. As the size of the atom increases, so do the effects of spin-orbit coupling that can favor the facilitation of intersystem crossing to the triplet state from the increased size of the positive charge in the nucleus. This is because the electrons in the outer shell are farther away from the nucleus and they experience less pull from the nucleus to maintain electron spin pairing. Overall, this means it would require less energy to flip the spin of an electron in a heavier atom compared to one in a lighter element.\(^{28}\) Platinum(II) is one example of a heavy metal. Platinum’s valence shell is far from the nucleus, and will be greatly affected by the
heavy atom effect to enhance spin-orbit coupling, with consequently increased intersystem crossing, and thus more probable phosphorescence. Although successful for phosphorescence production, fluorescence quenching can occur, so a balance must be achieved when using heavy metals like platinum in trying to improve OLED efficiency.\textsuperscript{11}

However, as with any metal atom, the extent to which emission from the triplet state occurs will depend on the contribution of the metal atomic orbitals to the excited state, as localization of the excited state with less contribution from the metal orbitals will result in observation of only the singlet state. Concern also needs to be paid to reducing the rate of non-radiative decay, $\Sigma k_{nr}$, to have optimal conditions to facilitate phosphorescence (Eq. 1). How the non-radiative decay and orbital mixing is promoted or suppressed depends heavily on the ligand field splitting diagram of the metal complex under consideration. In platinum(II) $d^8$ square planar complexes (Figure 1.1.5), the $d_{x^2-y^2}$ is very strongly antibonding, and any electron donated into that orbital would cause severe distortions of the square planar geometry by elongating the metal-ligand bonds.\textsuperscript{11}
These distortions will provide a favorable mechanism for promoting non-radiative decay to the ground state from an isoenergetic crossing point being at accessible energies (Figure 1.1.6A). Even when the ligand centered (LC) and metal to ligand charge transfer (MLCT) transitions are accessible, non-radiative decay can still be activated from thermal activation by the $d$-$d$ state if the energy states are close enough in energy (Figure 1.1.6B).  

**Figure 1.1.5:** Representation of simple ligand field splitting diagram for $d^8$ metals that have square planar geometry (A), with a corresponding structure example and plane definition (B).  

These distortions will provide a favorable mechanism for promoting non-radiative decay to the ground state from an isoenergetic crossing point being at accessible energies (Figure 1.1.6A). Even when the ligand centered (LC) and metal to ligand charge transfer (MLCT) transitions are accessible, non-radiative decay can still be activated from thermal activation by the $d$-$d$ state if the energy states are close enough in energy (Figure 1.1.6B).
From the above considerations, it is apparent that the most emissive platinum(II) compounds will be those that have the lowest excited energy state as an LC state, and where the energy gap between the $d-d$ and the lowest excited state is large to prevent thermally activated non-radiative decay. This means that strong-field ligands are needed to be coordinated about the metal center to ensure a large energy gap between the lowest excited state and the $d-d$ state.\textsuperscript{11}

The full effect of the strong field character of the ligands can best be understood by considering crystal field theory (CFT), which was developed in 1929 to describe the bonding in metal complexes better than valence bond theory, and would later have ligand field theory, which incorporated covalency, intertwined with its definition. CFT was premised upon mainly of one assumption: that the metal-ligand interactions were

\textbf{Figure 1.1.6:} Potential energy diagrams showing population of the $d_{x^2-y^2}$ orbital (A), and the thermally activated non-radiative transition from the $d$-$d$ state (B).\textsuperscript{11}
completely ionic in character. In this treatment, repulsions of orbital alignment due to the electrons present causes the molecular orbitals to reorder from highest to lowest energy, which is what gives rise to the observed order of orbital energies for square planar geometries in Figure 1.1.5. The difference in energy between the highest ordered energy level and the next highest is known as $\Delta$, which is controlled by the oxidation state and nature of the metal ion, and the number, nature, and geometry of the metal ligands.$^{29}$

As such, the higher the charge on the metal ion, or the higher the strength of the ligand, the larger the value of $\Delta$ will be. The strength of splitting exerted by a given ligand is determined by its electron-donating or -accepting ability. Those that are strong $\sigma$ donors are considered to be weak field ligands, and have lower $\Delta$ values. Strong field ligands are those that have more $\pi$ accepting capability from $\pi$-backbonding with the metal ion. With $\sigma$ donor and $\pi$ accepting capability in mind, ligands have been ordered in terms of their strength in what is known as the spectrochemical series:

$$\Gamma^- < Br^- < S^{2-} < Cl^- < N_3^- < F^- \ldots \text{CH}_3^- < \text{C}_6\text{H}_5^- < \text{CN}^- < \text{CO}.$$ $^{29}$

By looking at this series, the strongest field ligands would be those that have one pair of electrons to donate for a $\sigma$-bond and multiple $\pi$-bonds to have successful $\pi$-backbonding through the $\pi^*$ orbitals.$^{29}$ Such ligands would place the $d_{x^2-y^2}$ orbital significantly higher in energy to prevent thermal activation of non-radiative decay in platinum(II) complexes, while also stabilizing the electrons in the lower energy levels to prevent promotion into the highly antibonding orbital. In essence, ligands containing triple bonds in the vicinity of the metal would make ideal ligands to enhance the
efficiency of harnessing the triplet state for phosphorescence in hopes of further developing the overall efficiency of electronic devices like OLEDs.
REFERENCES CITED


(11) Murphy, L.; Williams, J. *Topics in Organometallic Chemistry*; Springer-Verlag: Berlin, 2010; 75-111.


Chapter 2: Novel Platinum(II) Acetylide Polymer

1.2.1: CURRENT WORK IN THE FIELD

Some of the earliest work on platinum(II) acetylide polymers was documented by Sonogashira, Takahashi, and coworkers in 1977 and 1978 (Figure 1.2.1), exhibiting stiff, rod-like polymers to study in the solution and solid state.\textsuperscript{1-3} Since this time, interest in these types of polymers have dramatically increased.

\begin{equation}
\begin{align*}
A & \quad \left( \begin{array}{c}
\text{P(n-Bu)}_3 \\
\vdots \\
\text{P(n-Bu)}_3 \\
\text{P(n-Bu)}_3 \\
\text{P(n-Bu)}_3 \\
\text{P(n-Bu)}_3 \\
\end{array} \right) \\
B & \quad \left( \begin{array}{c}
\text{P(n-Bu)}_3 \\
\vdots \\
\text{P(n-Bu)}_3 \\
\text{P(n-Bu)}_3 \\
\text{P(n-Bu)}_3 \\
\text{P(n-Bu)}_3 \\
\end{array} \right)
\end{align*}
\end{equation}

Figure 1.2.1: Representations of the first metallopolymers to incorporate a metal ion in the main chain of a polymer. The work of Sonogashira and coworkers from 1977 is shown in A, while the work of Takahashi and coworkers is shown in B.\textsuperscript{1-3}

Today, platinum(II) acetylide polymers are of great interest for their potential applications in photovoltaic cells.\textsuperscript{4-12} They are ideal for such applications due to their ability to access a long-lived, phosphorescent triplet state, which can be studied and monitored by photoluminescent spectroscopy.\textsuperscript{13-16} In addition, the rather high triplet yield and rate of triplet-singlet radiative decay rates suggest that these polymers could be useful in electrophosphorescent applications.\textsuperscript{17-20} All of these applications are becoming increasingly important due to the growing technological demand of the 21\textsuperscript{st} century.
Investigations have included probing phosphorescence quenching of platinum(II) acetylide polymers, exploring characteristics of the triplet excited state within the polymers, exploring intrachain energy transfer, exploring acetylide polymers with Si and Ge bridges, and probing the relationship between conjugated polymer structure and transfer of excitons and charge carriers. More recently, research had emphasized incorporating more variety of functional groups and aromatic linkers, or chromophores, into the polymer chains. In the last five years, the polymers looked very similar to those previously reported in 1977-1978, but with additions of different aromatic linkers, including porphyrins, to maintain conjugation throughout the polymer chain and to probe their potential photophysical properties, explore their ease of accessibility of the triplet state, and their potential applications for emissive materials (Figure 1.2.2).

![Chemical Structures](image)

**Figure 1.2.2:** Structural representations of conjugated metallopolymers containing platinum(II) that are very similar to the work reported in 1977-1978.
The examples of recent work shown in Figure 1.2.2 capture some of the structure and variety displayed by new platinum(II) acetylide polymers. There are many different aromatic linkers to choose from when designing such metallopolymers, however there have been relatively few platinum(II) metallopolymers incorporating phosphine conjugated materials into the backbone structure of the polymer. To date, phosphines have been used simply as place holders in the coordination about the platinum(II) metal and possibly as solubility units.\textsuperscript{1,2,5,23,25,27,38} In 2009, Tennyson and Smith reported a rational design and characterization of a novel diphosphine chromophore that coordinated to platinum(II) and palladium(II) metal centers (Figure 1.2.3). By designing their polymer to be able to host multiple chromophoric ligands if utilized appropriately, they had hoped to reduce lifetime values to allow the polymer to be viable for selected applications.\textsuperscript{39}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{Tennyson-Smith.jpg}
\caption{The metallopolymer reported by Tennyson and Smith.\textsuperscript{39}}
\end{figure}

These polymers exhibited rather low quantum yields where the platinum coordination polymer demonstrated a $\Phi$ value of $0.088 \pm 0.010$, and the palladium coordination polymer demonstrated a $\Phi$ value of $0.0210 \pm 0.0002$. Despite the fact that these low quantum yields would not make these polymers ideal for OLEDs, they could be
prime candidates for photovoltaic devices and other applications that do not require luminescence.\textsuperscript{39}

The design of Tennyson and Smith’s polymer allows for modification of the polymer post polymerization.\textsuperscript{39} By exchanging the chloride ligands (Figure 1.2.3) via Sonogashira-Hagihara coupling, the chloride ligands can easily be replaced with acetylide functional groups. Many researchers have reported novel platinum(II) acetylide complexes incorporating triphenylphosphine ligands in either the \textit{cis} or \textit{trans} conformation with acetylide ligands exhibiting a variety of functional groups incorporated into the acetylide structure\textsuperscript{40-51}. If any of these or additional acetylides with varying functional groups could be incorporated into similar polymers to that of Tennyson’s, then perhaps one would be able to synthesize novel polymers while exhibiting control over polymer properties by controlling acetylide functional group incorporation.

The work by Tennyson and Smith also demonstrates the ease with which phosphines can be included into the chromophores of the polymer chain, and opens a gateway into a new realm of polymer design and study. As such, it is the goal of this work to expand upon the beginning studies they have provided in this new realm. Investigations into the design and synthesis of a new diphosphine chromophore (Figure 1.2.4) incorporating a fluorene derivative will be discussed beginning in Chapter 2.
Upon obtaining this novel diphosphine, it was used in a plethora of polymerizations to investigate platinum(II) acetylide polymers (Chapter 2) with varying functional groups, design and study of crosslinked polymers (Chapter 3), and in the synthesis of phosphonium polyelectrolytes (Chapters 7-10). Photophysical data for these novel polymers will be compared to the phosphine monomer to investigate the effects of conjugation and heavy metal coordination. From these studies, it is expected that new information regarding the design of and potential application of these novel polymers can be elucidated and exploited to their full potential.

**Figure 1.2.4:** Representation of the novel disphosphine that current work will explore.
1.2.2: DISCUSSION AND RESULTS

Novel platinum(II) acetylide polymers were designed based on principles discussed in Chapter 1. Synthetic efforts began with the synthesis and characterization of novel diphosphine chromophore using a fluorene derivative to make 9,9-dihexyl-2,7-bis(4-[(diphenylphosphine oxide) phenyl] fluorene (FPO). Before FPO could be prepared, precursor (4-iodophenyl)diphenyl phosphine oxide (IPO1) (Scheme 1.2.1 A) was required.

Scheme 1.2.1: The synthetic scheme for the previously reported (4-iodophenyl)diphenyl phosphine oxide (IPO1) (A),\textsuperscript{39} and the synthesis of 9,9-dihexyl-2,7-bis(4-[(diphenylphosphine oxide) phenyl] fluorene (FPO) (B).

IPO1 was isolated as a bright white solid from a silica gel flash column eluting first with hexanes, until the starting material, 1,4-iodobenzene, was eluted, followed by switching the solvent to ethyl acetate to elute the product ($R_f = 0.451$). The $^1$H NMR spectrum supports the successful isolation and purification of IPO1, as a multiplet of peaks exist in the aromatic region of the spectrum. This multiplet of signals corresponds
to the equivalent protons on the benzene ring in the ortho and meta positions with relevance to the para iodine atoms, and to the protons on the three phenyl rings attached to the phosphorus atom (Figure A-1). This spectrum compares well with previous reported syntheses.\textsuperscript{39}

The $^{13}$C NMR spectrum shows eight characteristic signals for the unique carbons present in the compound, which also compares well with previous syntheses.\textsuperscript{37} All of the unique carbons fall in the aromatic region of the $^{13}$C NMR spectrum, and all signals except one singlet peak present as doublets with coupling constants ranging from 3 to 104 Hz. The coupling constant values are all attributable to phosphorus-carbon coupling, as the spectrum was not collected with phosphorus decoupling (Figure A-2, Figure A-3).

In addition to the $^1H$ and the $^{13}$C spectra collected, the $^{31}$P spectrum also supports the successful synthesis and characterization of IPO1. The spectrum shows one signal at 29.3 ppm, which, upon closer inspection, shows a weak triplet at that resonance ($J = 23.1$ Hz). This weak splitting could be due to carbon phosphorus coupling, as the spectrum was not collected with carbon decoupling. The spectrum not only agrees well with literature,\textsuperscript{39} but also serves as additional evidence that the IPO1 starting material was successfully synthesized (Figure A-4).

The synthesis of FPO was carried out via Suzuki coupling of a boronic ester of the fluorene derivative in the presence of base, [Pd(PPh$_3$)$_4$], and previously synthesized IPO1 in DMF (Scheme 1.2.1).

Upon using IPO1 to synthesize FPO, the synthetic success was assessed by the $^1H$ NMR spectrum. The aromatic region of the spectrum was similar to that of the $^1H$
NMR spectrum of \textbf{IOP1}, but there were three new signals between \(-0.7\text{-}2\) ppm. These new peaks correspond to the hexyl chains extending from the center of the fluorene unit between the two phosphorus atoms. The peak at \(2.04\) ppm corresponds to the protons closest to the aromatic rings of fluorene, and the other two peaks correspond to the other protons in groups moving further away from the aromatic rings due to less deshielding of the electrons (Figure 1.2.5, Figure A-5).

\textbf{Figure 1.2.5:} The \(^1\text{H}\) NMR spectrum (CDCl\(_3\), 300 MHz) of \textbf{FPO}. The increase in signals in the aliphatic region correspond the hexyl chain in the fluorene unit within \textbf{FPO}.

The \(^3\text{P}\) and \(^{13}\text{C}\) NMR spectra also supported the formation of \textbf{FPO}. The relative position of the signal in the \(^3\text{P}\) NMR spectrum should not shift significantly compared to that of \textbf{IPO1}, and this was the case with the signal present at \(29.5\) ppm (Figure A-6,
Figure A-7). In comparison, the $^{13}$C spectrum showed an increase in the signals present in the aromatic region of the spectrum, and again doublets were observed from phosphorus-carbon coupling (Figure A-8).

Despite many attempts, FPO crystals suitable for single crystal X-ray diffraction could not be obtained. Crystals could be grown easily in several different combinations of solvent systems via slow diffusion, but the crystals would lose solvent and become nondiffracting during or in the process of setting up the crystals for data collection. Solvent systems included higher boiling point solvents like toluene and benzene, but even these efforts were unsuccessful.

Once FPO was successfully synthesized and purified by triturating with ether, it was reduced via a previously published method using polymethylhydrosiloxane and titanium(IV) isopropoxide (Scheme 1.2.2). $^{52,53}$ This process yielded pure FP after simply triturating with pentane and ether.

![Scheme 1.2.2: Reduction of FPO to FP based on a previously published reduction method. $^{52,53}$](image)

The successful reduction of FPO to FP was most readily assessed by $^{31}$P NMR spectroscopy. Because the only change to the compound is loss of the oxygen atom bound to each phosphorus atom in the compound, the $^1$H and $^{13}$C NMR spectra should be
relatively similar to FPO starting material. This was indeed the case for the $^1$H NMR spectrum (Figure A-9, Figure A-10). There is, however, a significant chemical shift change in the $^{31}$P NMR spectrum from ~29 ppm for FPO to ~–5 ppm for FP (Figure 1.2.6, Figure A-11).

![Figure 1.2.6: The $^{31}$P NMR spectrum (CDCl$_3$, 121.4 MHz) of FP.]

Another synthetic approach to reduce the material includes using trichlorosilane in the presence of triethylamine in toluene (Scheme 1.2.3). This method is not preferred, because trichlorosilane is a more dangerous, difficult chemical to work with when compared with the reduction method proposed in Scheme 1.2.2.$^{52,53}$ Attempts to obtain analytically pure FP were also continued by recrystallizing FP.

![Scheme 1.2.3: An alternative reduction method to achieve FP.$^{52,53}$]
Eventually, crystals viable for collection of a crystal structure were obtained. Colorless crystals were grown using the slow diffusion of pentane into THF, and the results of single X-ray diffraction provided the structure in Figure 1.2.7 with refinement details given in Table 1.2.1. There is slight disorder in one of the hexyl chains off the fluorene unit.

**Figure 1.2.7:** ORTEP drawing 50% probability ellipsoids of the molecular structure of FP. Hydrogen atoms are omitted for clarity.
Table 1.2.1: Refinement details for crystal structure of FP

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<td>Empirical formula</td>
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<td>Unit cell dimensions</td>
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<tr>
<td>wR2</td>
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</tr>
<tr>
<td>R indices (all data)</td>
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<tr>
<td>R1</td>
<td>0.1409</td>
</tr>
<tr>
<td>wR2</td>
<td>0.2588</td>
</tr>
</tbody>
</table>
After obtaining pure FP for use in polymerization, FP was reacted with bis(benzonitrile)dichloroplatinum(II) in CH₂Cl₂ at room temperature to yield the functionalizable polymer, FPPtCl (Scheme 1.2.4).

Scheme 1.2.4: Synthetic route to synthesizing the functionalizable polymer, FPPtCl.

After performing the polymerization, an interesting feature was observed: the polymer contained cis and trans stereochemistry. The first polymerization was carried out following Scheme 1.2.4 while stirring at room temperature for one hour before removing the solvent. This procedure yielded a polymer with a 1.4:1 trans:cis ratio (Figure A-14) via ³¹P NMR spectroscopy. The stereochemistry ratio was determined from the signals at 20.3 and 14.4 ppm corresponding to trans and cis, respectively. The signals falling at 31.1, 29.5, 9.5, and 0.7 ppm are satellites due to splitting by the ¹⁹⁵Pt isotope (33.8%). The trans isomer has a P-Pt coupling constant of 2624 Hz, while that of the cis isomer is 3675 Hz, which were consistent with previously reported complexes and polymers.³⁹,⁵⁴,⁵⁵ The n, M_n, and p were unable to be determined for this polymer as the phosphine oxide endcaps were not visible. Overall, this was a very exciting result, as work by Tennyson showed predominantly all cis polymers.³⁹

Interestingly, upon letting the reaction stir overnight, the polymer had adopted a predominant cis stereochemistry (cis:trans, 8.5:1), which was determined by ³¹P NMR spectroscopy (Figure 1.2.8, Figure A-17). Identifying the phosphine oxide polymer end-
caps in the $^{31}$P NMR spectrum at 28.5 ppm allowed for an estimation of $n$ of 14, $M_n$ of 15,700, and an extent of polymerization of 0.93, similar to values noted for previous Pt-phosphine coordination polymers.\textsuperscript{39}

**Figure 1.2.8:** The $^{31}$P NMR spectrum (CDCl$_3$, 121.4 MHz) of cis FPPtCl from stirring the reaction overnight.

After the somewhat unexpected observation of polymers with different stereochemistries, investigations were undertaken to attempt to fully understand what factors dictate the stereochemistry of the polymer. The controlled time studies were performed at a concentration of 4.5 mM (FP), and stirring the reaction a set length of time at room temperature before solvent removal. The progressive time studies showed a fast formation of trans FPPtCl followed by the slow conversion of trans to cis by
observing only one signal at 20 ppm, followed by the slow emergence of the second signal at 14 ppm (Figure 1.2.9, Figure A-18). Concentration would also influence the rate of isomerization to cis, as observed from concentration dependent analysis. Where trans polymer was desired, minimal reaction time and low concentration are necessary.

From the $^{31}$P NMR spectral data presented in Figure 1.2.9, it is clear that the longer the polymer remains in solution the more cis stereochemistry that is formed. The trans isomer is the kinetic product, and the cis isomer is the thermodynamic product. The favorability of the cis isomer most likely derives from the ability of the polymer to form partial $\pi$-$\pi$ stacking between the fluorene units (Figure 1.2.10), but this formation is slow due to the steric hinderance from the hexyl chains attached to each fluorene unit preventing full $\pi$-$\pi$ stacking.

Figure 1.2.9: Overlay of $^{31}$P NMR spectra (CDCl$_3$, 121.4 MHz) from progressive reaction time of FPPtCl synthesis. Emergence of cis isomer is observed at 14 ppm.
Efforts were also undertaken to try to isolate a predominantly trans polymer, which was achieved by substituting CH$_2$Cl$_2$ for THF, removing the reaction solvent quickly, and using a low reaction concentration. The solvents were changed to stabilize one stereochemistry of the polymer versus the other. The predominantly cis polymer has a dipole moment, as both chlorides are on the same side of the metal, and the trans polymer does not have a dipole moment. In considering dielectric constants, these observations make sense as CH$_2$Cl$_2$ has a slightly larger dielectric constant than THF with values of 9.08 and 7.60, respectively.$^{56}$ If the donor/acceptor polarity scale suggested by Gutmann were considered, these results are still understandable,$^{57}$ as CH$_2$Cl$_2$ ($A_N = 20.4$)$^{57}$ has stronger hydrogen bonding character than THF ($A_N = 8.0$)$^{57}$ on one side of the molecule to stabilize a predominantly cis polymer.

The successful isolation of the trans FPPtCl was observed in the $^{31}$P NMR spectrum in Figure 1.2.11 (Figure A-20). The $n$, $M_n$, and $p$ values were estimated as 14 repeat units, 15,700 g/mol, and 0.93 from the $^{31}$P NMR spectrum (Figure 1.2.11, Figure

Figure 1.2.10: Representation of how fluorene chromophore units align for partial $\pi$-$\pi$ stacking within the polymer. The hexyl chains above and below the plane of the aromatics prevent full $\pi$-$\pi$ stacking of the chromophore units.
A-21) using the phosphine oxide end cap at 29.8 ppm. The \textit{cis:trans} ratio was determined to be 1:2 with coupling constant of 2465 Hz for \textit{trans} and 3871 Hz for \textit{cis}.

**Figure 1.2.11:** The $^{31}$P NMR spectrum (CDCl$_3$, 121.4 MHz) of \textit{trans FPPtCl} poly from performing synthesis using THF.

After the successful synthesis and isolation of both \textit{cis} and \textit{trans FPPtCl} polymers, \textit{FPPtCl} (X:Y, \textit{cis:trans}) polymer was used to synthesize novel platinum(II) acetylide polymer \textit{FPPtCCNO$_2$} via Sonogashira-Hagihara coupling with diisopropylamine, copper(I) iodide, and 1-ethynyl-4-nitrobenzene in toluene (Scheme 1.2.5).
In Scheme 1.2.5, a general reaction scheme is presented, as X will be substituted for \(-\text{NO}_2, -\text{CF}_3, -\text{F}, -\text{H}, -\text{C(CH}_3)_3, -\text{N(CH}_3)_2\), and \(-\text{C}_6\text{H}_5\). Currently only \text{FP}t\text{CCNO}_2 has been synthesized and characterized successfully. This is due to the effect that the electron donating/withdrawing capacity of X has on a side reaction during the synthesis.

The more electron donating ability the X functional group has, the more likely it is to break the Pt-P bond in the polymer. This is not to say that the Pt-P is particularly weak, but that the phosphine is more labile, which gives the ability to fluctuate between \textit{cis} and \textit{trans} stereochemistries. This lability is enhanced as the Pt already has an abundance of electron density from the acetylide ligand, which can push the donated electron density of the phosphine ligand from the metal center to break the bond. The bonds will break and reform during the process, allowing for extended periods of time between breaking the bond and reforming the bond. As the electron donating ability increases, so does the \(K_{eq}\) of breaking the Pt-P bond (Figure 1.2.12). In general, this can also lead to polymers with lower molecular weights in addition to fluctuating between stereochemistries.
An additional side reaction was also noted when an excess of acetylide was employed. It is these conditions to lengthen the time of reforming the Pt-P bond that allow for the side reaction to occur. Initial reactions were carried out with 20:1 ratio of copper(I) iodide catalyst: \( \text{FPtCl} \). The excess catalyst with the diisopropylamine base created the right conditions to form a phosphonium compound (Scheme 1.2.6).\(^{58,59}\)

![Figure 1.2.12: Representation of lability of the phosphine ligands coordinating with platinum(II). As the electron donating ability of the acetylide ligand increases, so does the \( K_{eq} \) of the bond breaking.](image)

\[
\begin{array}{c}
\text{P} \quad \text{P} \quad \text{Pt} \\
\text{P} \quad \text{Pt} \\
\end{array} \xrightleftharpoons{K_{eq}} \begin{array}{c}
\text{P} \quad \text{Pt} \\
\text{P} \quad \text{Pt} \\
\end{array} + \begin{array}{c}
\text{P} \quad \text{Pt} \\
\text{P} \quad \text{Pt} \\
\end{array}
\]

**Figure 1.2.12:** Representation of lability of the phosphine ligands coordinating with platinum(II). As the electron donating ability of the acetylide ligand increases, so does the \( K_{eq} \) of the bond breaking.

An additional side reaction was also noted when an excess of acetylide was employed. It is these conditions to lengthen the time of reforming the Pt-P bond that allow for the side reaction to occur. Initial reactions were carried out with 20:1 ratio of copper(I) iodide catalyst: \( \text{FPtCl} \). The excess catalyst with the diisopropylamine base created the right conditions to form a phosphonium compound (Scheme 1.2.6).\(^{58,59}\)

![Scheme 1.2.6: General reaction scheme for the phosphonium species formed as a side product in the \( \text{FPtCCX} \) syntheses.](image)

\[
\begin{array}{c}
\text{R} - \text{H} \\
\text{CuI} \\
\text{base} \\
\end{array} \xrightarrow{\text{CuI base}} \begin{array}{c}
\text{R} - \text{I} \\
\text{+ PR}_3 \\
\end{array} \xrightarrow{\text{PR}_3} \begin{array}{c}
\text{R} - \text{PR}_3 \\
\end{array}
\]

**Scheme 1.2.6:** General reaction scheme for the phosphonium species formed as a side product in the \( \text{FPtCCX} \) syntheses.\(^{58,59}\)

The side reaction outlined in Scheme 2.6 can be prevented through one of two ways. If the excess of base and copper(I) iodide catalyst are removed from the reaction,\(^{58,59}\) or if the reaction is longer than 24 hours. The former is harder to get ideal chloride ligand substitution and consistent results with the reaction. However, it was observed, that if excess amounts of acetylide and base were used while also allowing the
reaction to stir from 24-96 hours, the amount of the unwanted side reaction was decreased. Yields of the polymers without the unwanted side reaction were generally low, which was probably due to the phosphonium species precipitating out of the nonpolar solvent as the reaction progressed. All subsequent syntheses were carried out with a 1:2.5 ratio of \textit{FPPTCl}:copper(I) iodide and reacted for 24-96 hours to minimize formation of unwanted phosphonium compound. The salt is visible in the $^{31}$P NMR spectra, usually appearing as a singlet almost overlapping with another resonance near 26 or 14 ppm (Figure 1.2.13, Figure A-22).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{The $^{31}$P NMR spectrum (C$_6$D$_6$, 121.4 MHz) of \textit{FPPTCC}-tBu with the phosphonium side product present.}
\end{figure}

\textit{FPPTCCNO$_2$} can be purified to a high degree of purity, as determined by elemental analysis. Purity was also demonstrated through the $^1$H and $^{13}$C NMR spectra.
(Figure A-23, Figure A-24), and from the $^{31}$P NMR spectrum (Figure 1.2.14, Figure A-25). The $^{31}$P NMR spectrum shows one signal at 18.8 ppm for the single type of phosphorus in the polymer, and two other signals at 29.5 and 8.2 ppm for the platinum splitting with $J = 2587$ Hz. Only one signal is seen at 18.8 ppm, and has a coupling constant that compares well with $\text{trans FPPtCl}$ $J$ values and a previously synthesized $\text{trans}$ platinum(II) acetylide complexes, which supports that $\text{trans}$ is the only stereochemistry present.

![Figure 1.2.14](image)

**Figure 1.2.14:** The $^{31}$P NMR spectrum (CDCl$_3$, 121.4 MHz) for FPPTCCNO$_2$.

D’Amato and coworkers as well as others, have also used weak IR spectroscopic absorbances at 540 cm$^{-1}$ to discern between $\text{cis}$ and $\text{trans}$ stereochemistry in platinum(II) acetylide complexes. Efforts were made using ATR IR with a one bounce diamond crystal to attempt observation of the absorbance in FPPTCCNO$_2$, however, the
spectra did not show the characteristic peak at 540 cm$^{-1}$ due to a larger peak near 516 cm$^{-1}$ overshadowing the lower region (Figure C-1 to Figure C-6). Thus, we can say that the coupling constant observed for FPPtCCNO$_2$ is reasonable with trans platinum(II) acetylide complexes reported,$^{44}$ but it is difficult to say with complete certainty that our polymer is in the trans geometry.

Because the phosphine oxide end cap is clearly observable at 30.2 ppm in the $^{31}$P NMR spectrum (Figure 1.2.14, Figure A-22), $n$, $M_n$, and $p$ values were readily determined to be 17 repeat units, 22,800 g/mol, and 0.94 by using. The percent exchange of the chlorides for the acetylide ligands was determined to be 73% by comparing integrations of the peaks at 2.03 and 6.41 ppm. The peak at 2.03 corresponds to four protons that are the hexyl chain methylenes that are directly attached to the fluorene unit, whereas the peak at 6.41 ppm corresponds to four protons in the $-$C$_6$H$_4$NO$_2$ moiety, as noted by D’Amato and coworkers.$^{40}$

After the successful synthesis of FPPtCCNO$_2$, photophysical data were collected and compared with those FPO, FP, cis FPPtCl, trans FPPtCl, and FPPtCCNO$_2$ (Table 1.2.2, Figure 1.2.15). Unfortunately, no data for films of the polymers could be obtained, because the films emitted too weakly for reliable detection by our instrument at room temperature. Although a rather high photoluminescent quantum yield ($\Phi$) was observed for FPO (0.845), the phosphine analogue FP shows a much lower photoluminescence quantum yield (0.086), which is most likely due to the lone pair of electrons on the phosphorus atom that is easily polarizable and can facilitate nonradiative decay processes.$^{61}$ A second band in both the absorbance and emission spectra of FPPtCCNO$_2$. 
These new bands are attributable to the chromophore.\textsuperscript{40} The Pt acetylide unit is electronically insolated from the fluorene $\pi$-system and thus acts as an independent chromophore. Overall, the polymers synthesized have low quantum yields for fluorescence. This can be explained by the heavy atom effect due to the incorporation of platinum into the main chain of the polymer structure.

Table 1.2.2: Photophysical Data of Diphosphine Compounds

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\pi-\pi^*}$ (nm)</th>
<th>log $\varepsilon$</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>$\Phi$</th>
<th>$\tau$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FPO</td>
<td>338.9</td>
<td>4.82</td>
<td>379.0</td>
<td>0.845</td>
<td>0.70</td>
</tr>
<tr>
<td>FP</td>
<td>340.0</td>
<td>6.32</td>
<td>300.0</td>
<td>0.086</td>
<td>1.07</td>
</tr>
<tr>
<td>trans FPPTCl</td>
<td>343.0</td>
<td>5.97</td>
<td>396.9</td>
<td>0.013</td>
<td>0.80</td>
</tr>
<tr>
<td>cis FPPTCl</td>
<td>345.0</td>
<td>4.78</td>
<td>395.8</td>
<td>0.007</td>
<td>0.551</td>
</tr>
<tr>
<td>FPPTCCNO$_2$</td>
<td>343.0</td>
<td>4.91</td>
<td>400.0</td>
<td>0.011</td>
<td>0.163</td>
</tr>
</tbody>
</table>

As explained previously, the heavy atom effect can induce intersystem crossing to form the often nonemissive triplet state. This effect is observed when comparing the quantum yields of cis and trans FPPTCl and FPPTCCNO$_2$. For platinum(II) compounds to exhibit reasonably efficient phosphorescence, it is necessary to have strong field ligands coordinated to place the $dx^2-y^2$ orbital higher in energy and, thus, prevent a major mechanism for thermal initiation of non-radiative decay. The cis and trans FPPTCl
polymers lack such strong field ligands, as the chloride and phosphine ligands are strong σ donors and have no π accepting ability. These polymers might be expected to show little observable phosphorescence, but potentially lose energy through non-radiative decay from the d-d energy level being low enough in energy. Addition of the acetylide functional groups about the platinum, should thus increase the phosphorescence efficiency due to their being strong field ligands.

Both of these trends were observed from obtaining the phosphorescence spectra for trans FPPtCl and FPPtCCNO₂ polymers at 77 K in 2-methyltetrahydrofuran (Figure 1.2.15, Figure B-13, 14, 18, 19). Data were collected both at room temperature (298 K) and at the 77 K. Phosphoresence data could not be collected for cis FPPtCl because the polymer was not soluble in methyl THF. Comparison between the polymers and temperature shows the emergence of phosphorescent peak at 535 nm with a decrease in the fluorescence at 385 nm for FPPtCCNO₂. The fluorescent peak is severely decreased, even though the phosphine chromophore should still exhibit fluorescence at 77 K. This observation is most likely due to energy transfer from the remaining fluorescent signal to the phosphorescent signal. The trans FPPtCl polymer did not show and change between temperatures, as predicted from the lack of strong field ligands to induce phosphorescence instead of energy loss through non-radiative decay.
The phosphorescent quantum yield was determined to be 0.018, which is higher than the fluorescent quantum yield (0.011) of FPPtCCNO₂. As the quantum yields for all of the newly synthesized polymers, particularly for FPPtCCNO₂, are low in general, they have a low output of photons for light emission. Quantum yields indicate the number of photons emitted with respect to the number of photons absorbed. This means that when a quantum yield value is low, more photons are being absorbed than emitted. As more absorption is occurring, it is possible that these polymers could be employed in solar cell applications where absorption and storage are more important than energy emission.

**Figure 1.2.15:** Overlay of fluorescence and phosphorescence spectra for *trans* FPPtCl, and FPPtCCNO₂.
1.2.3: CONCLUSIONS AND FUTURE WORK

Thus far, synthesis and characterization of a novel chromophoric diphosphine and one of its platinum(II) coordination polymers have been shown. Photophysical data supports the facilitation of phosphorescence in a platinum(II) acetylide polymer (FPPTCCNO₂) from the addition of strong field ligands to the metal coordination sphere. Due to both the phosphorescent quantum yield and the fluorescence quantum yield being low for this polymer, FPPTCCNO₂ may be better suited for solar cell applications than for light emitting devices.

Further work needs to be carried out to investigate the effects of electron donicity of the acetylide ligand by synthesizing polymers with a variety of functional groups of the acetylide ligands (-CF₃, -F, -H, -C(CH₃)₃, -N(CH₃)₂, and -C₆H₅). As discussed previously, there were difficulties with a side reaction that led to the formation of an unwanted phosphonium species. Prevention of this unwanted formation appears accessible through control of reaction conditions, and full synthesis and characterization of these polymers will soon be underway. Characterization will include acquiring phosphorescence data as well as electrochemical data for each new polymer synthesized.

1.2.4: EXPERIMENTAL

General Considerations

All air-sensitive reactions were performed using standard Schlenk techniques or in an MBraun UNILab glovebox under nitrogen atmosphere. Anhydrous solvents were purchased from Fisher Scientific, and were further dried, degassed, and purified using an
MBraun solvent purification system. All other reagents were used as received unless otherwise stated. All NMR spectra were obtained using a Bruker Avance 300 MHz (operating at 300, 75.4, and 121.4 MHz for $^1$H, $^{13}$C, and $^{31}$P nuclei) or a Bruker Avance 500 MHz (operating at 500, 125.7, and 202.4 MHz for $^1$H, $^{13}$C, and $^{31}$P nuclei) NMR spectrometer. NMR spectra are reported in ppm referenced to residual solvent signal ($^1$H, $^{13}$C) or 85% phosphoric acid ($^{31}$P). UV-Vis absorption spectra were acquired on a Cary 50 Spectrophotometer, while all photoluminescence spectra were collected on a Varian Eclipse fluorimeter in quartz cuvettes with a pathlength of 1 cm in the appropriate solvent. Quantum yields ($\Phi$) for all compounds were calculated relative to quinine bisulfate in 0.1 M H$_2$SO$_4$ (aq) ($\Phi = 0.546$). Lifetime data were collected using an Easylife II Lifetime fluorometer from Photon Technology International.

**Synthesis of 4-iodophenyldiphenylphosphine oxide**

The reaction vessel was charged with 20.0 g (51.0 mmol) of 1,4-diiodobenzene and 400 mL of dry THF under inert atmosphere. The vessel was then cooled to –78 °C, followed by the addition of 20.8 mL (2.50 M in hexanes) of $n$-butyllithium. The reaction was stirred for 1 h before adding 13.5 g (61.0 mmol) of chlorodiphenylphosphine dissolved in 100 mL of dry THF. The resulting pale-yellow mixture was then stirred 24 h under inert atmosphere, while allowing the reaction to slowly warm to room temperature. After such time, the resultant clear-colored reaction was opened to air, diluted to 800 mL with CH$_2$Cl$_2$, and 50 mL of water were added. The reaction was stirred 20 min, then the water was removed, followed by washing 3 × more with 100 mL portions of water. The solvent
was then removed from the pale-yellow organic mixture via reduced pressure. The isolated yellow-white solid was re-dissolved in CH₂Cl₂, followed by adding 10 mL of 30% H₂O₂ to the organic mixture. The reaction was stirred or 24 h before the H₂O₂ was quenched by adding 22.0 g (175 mmol) sodium sulfite dissolved in 200 mL water and stirring 30 min. The organic mixture was then isolated, washed 3 × with water, dried over Na₂SO₄, and the solvent removed via reduced pressure to get yellow solid. The product was obtained from this yellow solid by purifying over a silica gel flash column by first eluting with pure hexanes, followed by ethyl acetate to yield the product as 9.67 g (47.0 % yield) of white solid (R_f = 0.451 in ethyl acetate). ᵃH NMR (300 MHz, CDCl₃): δ = 7.37-7.85 (m, 14 H, aromatic). ᵃ³C NMR ( 75 MHz, CDCl₃): δ = 137.8, 137.6 (d, J = 12 Hz); 133.5, 133.4 (d, J = 10.5 Hz); 132.8, 131.5 (d, J = 102.7 Hz); 132.5, 131.2 (d, J = 104.2 Hz); 132.2, 132.1 (d, J = 3 Hz); 132.0, 131.9 (d, J = 10.5 Hz); 128.7, 128.5 (d, J = 12.7 Hz); 99.7. ᵃ³¹P NMR (121.4 MHz, CDCl₃): δ = 29.3 (t, J = 23.1 Hz) (P=O).

**Synthesis of fluorene-based phosphine oxide (FPO)**

A mixture of 4.80 g (11.9 mmol) of 1,4-diodophenylphosphine oxide, 3.00 g (5.97 mmol) of 9,9-dihexylfluorene-2,7-bis(trimethyleneborate), 0.17 g (0.46 mmol) of [Pd(PPh₃)] catalyst, and 8.50 g (26.0 mmol) Cs₂CO₃ in 220 mL of DMF was heated to 80 °C under inert atmosphere. The reaction was stirred 12 h, then cooled to room temperature, and then 100 mL of CH₂Cl₂ were added. The reaction was then washed 5 × with water, 1 × with brine, and followed by 1 × more with water. The orange organic mixture was dried over Na₂SO₄, and the solvent removed via reduced pressure to yield an
orange-red oil. The product was isolated from the oil by triturating with diethyl ether to yield 3.80 g (72.0 % yield) of white solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 0.74$ (t, 10 H, $-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3 \times 2$), 1.09 (s, 12 H, $-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3 \times 2$), 2.04 (s, 4 H, $-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3 \times 2$), 7.46-7.75 (m, 34 H, aromatic). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 151.9; 145.0; 140.7; 138.9; 133.1, 132.3$ (d, $J = 102.5$ Hz); 132.7, 132.6 (d, $J = 12.5$ Hz); 132.1, 132.0 (d, $J = 10$ Hz); 131.9; 131.4, 130.61 (d, $J = 105$ Hz); 128.6, 128.5 (d, $J = 12.5$ Hz); 127.2, 127.1 (d, $J = 12.5$ Hz); 126.4; 55.4; 40.38; 31.4; 29.6; 23.8; 22.5; 13.9. $^{31}$P NMR (121.4 MHz, CDCl$_3$): $\delta = 29.5$ (P=O). Anal. Cacld. for C$_{61}$H$_{60}$P$_2$O$_2$: C, 82.59; H, 6.82; Found: C, 82.01; H, 6.81. mp = 205-207 °C.

**Reduction of FPO to fluorine-based phosphine (FP)**

The reduction of FPO was adapted from previously reported literature.$^{52,53}$ Under inert atmosphere, 2.50 g (2.80 mmol) of FPO, 4.02 mL (14.1 mmol) titanium(IV) isopropoxide, and 8.48 mL (141 mmol) of polymethylhydrosiloxane were combined in dry THF and heated to reflux for 12 h. After such time, 100 mL degassed CH$_2$Cl$_2$ and 30 mL of degassed, saturated Na$_2$CO$_3$ solution were added to the reaction, and stirred until a dark blue jelly formed. The reaction was then opened to air, the jelly filtered away, and the pale yellow organic mixture was washed 2 × with 100 mL of saturated Na$_2$CO$_3$ solution, dried over Na$_2$SO$_4$, and the solvent removed by reduced pressure. The resulting yellow-white solid was brought under inert atmosphere. The product was obtained by triturating the solid in pentane, and filtering away the solvent to obtain the product as
yield bright white solid 1.70 g (70.0 % yield). $^1$H (300 MHz, CDCl$_3$): $\delta = 0.74$ (t, 10 H, $J = 9$ Hz, -CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$ $\times$ 2), 1.07 (s, 12 H, -CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$ $\times$ 2), 2.03 (s, 4 H, -CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$ $\times$ 2), 7.38- 7.80 (m, 34 H, aromatic).

$^{31}$P NMR (121.4 MHz, CDCl$_3$): $\delta = -5.5$. Anal. Cacld. for C$_{61}$H$_{60}$P$_2$: C, 85.68; H, 7.07; Found: C, 82.77; H, 7.09. mp = 176-178 °C.

Synthesis of cis FPPTCl polymer

A mixture of 0.47 g (0.55 mmol) FP and 0.25 g (0.53 mmol) dichlorobis(benzonitrile)platinum (II), dissolved in dry CH$_2$Cl$_2$, was prepared under inert atmosphere. The mixture stirred at room temperature 2 d, followed by removing the solvent in vacuo to yield a dark brown gel. The gel was purified by triturating in pentane to yield 0.49 g (0.44 mmol, 79.0 % yield) of brown polymer powder. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 0.71$ (s, 10 H, -CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$ $\times$ 2), 1.09 (s, 12 H, -CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$ $\times$ 2), 2.05 (s, 4 H, -CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$ $\times$ 2), 7.37-7.76 (m, 34 H, aromatic). $^{31}$P NMR (121.4 MHz, CDCl$_3$): $\delta = 14.3$ ($J_{P,Pt} = 3674$ Hz), 20.3 ($J_{P,Pt} = 2631$ Hz), 28.5 ($J_{P,Pt} = 3002$ Hz) (P=O).

Synthesis of trans FPPTCl polymer

Under inert atmosphere, 0.037 g (0.043 mmol) of FP and 0.020 g (0.042 mmol) dichlorobis(benzonitrile)platinum (II) were dissolved in 10 mL THF. Upon dissolavation, the mixture was stirred while the solvent was removed in vacuo to yield a yellow-green glassy gel. The gel was purified by trituration in pentane, while open to the air, to yield
0.036 g (75.0 % yield) of light yellow-green powder. $^1$H NMR (300 MHz, CDCl$_3$): $\delta =$ 0.76 (s, 10 H, -CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$ $\times$ 2), 1.07 (s, 12 H, -CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$ $\times$ 2), 2.05 (s, 4 H, -CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$ $\times$ 2), 7.41-7.85 (m, 34 H, aromatic). $^{31}$P NMR (121.4 MHz, CDCl$_3$): $\delta =$ 14.3 ($J_{P, Pt} = 3871$ Hz), 20.3 ($J_{P, Pt} = 2465$ Hz), 29.8 (P=O). Anal. Cacld. for C$_{61}$H$_{60}$P$_2$Cl$_2$Pt (monomer repeat unit ignoring end groups): C, 65.35; H, 5.39; Found: C, 60.51; H, 5.18.

**Synthesis of FPPTCCNO$_2$ polymer**

FPPTCl, 0.10 g (0.09 mmol), 0.52 g ( 3.57 mmol) of 1-ethynyl-4-nitrobenzene, 0.042 g (0.22 mmol) copper(I) iodide, and 2.50 mL (17.8 mmol) diisopropylamine were stirred for 24 h. The resultant brown-red reaction mixture was opened to the air, all solid was filtered away, and the solvent removed by reduced pressure to give a yellow-orange gel. The gel was purified by triturating separately in pentane, methanol, and ether to give 0.094 g (0.07 mmol, 78.0 % yield) yellow-orange powder. $^1$H NMR (300 MHz, CDCl$_3$): $\delta =$ 0.72 (s, 10 H, -CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$ $\times$ 2), 1.05 (s, 12 H, -CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$ $\times$ 2), 2.03 (s, 4 H, -CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$ $\times$ 2), 6.41 ( s, 3 H , aromatic C$_6$H$_4$NO$_2$) 7.47-7.88 (m, 36 H, aromatic). $^{31}$P NMR (121.4 MHz, CDCl$_3$): $\delta =$ 18.8 ($J_{P, Pt} = 2587$ Hz), 30.2 (P=O).
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Chapter 3: Continuation of Novel Platinum Acetylide Polymers With Varied Functional Groups to Explore Electrochemical Properties

1.3.1: DISCUSSION AND RESULTS

The same synthetic strategy will be employed in this chapter, as it was in Chapter 2 to synthesize a novel platinum (II) acetylide polymer containing a nitro group on the acetylide ligand. FPPtCl (discussed in Chapter 2) was reacted via Suzuki coupling with diisopropylamine, copper(I) iodide, and various acetylides to make a variety of platinum(II) acetylide polymers (Scheme 1.3.1).

To date, the synthesis and characterization of the six remaining platinum(II) acetylide polymers that contain -F, -CF₃, -C₆H₅, -H, -tBu, and -NMe₂ remains to be finished. Progress has been made on three of these remaining polymers (-C₆H₅, -tBu, and -NMe₂), and they currently need to be fully characterized.

The ¹H NMR spectrum for FPPtCCPh shows successful synthesis of the polymer with reasonable purity. The major impurities in the sample are at 3.51 and 1.26 ppm, which correspond to ether from triturating the polymer to remove impurities from the
ligand substitution reaction (Figure 1.3.1). All important peaks of interest from the fluorene chromophore in FPPtCl are observed at 1.99, 1.01, and 0.69 ppm. The large mass of overlapping peaks in the aromatic region correspond to the aromatics in the polymer, however, they are not too helpful in determining polymer identification. Only one peak, at 6.45 ppm is helpful, as it corresponds to the protons on the acetylide-bearing aromatic ring.

Figure 1.3.1: The $^1$H NMR spectrum of FPPtCCPh (CDCl$_3$, 300 MHz).

The $^{31}$P NMR spectrum shows a strong peak at 18.8 ppm, which indicates successful polymerization from the peaks at 14 and 20 ppm of FPPtCl disappearing (Figure 1.3.2). Satellite peaks from P-Pt splitting are located at 8.0 and 29.9 ppm, the latter of which overlaps with the phosphine oxide endcaps of the polymer.
The $^1$H and $^{31}$P NMR spectrum of FPPtCCPh also show successful synthesis of the desired platinum(II) acetylide polymer (Figure 1.3.3). The major impurity in the polymer, according to the $^1$H NMR spectrum is ether from purifying the polymer post ligand exchange (Figure 1.3.3 A). The $^{31}$P NMR spectrum clearly shows the desired has been synthesized from the peaks at 19.5 and 18.0 ppm. Not only does this indicate that ligand exchange was successful, it also indicates that the polymer contains cis and trans character. The peak at 18.3 ppm corresponds to trans with a coupling constant of 2162 Hz, and the peak at 19.5 ppm corresponds to cis with a coupling constant of 2050 Hz (Figure 1.3.3 A).
Figure 1.3.3: The $^1$H NMR ($C_6D_6$, 300 MHz) (A) and the $^{31}$P NMR spectra ($C_6D_6$, 121.4 MHz) (B) of FPtCC$^t$Bu.
The synthesis of \textbf{FPPlCCNMe}_2 has proven to be a little more difficult than the other platinum(II) acetylide polymers. Initial syntheses had issues with very low molecular weight polymers, as there was an almost equal amount of phosphine oxide and polymer peaks in the \textsuperscript{31}P NMR spectrum. This observation was due to the electron donating strength of the acetylide ligand. The NMe\textsubscript{2} functional group on the acetylide group is a very strong electron donator, which can influence pushing off the phosphine ligand from the metal center, allowing it to become oxidized. Henceforth, all syntheses of the polymer were carried out completely under nitrogen in the glove box.

Since amending the synthesis to include air-free storage techniques, the synthesis results look more promising. The \textsuperscript{1}H NMR spectrum looks rather dirty, but shows the expected peaks are present (Figure 1.3.4 A). The more interesting results are shown in the \textsuperscript{31}P NMR spectrum (Figure 1.3.4 B), as the molecular weight of the polymer has increased, which is due to the eliminating exposure to oxygen.
Figure 1.3.4: The $^1$H NMR ($C_6D_6$, 300 MHz) (A) and the $^{31}$P NMR spectra ($C_6D_6$, 121.4 MHz) (B) of FPPtCCNMe$_2$. 
1.3.2: CONCLUSIONS AND FUTURE WORK

There is still a lot of work to be done with these polymers. Currently, only three have preliminary results, but they still require purification before they can be fully characterized. Synthesis still needs to be completed for the remaining three polymers, and a full characterization will also need to be carried out for those as well.

Future work for these polymers should be based on the comparison of the all the platinum(II) acetylide polymers as a collection. For it will be from comparing the properties of these polymers that potential modifications could be made to design platinum(II) acetylide polymers for specific applications.

1.3.3: EXPERIMENTAL

Proposed Synthesis of FPPTCCPh

FPPTCl, (0.10 g, 0.09 mmol), 0.32 g ( 3.57 mmol) of 4-ethynylbiphenyl, 0.04 g ( 0.22 mmol) copper(I) iodide, and 2.5 mL (17.8 mmol) diisopropylamine were stirred for 36 h. The resultant brown-red reaction mixture was opened to the air, all solid was filtered away, and the solvent removed by reduced pressure to give a brown gel. The gel was purified by triturating in ether to give brown polymer powder. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 0.62$ (s, 6 H, -CH$_2$-CH$_2$CH$_2$-CH$_2$-CH$_2$-CH$_3$ × 2), 1.01 (s, 4 H, -CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$ × 2), 1.99 (s, 4 H, -CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$ × 2), 6.47 ( s, 3 H , aromatic C$_6$H$_4(C_6H_5)$) 6.47-8.00 (m, 36 H, aromatic). $^{31}$P NMR (121.4 MHz, CDCl$_3$): $\delta = 18.8; 30.2$ (P=O).
Proposed Synthesis of FPPTCCNMe₂

FPPTCl, 0.10 g (0.09 mmol), 0.26 g (3.57 mmol) of 1-ethynyl-4-dimethylaniline, 0.04 g (0.22 mmol) copper(I) iodide, and 2.5 mL (17.8 mmol) diisopropylamine were stirred for 36 h. The resultant brown-red reaction mixture was opened to the air, all solid was filtered away, and the solvent removed by reduced pressure to give a black gel.

Proposed Synthesis of FPPTCC'Bu

FPPTCl, 0.10 g (0.09 mmol), 0.34 g (2.30 mmol) of 1-ethynyl-4-dimethylaniline, 0.04 g (0.22 mmol) copper(I) iodide, and 2.5 mL (17.8 mmol) diisopropylamine were stirred for 36 h. The resultant brown-red reaction mixture was opened to the air, all solid was filtered away, and the solvent removed by reduced pressure to give a brown gel. The gel was purified by triturating in ether to give brown polymer powder.
Chapter 4: Crosslinking of Functionalizable FPPtCl polymer with Diethynylbenzene

1.4.1: DISCUSSION AND RESULTS

The functionalizable polymer FPPtCl was reacted with controlled amounts of diethynyl benzene and 4-(tert-butyl)phenylacetylene to create 0.5%, 1%, and 3% crosslinked polymers (Scheme 1.4.1).

![Scheme 1.4.1: General schematic representation of reacting the FPPtCl to form crosslinked polymers.](image)

Initial syntheses of these polymers proved to be unsuccessful, as the polymers produced were insoluble in all of the most common organic solvents. The percentages of crosslinking were initially 3%, 5% and 7%, but while troubleshooting the synthesis, it...
was found that anything that contained 5% or higher crosslinking was completely insoluble. The insolubility was due to the polymer being very rigid before crosslinking, as the only flexibility existed primarily in the hexyl sidechains of the fluorene chromophore, and from adding triple bond-containing links between rigid polymer chains. This has the potential to create a rigid network that will not easily dissolve in solution, which was observed to be the case in multiple preparations. Therefore, these syntheses need to have small percentages of crosslinking achieved to obtain soluble crosslinked polymers, which in effect are more useful for applications.

As of right now only preliminary data is presented here, as the polymers have limited solubility. The two solvents they are most soluble in are DMF followed by CH$_2$Cl$_2$, and the work-up post crosslinking has been adapted to include a CH$_2$Cl$_2$ extraction of a DMF-water mixture to attempt reasonable isolation of the polymers. DMF was chosen as the reaction solvent because the different ratios of cis and trans in FPPtCl have slightly different solubility characteristics. For example, when more cis character is present the polymer is less soluble in toluene, and takes a long time of stirring and gentle heating to force the polymer into solution. Regardless of cis:trans ratios, FPPtCl is readily soluble in DMF to perform crosslinking.

The preliminary data collected thus far centers around the $^{31}$P NMR spectra for FPPtCl before crosslinking, 0.5%, and 1% crosslinking. The data presented in Figure 1.4.1 is for crosslinked polymers synthesized with both the diethynylbenzene, for crosslinking, and the 4-(tert-butyl)phenylacetylene in the reaction mixture at the same time. The 3% polymer with both reactants, and the reactions with only crosslinking
occurs first and a second reaction is carried out to add 4-(tert-butyl)phenylacetylene are not ready to present here at this time.

![NMR spectra](image)

**Figure 1.4.1:** The preliminary $^{31}$P NMR spectra (DMF, CDCl$_3$, 121.4 MHz) for 0.5% and 1% crosslinking with both 4-(tert-butyl)phenylacetylene and diethynylbenzene in the reaction setup.

The $^{31}$P NMR spectra in Figure 1.4.1 show that the crosslinking and acetylide group addition at the same time allows for successful crosslinked polymers to occur. The disappearance of the peak at ~14 ppm is the decrease of a *cis FPPtCl* unsubstituted chlorides as the crosslinking increases, and it its place there is another signal ~26 ppm that increases. There are some signals present in the spectra that are unclear as to if they
are satellite peaks from platinum coupling causing a doublet to form about a phosphorus signal, an actual phosphorus signal, or a side reaction occurring, as these polymers are subject to the same potential side reaction that occurs during the synthesis of the platinum acetylide polymers in Chapter 2 (Scheme 1.2.6). As such, further investigation needs to be carried out to determine if the peaks observed at ~26 ppm are from the crosslinked polymer or if they are from the unwanted phosphonium species.

1.4.2: CONCLUSIONS AND FUTURE WORK

Thus far it has been shown that the crosslinked polymers can be synthesized, and a suitable work-up has been found to isolate the polymers after reaction completion. A full characterization needs to be carried out on these polymers, however, they are subject to the same side reaction as the FPPtCCX polymers in Chapter 2, so more investigation needs to be carried out to determine if the crosslinked polymers are also affected in the same manner.

1.4.3: EXPERIMENTAL

General Considerations

All air-sensitive reactions were performed using standard Schlenk techniques or in an MBraun UNILab glovebox under nitrogen atmosphere. Anhydrous solvents were purchased from Fisher Scientific, and were further dried, degassed, and purified using an MBraun solvent purification system. All other reagents were used as received unless otherwise stated. All NMR spectra were obtained using a Bruker Avance 300 MHz
(operating at 300, 75.4, and 121.4 MHz for $^1\text{H}$, $^{13}\text{C}$, and $^{31}\text{P}$ nuclei) or a Bruker Avance 500 MHz (operating at 500, 125.7, and 202.4 MHz for $^1\text{H}$, $^{13}\text{C}$, and $^{31}\text{P}$ nuclei) NMR spectrometer. NMR spectra are reported in ppm referenced to residual solvent signal ($^1\text{H}$, $^{13}\text{C}$) or 85% phosphoric acid ($^{31}\text{P}$). UV-Vis absorption spectra were acquired on a Cary 50 Spectrophotometer, while all photoluminescence spectra were collected on a Varian Eclipse fluorimeter in quartz cuvettes with a pathlength of 1 cm in the appropriate solvent. Quantum yields ($\Phi$) for all compounds were calculated relative to quinine bisulfate in 0.1 M $\text{H}_2\text{SO}_4$ (aq) ($\Phi = 0.546$). Lifetime data was collected using an Easylife II Lifetime fluorimeter from Photon Technology International.

**Proposed Synthesis of 0.5% Diethynylbenzene Crosslinked FPPtCl (CLP1)**

A mixture of 0.1 g FPPtCl (0.09 mmol), 0.22 mL of a $1.79 \times 10^{-7}$ M solution of diethynylbenzene in DMF, 0.04 g copper(I) iodide, and 0.5 mL diisopropylamine were reacted in 8 mL DMF. The reaction stirred at room temperature for 24 h under inert atmosphere, followed by opening to the air, and filtering away any solid. The dark brown DMF solution was then mixed with 50 mL of water, and extracted three times with 50 mL CH$_2$Cl$_2$. The solvent was removed from collected organic solution, and dried in vacuo overnight yield a brown gel. Triturating in pentane and methanol, separately, purified the product to yield dark brown gel.

**Proposed Synthesis of 1.0% Diethynylbenzene Crosslinked FPPtCl (CLP2)**
A mixture of 0.1 g FPPtCl (0.09 mmol), 0.23 mL of a $8.9 \times 10^{-5}$ M solution of diethynylbenzene, 0.04 g copper(I) iodide, and 0.5 mL diisopropylamine were reacted in 8 mL DMF. The reaction stirred at room temperature for 24 h under inert atmosphere, followed by opening to the air, and filtering away any solid. The dark brown DMF solution was then mixed with 50 mL of water, and extracted three times with 50 mL CH$_2$Cl$_2$. The solvent was removed from collected organic solution, and dried in vacuo overnight yield a brown gel. Triturating in pentane and methanol, separately, purified the product to yield brown polymer gel.

**Proposed Synthesis of 3.0% Diethynylbenzene Crosslinked FPPtCl (CLP3)**

A mixture 0.10 g FPPtCl (0.09 mmol), 0.34 mL of a $8.0 \times 10^{-6}$ M solution of diethynylbenzene in DMF, 0.04 g copper(I) iodide, and 0.5 mL diisopropylamine were mixed in 8 mL DMF. The reaction stirred at room temperature for 24 h under inert atmosphere, followed by opening to the air, and filtering away any solid. The dark brown DMF solution was then mixed with 50 mL of water, and extracted three times with 50 mL CH$_2$Cl$_2$. The solvent was removed from collected organic solution, and dried in vacuo overnight yield a brown gel. Triturating in pentane and methanol, separately, purified the gel to yield dark brown gel.

**Proposed Synthesis of 0.5% Diethynylbenzene Acetylide Crosslinked FPPtCl (CLAP1)**
A mixture of 0.1 g FPPtCl (0.09 mmol), 0.22 mL of a $1.79 \times 10^{-7}$ M solution of diethynylbenzene in DMF, 0.03 g 4-(tert-butyl)phenylacetylene, 0.04 g copper(I) iodide, and 0.5 mL diisopropylamine were reacted in 8 mL DMF. The reaction stirred at room temperature for 24 h under inert atmosphere, followed by opening to the air, and filtering away any solid. The dark brown DMF solution was then mixed with 50 mL of water, and extracted three times with 50 mL CH$_2$Cl$_2$. The solvent was removed from collected organic solution, and dried in vacuo overnight yield a brown gel. Triturating in pentane and methanol, separately, purified the product to yield dark brown gel.

**Proposed Synthesis of 1.0% Diethynylbenzene Acetylide Crosslinked FPPtCl (CLAP2)**

A mixture of 0.1 g FPPtCl (0.09 mmol), 0.23 mL of a $8.9 \times 10^{-5}$ M solution of diethynylbenzene in DMF, 0.03 g 4-(tert-butyl)phenylacetylene, 0.04 g copper(I) iodide, and 0.5 mL diisopropylamine were reacted in 8 mL DMF. The reaction stirred at room temperature for 24 h under inert atmosphere, followed by opening to the air, and filtering away any solid. The dark brown DMF solution was then mixed with 50 mL of water, and extracted three times with 50 mL CH$_2$Cl$_2$. The solvent was removed from collected organic solution, and dried in vacuo overnight yield a brown gel. Triturating in pentane and methanol, separately, purified the product to yield dark brown gel.

**Proposed Synthesis of 3.0% Diethynylbenzene Acetylide Crosslinked FPPtCl (CLAP3)**
A mixture 0.1 g \texttt{FPtCl} (0.09 mmol), 0.34 mL of a $8.0 \times 10^{-6}$ M solution of diethynylbenzene in DMF, 0.03 g 4-(tert-butyl)phenylacetylene, 0.04 g copper(I) iodide, and 0.5 mL diisopropylamine were mixed in 8 mL DMF. The reaction stirred at room temperature for 24 h under inert atmosphere, followed by opening to the air, and filtering away any solid. The dark brown DMF solution was then mixed with 50 mL of water, and extracted three times with 50 mL CH$_2$Cl$_2$. The solvent was removed from collected organic solution, and dried in vacuo overnight yield a brown gel. Triturating in pentane and methanol, separately, purified the product to yield dark brown gel.
SECTION 2: THE STUDY OF FLUORENE-BASED PHOSPHONIUM POLYELECTROLYTES
Chapter 5: Light Harvesting Phosphonium Polymer containing 1,4-dibromomethyl-2,5-dihexyloxybenzene (FPOHx)

2.5.1: CURRENT WORK IN THE FIELD

For some time now, π-conjugated materials have received incredible interest due to their exhibition of metal-like conductivities upon doping, and several others that show semiconducting properties.\textsuperscript{1-11} From this extensive research, many new applications of π-conjugated materials have arisen, including organic light emitting diodes,\textsuperscript{12-17} photovoltaic cells,\textsuperscript{18-22} nonlinear optical devices,\textsuperscript{1-21} polymeric sensor,\textsuperscript{1-21} and biological and medicinal applications,\textsuperscript{23-25} all of which have become increasingly more important with growing technological demand.

Despite such growth, however, few organophosphorus π-conjugated materials, specifically phosphonium polyelectrolytes, have been reported,\textsuperscript{26-35} which is surprising, as these polyelectrolytes have shown high quantum efficiency that could be harnessed for electronic device applications.\textsuperscript{36,37} More surprisingly, even fewer phosphonium polyelectrolytes with the phosphonium incorporated into the main chain of the polymer have been reported, except for the recent submitted work from our group, and Durben (Figure 2.5.1).\textsuperscript{35,38} Compared to phosphines, phosphonium salts are much easier to manipulate in a laboratory setting. They are very air stable, and can easily undergo a phosphonium linkage from a phosphine reacting with a benzyl or alkyl halide. As such, it would be rather facile to capitalize on polymerization from benzyl halide routes to achieve high yielding polymer reactions.\textsuperscript{38}
These polyelectrolytes polymerized from benzyl halides with the phosphonium incorporated into the main chain of the polymer or chromophoric species by Tennyson have been observed to have interesting red shift properties in absorption spectra from the phosphonium adding to the conjugation of the species, be readily layered with other charged species to create multilayer films for study, and they have shown interesting behavior like solvatochromism and aggregation in solution.\textsuperscript{38}

Capitalizing on this straightforward polymerization scheme, the emphasis of this chapter focuses on adding to the sparse knowledge of phosphonium polyelectrolytes with the charges incorporated into the main chain of the polymer. New phosphonium polyelectrolytes will be synthesized using a novel fluorene-based diphosphine (FP, discussed in Chapter 2) to design such polymers with a variety of conjugated linkers for study. These new polymers will also be used in layer-by-layer studies to investigate their film and charge transfer properties.
2.5.2: RESULTS AND DISCUSSION

Using the fluorene-based phosphine monomer (FP, Chapter 2), a new phosphonium polymer (FPOHx) was synthesized by reacting FP with 1,4-dibromomethyl-2,5-dihexyloxybenzene for 48 h in DMF at 90 °C (Scheme 2.5.1).

Scheme 2.5.1: The synthetic pathway to FPOHx.

Synthetic success for obtaining FPOHx was assessed via $^1$H and $^{31}$P NMR spectroscopy (Figure A-26, 27, 28). The $^1$H NMR spectrum was very similar to the spectrum presented for FP (Figure A-9), however, there were the emergence of signals at 6.93, 6.78, 5.25, 3.08, and 1.84 ppm. These new signals corresponded to the phenyl ring of the hexyloxy repeat unit, the methyl group off the hexyloxy unit, and the hexyloxy protons, respectively. The signals in the spectrum are also broad, indicating a polymer from the rise of an average of several signals in the same ppm range.

The $^{31}$P NMR spectrum also supported polymerization as the peak at −5.5 ppm shifted to a broad signal centered at ~21 ppm. The broadness of the signal for the phosphonium polymer is typical for polymers because the phosphorus centers have slightly different stereochemistry and environments about the phosphorous atom depending on their position in the chain (Figure 2.5.1). The signal at 29.9 ppm corresponds to the phosphine oxide end caps of the polymer. As the molecular weights of polyelectrolytes are well known for characterization challenges using standard
techniques like GPC,\textsuperscript{39} the degree of polymerization, $M_n$, and extent of polymerization (from the Carother’s equation) were calculated to be 27 repeat units, 35,700 Da, and 0.96, respectively, from utilizing the phosphine oxide end caps in the $^{31}$P NMR spectrum.

Photophysical data were collected for FPOHx with the help of Samantha Kristufek in the Summer Undergraduate Research Program (SURP) at Clemson University. As this polymer was very similar to the phosphonium polymer recently studied by Tennyson in our group (Figure 2.5.1 B),\textsuperscript{38} a comparative study was performed.

Tennyson’s polymer demonstrated a few interesting properties of solvatochromism, aggregation, and easy layer-by-layer assembly when paired with an oppositely charged species like poly(acrylic acid) (PAA). All of the phosphorous containing species produced by Tennyson, the phosphine and polymer, demonstrated a

\textbf{Figure 2.5.2:} The $^{31}$P NMR spectrum (CDCl$_3$, 121.4 MHz) of FPOHx.
red shift in absorption and emission maxima when compared to 1,4-dihexyloxy-2,5-bis(2-phenylethynyl)benzene, which featured the same \( \pi \)-system as the phosphorous analogues.\textsuperscript{38} The shifts in the spectra were determined to be effects of induction within the polymer, as participation of phosphorous lone pairs with appended \( \pi \)-systems is not generally strong.\textsuperscript{36-38,40,41} The red shift followed increasing electron withdrawing strength from phosphine, phosphine oxide, and to the phosphonium polymer.\textsuperscript{38}

The polymer synthesized for this chapter, FPOH\textsubscript{x}, also showed similar properties to the one synthesized by Tennyson and Smith. Photophysical data comparison of FPO, FP, and FPOH\textsubscript{x} show the progressive red shift like Tennyson observed (Figure 2.5.3).\textsuperscript{38}

\[\text{Figure 2.5.3:} \text{ The absorbance data for FP (} 2.92 \times 10^{-7} \text{ M), FPO (} 9 \times 10^{-6} \text{ M), and FPOH} \textsubscript{x} (1.17 \times 10^{-5} \text{ M) in CH} \textsubscript{2} \text{Cl} \textsubscript{2} \text{ demonstrating a progressive red shift.}\]

The investigations into solvatochromic properties were also performed, by collecting UV-Vis and photoluminescence spectra in acetonitrile, dichloromethane, tetrahydrafuran, water, and toluene (Table 2.5.1). FPOH\textsubscript{x} was not found to be soluble in
water or toluene without the presence of acetonitrile, however, FPOHx was found to be highly soluble in acetonitrile, THF, and CH₂Cl₂ in addition to the reaction solvent, DMF. As such, data were collected by dissolving FPOHx in acetonitrile, and then diluted in water and toluene until acetonitrile concentration was 5% \((1.75 \times 10^{-5} \text{ M})\) to induce solubility. All other solutions with only acetonitrile, dichloromethane, and tetrahydrofuran were prepared and diluted to \(1.75 \times 10^{-5} \text{ M}\) as well. The estimated optical band gap \((E_{\text{opt}})\) was determined by using wavelengths that were at \(\sim 0.05\) absorbance, and converted to electron volts. The \(E_{\text{opt}}\) values for FPOHx were larger than those reported for Tennyson’s polymer. This indicates that a larger band gap is observed with FPOHx, and hence more energy is required to place an electron in an excited state.

The variation of Stokes shifts for FPOHx in varying solvents was much lower

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>(\lambda_{\pi-\pi^*}^a)</th>
<th>(\log \epsilon)</th>
<th>(E_{\text{opt}}) (eV)(^b)</th>
<th>Stokes Shift(^a)</th>
<th>(\lambda_{\text{emit}}^a)</th>
<th>(\Phi)</th>
</tr>
</thead>
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<tr>
<td>FPO</td>
<td>CH₂Cl₂</td>
<td>339</td>
<td>4.82</td>
<td>3.32</td>
<td>40</td>
<td>379</td>
<td>0.845</td>
</tr>
<tr>
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<td>CH₂Cl₂</td>
<td>340</td>
<td>6.32</td>
<td>3.27</td>
<td>61</td>
<td>401</td>
<td>0.086</td>
</tr>
<tr>
<td>FPOHx</td>
<td>CH₃CN</td>
<td>349</td>
<td>4.81</td>
<td>3.19</td>
<td>71</td>
<td>420</td>
<td>0.350</td>
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<tr>
<td></td>
<td>CH₂Cl₂</td>
<td>352</td>
<td>4.75</td>
<td>3.13</td>
<td>68</td>
<td>420</td>
<td>0.017</td>
</tr>
<tr>
<td></td>
<td>THF</td>
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</tr>
<tr>
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<td>H₂O(^c)</td>
<td>346</td>
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<td>3.22</td>
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<td>0.006</td>
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<tr>
<td></td>
<td>CH₃Ph(^c)</td>
<td>361</td>
<td>4.58</td>
<td>2.67</td>
<td>48</td>
<td>409</td>
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</tr>
<tr>
<td>Film(^d)</td>
<td>356</td>
<td>NA</td>
<td>3.23</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

\(a\). Absorption / emission wavelengths and Stokes shift are provided in nm.

\(b\). The optical band gap in eV.

\(c\). Solutions contain 0.5% acetonitrile by volume from a concentrated stock solution to improve solubility for absorption spectra.

\(d\). Data provided from the tenth polymer layer (middle of the 20 bilayer assembly).

Table 2.5.1: Photophysical data for FPOHx and small molecule precursors in various solvents

than the polymer reported by Tennyson.\(^{38}\) Overall, this indicates that less energy should
be lost as heat, and emitted as photons instead. The quantum yields compare to those of
Tennyson,\textsuperscript{30} however, \textbf{FPOHx} had a higher quantum yield in both acetonitrile and
tetrahydrofuran. Despite lower stokes shifts, lower quantum yields were observed with
\(\text{CH}_2\text{Cl}_2\), \(\text{H}_2\text{O}\), and toluene. This observation can be attributed to fluorescence quenching
from heavy atom effects from increased counterion interaction with the phosphonium
polymer, which has been previously observed.\textsuperscript{42,43} Improvements to the quantum yields
of the polymer should be possible if the heavy atom effect can be removed, which will be
explored in Chapter 9.

Unfortunately, photoluminescent data for dropcasted films of \textbf{FPOHx} were not
obtainable due to our instrument not being able to detect such low fluorescence. However,
photoluminescent solution experiments demonstrated the polymer has solvatochromic
properties (Figure 2.5.4), which is not surprising due to the highly polar nature of the
polymer, and its range of solubility. In general there is a progressive red shift with
increasing solvent polarity, with the only exception being the water solution.

Despite the polar nature of water, a blue shift was observed compared to the other
solvents. This can best be explained by aggregation, which is indicated by the
significantly low quantum yield (0.006) and the rather broad emission band in the
photoluminescence spectra,\textsuperscript{38} as others have also observed a blue shift with increasing
aggregation of polyelectrolytes.\textsuperscript{44,45}
Layer-by-layer (LBL) experiments were also performed with FPOHx. The polymer was deposited on glass microscope slides with poly(acrylic) acid (PAA) or sodium poly[2-(3-thienyl)ethyloxy-4-butylsulfonate] (APT) as anionic placeholders between each FPOHx deposition. PAA was selected due to its nonemissive character, so the layering ability of the polymer could be monitored photophysically. The FPOHx/PAA LBL studies showed that the formed layers were well behaved with a linear increase in absorbance upon the addition of each new layer (Figure 2.5.5). Unfortunately, the linear increase of layering does not have a completely consistent increase in absorbance, which can be due to imperfections of the substrate or poor layering ability of the polyelectrolyte. As no or minimal shifting of absorbance maxima occurred, this shows that the top-most layer interacts with the previously added top layer in the same manner for every addition, suggesting that no π-system distorting conformational changes of the polyelectrolyte embedded chromophore are occurring.

**Figure 2.5.4:** Luminescence solvatochromism data, which also shows evidence of aggregation in water, and a progressive red shift with increasing solvent polarity.
Fluorescent spectra were also obtained for the LBL study; however, the data were too weakly emissive for our spectrometer to detect. In effect, fluorescent data was not considered for this study.

A.

![Fluorescent spectra graph]

B.

![Absorbance vs. Number of Bilayers graph]

**Figure 2.5.5:** The spectral data for the FPOHx/PAA LBL study showing UV-Vis spectra (A) and a plot of each additional layer added (B).
The FPOHx/APT showed similar results to the FPOHx/PAA LBL studies (Figure 2.5.5). The addition of each new bilayer increased in a linear fashion, and the layers also seem to be well behaved. Again, there are some problems with a very consistent increase in absorbance, which can be due to imperfections of the substrate or poor layering ability of the polyelectrolyte. As with the FPOHx/PAA bilayer study, there was little to no shift in absorption maxima after the addition of each new layer, demonstrating that each layer is interacting with the previously deposited layer and that no π-sytem distorting conformational changes of the polyelectrolyte embedded chromophore were present. All films still need to be assessed for uniformity and roughness, and will also be initially probed using AFM studies.
Figure 2.5.6: The spectral data for the FPOHx/APT LBL study showing UV-Vis spectra (A) and a plot of each additional layer added (B).
After performing the LBL studies of FPOHx with APT and PAA, 1:1 solutions of FPOHx:anionic polymer were made to investigate energy transfer ability between FPOHx and APT in solution. As PAA is not a luminescent anionic polymer, it was used as a control in comparing energy transfer between FPOHx and APT. The 1:1 solution of FPOHx:PAA when compared with just FPOHx in solution showed no shift in maximum emission, as expected (Figure 2.5.7).

![Emission Spectrum](image)

**Figure 2.5.7:** The FPOHx:PAA 1:1 solution (9 × 10^{-6} M:0.5% wt%) emission spectrum.

However, when the 1:1 FPOHx:APT and FPOHx solution were compared, there was a noticeable shift in the emission bands. A series of excitation wavelengths were used, and all the excitation wavelengths used to excite the 1:1 FPOHx:APT showed a single, broad emission band at 600 nm (Figure 2.5.8), which corresponds to the emission of APT provided by American Dye Source. By itself, FPOHx shows a strong emission band at 420 nm, and this band was not visible in any of the excitation wavelengths of the
1:1 solution. This indicates that full energy transfer is occurring in solution between FPOHx and APT, which is an exciting result. The relatively identical emission intensities from exciting at the optimal excitation wavelength for APT (435 nm) and FPOHx (350 nm) shows 100% energy transfer is occurring in the solution.

2.5.3: CONCLUSIONS AND FUTURE WORK

The newly synthesized and characterized FPOHx demonstrates comparable data with previous reported polyelectrolytes from our group. FPOHx demonstrates a higher quantum yield in acetonitrile and tetrahydrafuran, exhibiting lower stokes shift values, and higher band gap values, and aggregation was also observed in water solution with 5% acetonitrile, which was indicated by broad emission bands and rather low quantum yield.
values. In this case, the aggregation caused a visible blue shift of the emission maximum of the water solution compared to other polar solvents used in the study.

**FPOHx** also shows excellent behavior in LBL assemblies with PAA and APT, demonstrating a uniform addition of layers with little shifting of the absorbance bands, indicating that conformational changes are not occurring upon layering polyelectrolytes (Figures 2.5.6 and 2.5.7). In solution phase, complete energy transfer from **FPOHx** to APT was observed, which is an exciting observation, as the ability to promote energy transfer across the visible spectrum could be very useful in future design of light emitting diodes and solar cells.

Future investigations should include changing the counteranion of the polymer to probe the effects, especially if the counteranion were emissive rather than a deterrent for emission. This could lead to improvements in quantum yields, polymer properties, and potentially lead to more investigations into energy transfer in emission spectra. Chapter 9 will focus on investigations into this counteranion exchange along with the effects of such an occurrence with **FPOHx**.

2.5.4: EXPERIMENTAL

**General Considerations**

All air-sensitive reactions were performed using standard Schlenk techniques or in an MBraun UNILab glovebox under nitrogen atmosphere. Anhydrous solvents were purchased from Fisher Scientific, and were further dried, degassed, and purified using an MBraun solvent purification system. All other reagents were used as received unless
otherwise stated. All NMR spectra were obtained using a Bruker Avance 300 MHz (operating at 300, 75.4, and 121.4 MHz for $^1$H, $^{13}$C, and $^{31}$P nuclei) or a Bruker Avance 500 MHz (operating at 500, 125.7, and 202.4 MHz for $^1$H, $^{13}$C, and $^{31}$P nuclei) NMR spectrometer. NMR spectra are reported in ppm referenced to residual solvent signal ($^1$H, $^{13}$C) or 85% phosphoric acid ($^{31}$P). UV-Vis absorption spectra were acquired on a Cary 50 Spectrophotometer, while all photoluminescence spectra were collected on a Varian Eclipse fluorimeter in quartz cuvettes with a pathlength of 1 cm in specified solvents. Quantum yields ($\Phi$) for all compounds were calculated relative to quinine bisulfate in 0.1 M H$_2$SO$_4$ (aq) ($\Phi = 0.546$). Lifetime data were collected using an Easylife II lifetime fluorometer from Photon Technology International.

**Synthesis of Phosphonium phenyl-hexyloxy polymer (FPOHx)**

Fluorene diphosphine derivative (FP) was synthesized as described in Chapter 2. FP (0.202 g, 23.6 mmol) was mixed with 1,4-bromomethyl-2,5-hexyloxybenzene (0.100 g, 0.23 mmol) in 10 mL of DMF under inert atmosphere. The reaction was heated to 100 °C and stirred 48 hrs. After such time, the reaction was opened to the air, and the DMF removed via reduced pressure. The resulting brown goo was then dissolved in 20 mL of acetonitrile, followed by filtering away all solid, to get a pale amber-yellow solution mixture. The solvent was removed to get an off-white gel. The gel was purified further by trituration in an ether/pentane mix (1:1) to yield 0.201 g (65.0% yield) of white polymer powder. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 0.73$ (m, 10 H, fluorene-CH$_2$CH$_3$ hexyl chain $\times$ 2), 1.05 (s, 30 H, fluorene-CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$ $\times$ 2, phenyl-O-
CH₂CH₂CH₂CH₂CH₂CH₃ × 2), 1.84 (s, 4H, phenyl-O-CH₂CH₂CH₂CH₂CH₂CH₃ × 2), 2.06 (s, 4H, fluorene-CH₂CH₂CH₂CH₂CH₂CH₃ × 2), 3.08 (s, 4H, O-CH₂CH₂CH₂CH₂CH₂CH₃ × 2), 5.25 (m, 4H, phenyl-CH₂-P- × 2), 6.78 (s, 1H, aromatic), 6.93 (s, 1H, aromatic), 7.28-7.98 (m, 34 H, aromatic). ³¹P NMR (121.4 MHz, CDCl₃): δ = 29.9, 21.9, 21.3.

Layer-by-layer study of FPOHₓ and poly(acrylic acid)

A 1.75 x 10⁻⁵ M solution of FPOHₓ in acetonitrile and a 0.1% wt% solution of poly(acrylic acid) (PAA) in water (pH = 4) were prepared. Glass microscope slides (Fisher Brand) were cleaned by sonicating in CH₂Cl₂ for 15 min, followed by sonicating in HPLC grade water for 10 min. The microscope slide was allowed to air dry, then placed in a Cary UV-Vis spectrometer for blanking purposes. All experiments from this point forward were collected from 285 to 800 nm. FPOHₓ was first deposited on the microscope slide by dipping the glass into the FPOHₓ solution with a deposition time of a few seconds. The glass was air dried, and then an absorption spectrum was obtained. The microscope slide was then dipped into the 0.1% wt% solution of PAA for a few seconds, air dried, then an absorption spectrum was obtained. This process was repeated until the desired number of bilayers were deposited.

Layer-by-layer study of FPOHₓ and sodium poly[2-(3-thienyl)ethyloxy-4-butylsulfonate] (APT)
A 1.75 x 10^{-5} M solution of FPOHx in acetonitrile and a 0.1% wt% solution of poly[2-(3-thienyl)ethyloxy-4-butylsulfonate] (APT) in water (pH = 10) were prepared. All pH adjustments were made using Fisher pH 10 standard buffer solution. Glass microscope slides (Fisher Brand) were cleaned by sonicating in CH$_2$Cl$_2$ for 15 min, followed by sonicating in HPLC grade water for 10 min. The microscope slide was allowed to air dry, then placed in a Cary UV-Vis spectrometer for blanking purposes. All experiments from this point forward were collected from 285 to 800 nm. FPOHx was first deposited on the microscope slide by dipping the glass into the FPOHx solution with a deposition time of a few seconds. The glass was air dried, and then an absorption spectrum was obtained. The microscope slide was then dipped into the 0.1% wt% solution of APT for a few seconds, air dried, then an absorption spectrum was obtained. This process was repeated until the desired number of bilayers were deposited.

**Atomic Force Microscopy (AFM)**

AFM images were acquired using a Digital Instrument Multimode imaging in tapping mode with Olympus cantilevers of 170, spring constant of 42 N/m, and with resonance frequency at 300 kHz.
REFERENCES CITED


(41) Lucht, B. L.; St Onge, N. O. *Chem. Commun.* **2000**, *2097*.


Chapter 6: Counterion Exchange of FPOHx from Bromide to Fluorescein

2.6.1: CURRENT WORK IN THE FIELD

The effects of counterions on polyelectrolytes are well studied and recognized as having significant influence on polymer properties.\textsuperscript{1-4} The ions within the composition of the polyelectrolytes provide the electronic function that is not attainable from their neutral counterparts, like redistribution of electric fields within a device, for example.\textsuperscript{4}

From careful selection and design of polyelectrolytes paired with specific counterions, unique features can be emphasized for using such polymers in dye-sensitized solar cells (DSSCs),\textsuperscript{4,8-10} bulk heterojunction (BHJ) solar cells,\textsuperscript{4,8-10} light-emitting diodes (LED),\textsuperscript{4,11-13} light-emitting electrochemical cells (LECs),\textsuperscript{4} and organic thin film resistor (OTFR) applications.\textsuperscript{4,14-18}

The choice of counterion with the polyelectrolytes can also affect the photophysical properties and manipulation of polyelectrolytes. The Woo group have documented using conjugated polyelectrolytes as DNA sensors in solution by assessing the fluorescence resonant energy transfer (FRET) of polyelectrolytes with different counterions.\textsuperscript{19,20} The interaction of DNA with the polyelectrolyts of the Woo group is possible from the exchange of the counterions associated with the polymer for the negatively charged phosphate groups on DNA. The rate at which these counterions exchange has also been of interest in polyelectrolyte research.\textsuperscript{21-25}

Surprisingly, few phosphonium polyelectrolytes have been reported,\textsuperscript{26-36} and none of them have been studied to probe the effects of the counterion on the polyelectrolyte. Drawing inspiration from all of these previous findings, we chose to investigate the
effects of exchanging counterions of $\text{FPOH}_x$ (Chapter 5) by replacing the bromide counterion with fluorescein. By comparing $\text{FPOH}_x$ before and after the counterion exchange, we will observe any photophysical changes that occur as a result of the exchange. The goal is to improve the polyelectrolyte’s properties and range of absorption and emission by removing heavy atom counterions that can quench fluorescence, and replace the heavy atoms with strongly fluorescent counteranions.\textsuperscript{37-39} By carefully selecting the fluorescent counterion, we will demonstrate FRET between $\text{FPOH}_x$ and the fluorescein counterion, showing energy transfer across a wide range of the visible spectrum.

2.6.2: DISCUSSION AND RESULTS

Investigating the effects of changing the counteranion of $\text{FPOH}_x$ began by exchanging the bromide counterions for fluorescein dianion. The exchange was performed by stirring the polymer and fluorescein disodium salt in ethanol, driving the exchange by precipitation of sodium bromide to yield the counteranion exchanged polymer, $\text{FPOH}_x\text{F}$ (Scheme 2.6.1).

![Scheme 2.6.1: Reaction scheme for anion exchange to form $\text{FPOH}_x\text{-F}$](image)

$\text{FPOH}_x$ $\xrightarrow{\text{ethanol}}$ $\text{FPOH}_x\text{-F}$

$\text{Br}^-$ $\rightarrow$ Fluorescein $\rightarrow$ $\text{FPOH}_x\text{-F}$

$\text{Na}^+\text{Br}$
Exchange of the counterions was difficult to achieve, as solubility issues were a constant challenge. According to the work of Pinho and coworkers, sodium bromide is insoluble in ethanol.\textsuperscript{41} In the current work, we observed that it was essential to use anhydrous ethanol. However, anhydrous ethanol does not dissolve fluorescein disodium salt at all, even after stirring and gentle heating. Thus, a residual amount of water was necessary in the ethanol to dissolve the fluorescein salt. Consequently, the increased water in the solvent allowed the sodium bromide byproduct to remain soluble in solution, which was also observed by Pinho and coworkers.\textsuperscript{41}

The removal of the sodium bromide salt was achieved by mixing the ethanol reaction mixture with chloroform, followed by washing the mixture with water. As sodium bromide is far more soluble in water compared to chloroform, the byproduct could be removed while maintaining the desired product in the chloroform layer. When the chloroform layer was isolated and the solvent removed, the resultant bright red polymer was not soluble in water or chloroform without ethanol present. To remove excess fluorescein salt from the polymer, $\text{FPOH}_x\text{F}$ was triturated in water, which resulted in a bright red polymer.

This process was very successful in yielding the fluorescein exchanged polymer, $\text{FPOH}_x\text{-F}$. Success of exchange was monitored via color, solubility, $^1$H NMR spectroscopy, and UV-Vis and fluorescence spectroscopy. In terms of color, it was clear the polymer had undergone an exchange as $\text{FPOH}_x$ is white, and the addition of fluorescein caused $\text{FPOH}_x\text{-F}$ to be a bright cherry red, indicating fluorescein was present. As for solubility, $\text{FPOH}_x$ is highly soluble in chloroform, and after the
introduction of fluorescein, the solubility decreased to partial and or not soluble at all, unless ethanol was present. The exchanged polymer was found to be soluble in a 2.5:1 ethanol:chloroform mixture.

These observations coincided with the $^1$H NMR spectrum obtained for FPOHx-F (Figure 2.6.1, Figure A-30). The proton spectrum was similar to the spectrum obtained for FPOHx (Figure A-27), however, there were an increase of signals in the aromatic region between 6 and 7 ppm. The increase in peaks is due to the introduction of fluorescein as the counterion in the polymer. From these peaks, the extent of counterion exchange was determined by comparison to a signal at 2.14 ppm, (four protons in the hexyl chains off the fluorene unit) to indicate a 61% counterion exchange.

![Figure 2.6.1](image)

**Figure 2.6.1:** The $^1$H NMR spectrum (EtOD, 300 MHz) of FPOHx-F. Residual solvent and water peaks are marked with asterisks.
The $^{31}$P NMR spectrum for **FPOHX-F** did not change in comparison with the $^{31}$P NMR spectrum of **FPOHx**. This result was expected as the general environment bound to the phosphorous in the polymer did not change. However, instead of observing two averaged signals as with **FPOHx** (Figure A-29), only one averaged signal is observed for **FPOHx-F** (Figure 2.6.2). From the peak at 32.8 ppm, the $n$, $M_n$, and $p$ values were determined to be 9 repeat units, 11,768 g/mol, and 0.88.

![Figure 2.6.2: The $^{31}$P NMR spectrum (EtOD, 300 MHz) of FPOHx-F.](image)

Photophysical data were collected for **FPOHx-F** to probe energy transfer and quantum yield improvements by removing a heavy atom counterion (Table 2.6.1). The data in Table 2.3.1 indicate that there is an increase in the quantum yield between **FPOHx** and **FPOHx-F**, as the quantum yield of **FPOHx** in ethanol is significantly lower.
than FPOHx-F. All other values were relatively the same between FPOHx and FPOHX-F.

Further investigations into the extent of energy transfer between the polymer and the fluorescent counterion were carried out through fluorescence spectra (Figure 2.6.3, Figure 2.6.4, Figure B-34-36). Both fluorescein and FPOHx-F were excited at three wavelengths while maintaining the same slit widths. The wavelengths chosen were 349, 400, and 496 nm to observe how the spectra change from exciting at the ideal wavelength for FPOHx, a wavelength between the ideal wavelength of FPOHx, and fluorescein, and at the optimal excitation wavelength for fluorescein.

<table>
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<th>log $\varepsilon$</th>
<th>$E_{\text{opt}}$ (eV)</th>
<th>Stokes</th>
<th>$\lambda_{\text{emit}}$ (nm)</th>
<th>$\Phi$</th>
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<td>418</td>
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<td>71</td>
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<tr>
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<td>496</td>
<td>5.27</td>
<td>2.37</td>
<td>29</td>
<td>525</td>
<td>0.79$^a$</td>
</tr>
</tbody>
</table>

$^a$previously reported value$^{40}$

Further investigations into the extent of energy transfer between the polymer and the fluorescent counterion were carried out through fluorescence spectra (Figure 2.6.3, Figure 2.6.4, Figure B-34-36). Both fluorescein and FPOHx-F were excited at three wavelengths while maintaining the same slit widths. The wavelengths chosen were 349, 400, and 496 nm to observe how the spectra change from exciting at the ideal wavelength for FPOHx, a wavelength between the ideal wavelength of FPOHx, and fluorescein, and at the optimal excitation wavelength for fluorescein.
Figure 2.6.3: The fluorescence spectra for FPOHx-F obtained upon excitation at three different wavelengths.

Figure 2.6.4: The fluorescence spectra of fluorescein excited at three different wavelengths.
The fluorescence data shows successful energy transfer between the polymer and the fluorescent counterion. This is indicated in Figure 2.6.3 in how excitation at the optimal wavelength for \textbf{FPOHx} fluorescence at 349 nm gives almost equal intensity peaks for the polymer and fluorescein. When the intensities of the spectrum at 349 nm are compared with the other two wavelengths of 400 and 496, there is decreased fluorescence in general when excited at 400 nm, and only fluorescein is observed when excited at 496 nm. Comparing this data with the fluorescence data for fluorescein in Figure 2.6.4, decreased fluorescence is observed at 349 and 400 nm, while at 496 nm a strong peak is observed. Together, these spectra indicate that for fluorescein to be fluorescent while exciting at 349 nm that there needs to be energy transferred from the polymer to fluorescein. Thus, the goal of demonstrating energy transfer between \textbf{FPOHx} and fluorescein was achieved.

On a side note, the strength of the fluorescein emission band can be affected by making the solution more basic (Figure 2.6.5). Even by making the sample to contain 10% pH 10 buffer, the fluorescein emission dramatically increases when excited at 350, 400, and 496 nm. This shows we can effectively control the strength of the fluorescein emission even when it is interacting with \textbf{FPOHx}. 
As FPOHxF is a positively charged polyelectrolyte, the next set of experimentation included how well it could be used in layer-by-layer (LBL) studies. FPOHxF was subjected to dropcasted LBL deposition with poly (acrylic acid) (PAA) and sodium poly[2-(3-thienyl)ethyloxy-4-butylnsulfonate] (APT) on Fisher band microscope slides. Dropcast deposition was used in place dipping the slides for LBL deposition due to inconsistency in layering FPOHxF with the anionic polymers, which included FPOHxF washing off the microscope slide from dipping the microscope slide to add each layer. Where the absorbance and emission of fluorescein can be influenced by protonation (Figure 2.6.5), the LBL studies were performed in both acidic (pH = 4) and basic (pH = 10) for FPOHxF/PAA LBL studies, and only basic conditions for FPOHxF/APT LBL studies to show exhibited control of fluorescein in LBL studies.

Figure 2.6.5: Overlay of emission spectra of FPOHxF with and without 10% base in the samples excited at several wavelengths.
The FPOHxF/PAA LBL study showed a general linear trend in both the basic and acidic LBL studies (Figures 2.6.6-2.6.8). However, the absorbance is not perfectly linear in absorbance increase upon the addition of each new layer. This is due to the dropcasted LBL deposition perhaps not evenly spreading across the slide, or redistribution of FPOHxF layers on the slide from adding each layer. This indicates that FPOHxF does not behave ideally for LBL assembly, but can be manipulated to create the desired effects with some manner of consistency. Where the absorbance maxima does not shift with the addition of each additional layer, this shows that the layers are interacting with the previously deposited layer in the same manner, suggesting that there are no π-system distorting changes of the polyelectrolyte-embedded chromophore are not occurring.

These same observations were made for the FPOHxF/APT LBL studies. Overall, the absorbance increased in a general linear manner after the addition of each additional bilayer, suggesting that the top layer interacts with the layer previously deposited (Figure 2.6.8). The absorbance does not increase perfectly linear, which is due to the polymers not distributing evenly on the microscope slide, or due to redistribution during the addition of the next layer. Only basic (pH = 10) LBL studies were performed with APT, as we hoped to view energy transfer between FPOHxF and APT through emission spectra.

All films still need to be examined for their uniformity and roughness, and will be done so using AFM studies.
Figure 2.6.6: The spectral data for the FPOHxF/PAA (pH = 4) LBL study showing UV-Vis spectra (A) and a plot of each additional layer added (B) with outlier layers omitted.
Figure 2.6.7: The spectral data for the FPOHxF/PAA (pH = 10) LBL study showing UV-Vis spectra (A) and a plot of each additional layer added (B) with outlier layers omitted.
Figure 2.6.8: The spectral data for the FPOHxF/APT (pH = 10) LBL study showing UV-Vis spectra (A) and a plot of each additional layer added (B) with outlier layers omitted.
After completing the LBL studies of FPOHxF with PAA and APT, the energy transfer the FPOHxF to APT upon excitation with the appropriate wavelength. Again, a 1:1 ratio was used, to mix FPOHxF:PAA and FPOHxF:APT solutions (Figure 2.6.10). Solutions made with PAA were used as a control, where PAA is nonemissive. When comparing the two samples, it is clear that energy transfer is occurring between FPOHxF and APT, as in the emission spectra of the 1:1 FPOHxF:APT solution, there is a rather large emission band spanning from 480-680 nm, and no emission band present near 420 nm for FPOHx. The broadness of the band from 480-680 nm could be due to the APT and the fluorescein overlapping, which would allow the band to span over 525 and 600 nm, the emission wavelengths of APT and fluorescein. Overall, this demonstrates excellent FRET between FPOHxF and APT.
Figure 2.6.9: The emission spectra of the 1:1 solutions of \textbf{FPOHxF}:PAA (A) and \textbf{FPOHxF}:APT (B). Sharp emissions correspond to excitation of the sample.
2.8.2: CONCLUSIONS AND FUTURE WORK

By performing the counteranion exchange of bromide for fluorescein with FPOHx to make FPOHxF, successful energy transfer between the polymer and counterion, and an increase in quantum yield from counterion exchange, were demonstrated. This energy transfer allows for the emission of energy at two different wavelength ranges in the fluorescence spectrum (Figure 2.8.3).

Being able to control and provide a variety of wavelength ranges of emission energy is very important, as one of the biggest challenges with designing electronic devices like solar cells and OLEDs is achieving the desired wavelength range of absorption and emission.10 FPOHxF can contribute to defeating this challenge, and its polyelectrolyte nature can also be employed.

Layer-by-layer studies with FPOHxF show the polymer can behave in a desired manner, although not perfectly. FPOHxF needs to be dropcasted for LBL studies, as the polymer tends to be washed away from the dipping deposition technique. Despite, this difficulty, FPOHxF can be layered with anionic polymer such as APT and PAA with some degree of good behaviour. Solution experiments with FPOHxF and APT in a 1:1 ratio show energy transfer occurring between FPOHxF and APT, which is a very important result for future studies.
2.6.3: EXPERIMENTAL

General Considerations

All air-sensitive reactions were performed using standard Schlenk techniques or in an MBraun UNILab glovebox under nitrogen atmosphere. Anhydrous solvents were purchased from Fisher Scientific, and were further dried, degassed, and purified using an MBraun solvent purification system. All other reagents were used as received unless otherwise stated. All NMR spectra were obtained using a Bruker Avance 300 MHz (operating at 300, 75.4, and 121.4 MHz for $^1$H, $^{13}$C, and $^{31}$P nuclei) or a Bruker Avance 500 MHz (operating at 500, 125.7, and 202.4 MHz for $^1$H, $^{13}$C, and $^{31}$P nuclei) NMR spectrometer. NMR spectra are reported in ppm referenced to residual solvent signal ($^1$H, $^{13}$C) or 85% phosphoric acid ($^{31}$P). UV-Vis absorption spectra were acquired on a Cary 50 Spectrophotometer, while all photoluminescence spectra were collected on a Varian Eclipse fluorimeter in quartz cuvettes with a pathlength of 1 cm in appropriate solvents. Quantum yields ($\Phi$) for all compounds were calculated relative to quinine bisulfate in 0.1 M H$_2$SO$_4$ (aq) ($\Phi = 0.546$). Lifetime data was collected using an Easylife II lifetime fluorometer from Photon Technology International.

Synthesis of Fluorescein anion exchanged Phosphonium Hexyloxy polymer (FPOHxF)

FPOHxF (0.10 g, 0.08 mmol) and fluorescein sodium salt (0.03 g, 0.08 mmol) were dissolved in 10 mL of ethanol. The reaction mixture was stirred at room temperature for two hours, followed by adding 25 mL of CHCl$_3$. The orange solution was then washed with water until all washings were clear (5 × 100 mL). The solvent was removed via
reduced pressure, followed by trituration of the resulting red polymer in water for 12 hrs. The red polymer powder was collected and dried by vacuum to yield 0.90 g (0.6 mmol, 80% yield) of red-orange polymer powder. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 0.67$-$1.32$ (m, 55 H, hexyl chain, flourene$\_CH_2$CH$_2$CH$_2$CH$_2$CH$_3$ $\times$ 2, phenyl-O-CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$ $\times$ 2), 2.14 (s, 4H, fluorene$\_CH_2$CH$_2$CH$_2$CH$_2$CH$_3$ $\times$ 2), 3.14 (s, 4H, O-CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$ $\times$ 2), 5.25 (m, 4H, phenyl-CH$_2$-$P\_\times$ 2), 6.48-$6.97$ (m, 6H, aromatic fluorescein, ph-CH$_2$-ph $\times$ 2), 7.49-$8.05$ (m, 40 H, aromatic. $^{31}$P NMR (121.4 MHz, CDCl$_3$): $\delta = 21.5$ (phophonium polymer main chain), 32.8 (phosphine oxide endcaps).

**Layer-by-layer study of FPOHxF and poly(acrylic acid) (PAA)**

A 1.9 x $10^{-5}$ M solution of FPOHxF in ethanol and a 0.1% wt% solution of poly(acrylic acid) (PAA) in water (pH = 4, and pH = 10) were prepared. Adjustments to the pH were made using Fisher pH 10 buffer solution for the basic solution. Glass microscope slides (Fisher Brand) were cleaned by sonicating in CH$_2$Cl$_2$ for 15 min, followed by sonicating in HPLC grade water for 10 min. The microscope slide was allowed to air dry, then placed in a Cary UV-Vis spectrometer for blanking purposes. All experiments from this point forward were collected from 285 to 800 nm. FPOHxF was first deposited on the microscope slide by dropping the FPOHxF solution onto the glass slide, which was then air dried before obtaining an absorption spectrum. Then, the 0.1% wt% solution of PAA was dropped onto the glass slide, followed by air drying and obtaining an absorption spectrum. This process was repeated until the desired number of bilayers were deposited.
Layer-by-layer study of FPOHx-F and polythiophene (PT or APT)

A $1.9 \times 10^{-5}$ M solution of FPOHx in actetonitrile and a 0.1% wt% solution of polythiophene (PT) in water were prepared. Glass microscope slides (Fisher Brand) were cleaned by sonicating in CH$_2$Cl$_2$ for 15 min, followed by sonicating in HPLC grade water for 10 min. The microscope slide was allowed to air dry, then placed in a Cary UV-Vis spectrometer for blanking purposes. All experiments from this point forward were collected from 285 to 800 nm. FPOHx was first deposited on the microscope slide by dipping the glass into the FPOHx solution with a deposition time of a few seconds. The glass was air dried, and then an absorption spectrum was obtained. The microscope slide was then dipped into the 0.1% wt% solution of PT for a few seconds, air dried, then an absorption spectrum was obtained. This process was repeated until the desired number of bilayers were deposited. This process was performed for APT in basic (pH = 10) solution, which was adjusted using Fisher pH 10 buffer solution. Adjustments to the pH were made using Fisher pH 10 buffer solution.

Atomic Force Microscopy (AFM)

AFM images were acquired using a Digital Instrument Multimode imaging in tapping mode with Olympus cantilevers of 170, spring constant of 42 N/m, and with resonance frequency at 300 kHz.
REFERENCES CITED


(4) Duarte, A. P., Kan-Yi; Liu, Bin; Bazan, Guillermo *Chem. Mater. Rev.* **2010**.


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Chapter 7: Continued Study of Light Harvesting Phosphonium Polymers: 
Incorporation of 4,10-dibromomethyl bipyridine unit (FPBipy)

2.7.1: Introduction

Interest in organic polymers as potential semiconductors for a variety of applications began with the discovery of the electrical conductivity of polyacetylene (PA) (Figure 2.7.1) in 1977.¹ It was clear that the key to organic semiconductors was in furthering research of the design and development of new compounds with a conjugated backbone.¹,²

![Figure 2.7.1: The structure of polyacetylene (PA).](image1)

Shortly after the first work to produce PA films, research efforts began to focus on the synthesis and design of new PAs. New PAs were needed to overcome the challenges of insolubility, stability, and difficulties in isolation and characterization of the parent PAs.¹,³ This interest in designing more functional PAs continues to the present day, with a surge of design and development starting to take flight in the 1990s.¹

By this time, it was well documented that the design of the polymer could allow fine-tuning of the electro-optical properties of the polymer. More specifically, the choice of the monomer, steric hindrance within the polymer structure, and the addition of side chains in the monomer unit could control many properties, like solubility, which could dictate the potential application of the polymers. For example, organic field effect
transistors (FET) are devices that are very dependent upon the $\pi-\pi$ interactions for governing the mobility of the carrier, so design of an ideal FET would include strong orbital overlap among the $\pi$-backbone of the molecules.\textsuperscript{1,4} However, if a highly luminescent OLED were desired, then the strong interactions within the polymer chain should be avoided, as they can decrease luminescence efficiency, and materials with longer interchain distances should be employed instead.\textsuperscript{1,5}

The color that is absorbed or emitted from different polymeric species relates back to understanding the energy necessary to promote an electron to an excited state, which was founded by Max Planck and Albert Einstein. Planck was the German physicist that proposed the theory of quanta, or discrete packets of energy that can be emitted or absorbed as electromagnetic radiation, and Einstein developed the theory a step further by introducing the photoelectric effect. Einstein hypothesized that small, discrete packets of energy, or photons, bombarding a metal surface were responsible for emitting electrons, and a minimum frequency of light was required for emission to occur. He further hypothesized that these photons were the “quantized” energy packets proposed by Planck, and that they had energy that was proportional to the frequency of light, and thus, Equation 4 was born:

$$E = h\nu$$  \hspace{1cm} (4)\textsuperscript{6,7}

There are wide ranges of energies that can excite an electron to a higher energy state, all of which compose the electromagnetic spectrum (Figure 2.7.2). They range from gamma rays to radio waves, and are determined by the energy of photons absorbed based on the frequency of light of their origin. Various spectroscopic techniques can be
employed to study each range of light frequency in the electromagnetic spectrum,\textsuperscript{6,7} however, the focus here will be emphasized upon the ultraviolet and visible light spectra (UV-vis), which are important to consider, with regard to conjugated polymers, for OLED and photovoltaic applications.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{em_spec.png}
\caption{The electromagnetic spectrum showing the relationship between wavelength and photon energy.\textsuperscript{6,7}}
\end{figure}

The effects of conjugation within the polymer structure have a major impact on the applications of conjugated polymers (CP), especially in OLED and photovoltaic cells, as conjugation controls the color absorption and emission of a species. The effects of added conjugation within the polymer chain can best be understood from a molecular orbital standpoint. When adsorption or emission occur within a species, this deals directly from the promotion and relaxation of an electron between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Within each chemical species, there are relative energies to overcome for the electron promotion and relaxation, all of which deal directly with the type of bonds present, and where the HOMO and LUMO are ordered with respect to energy.\textsuperscript{8,9}
The energy of a single C-C bond to promote an electron from a σ to a σ* orbital is very high, as a σ–bond is a very strong bond due to the electron density lying between the two nuclei of the bonded atoms. When π-bonds are added to the system, this will change the relative energies to promote an electron from a ground state to an excited state, as the π-bonds are above and below the internuclear axis. This makes the π-bonds weaker in comparison to σ-bonds, from the electrons not being directly between the nuclei, and lowers the energy required for promotion from the HOMO to the LUMO, or from π–π* orbitals (Figure 2.7.3).\(^8,9\)

As the number of conjugated π-bonds increase within a chemical species, the more the conjugation will affect the absorbance and emission spectra for a given species. Conjugation causes the π and π* orbitals of each multiple bond in the species to combine
orbitals, and create new ordered energy sets for the bonding and antibonding orbitals. The result of this recombination causes the energy between the HOMO an LUMO to be significantly decreased in comparison to systems that have only σ–bonds or one π–bond (Figure 2.7.3). Due to this decrease in energy for electron promotion, the observation of light absorption and emission will shift in the electromagnetic spectrum. This shift observation can be seen Figure 2.7.2, where as the photon energy decreases, this leads to longer wavelengths of light absorbance and emission for a given chemical species.

The ability to control the shift of absorbance and emission from shorter to longer wavelengths is a key feature to designing CPs for different applications, because it allows for the CPs to be designed to absorb and emit at certain wavelengths within UV-Vis spectra. This ability to control the absorption and emission is not only important for color emission or energy storage purposes, like in OLEDs and solar cells, but to match the HOMO/LUMO energies, or have band gap overlap, with the anode and cathode within the device to allow for reduction and oxidation of CP material to occur. Achieving the desired band gap to optimize any CP emissive material is one of the greatest challenges in designing and utilizing new CPs, and is only one of the many considerations to incorporate into current research on CPs.

The properties of a CP can further be controlled by the functional groups present within the backbone structure of the polymer through electronic (electron donation or withdrawal) or via steric (from the interchain organization) effects. As such, much effort has been focused on efficiently tuning the optoelectronic structure for desired functions. One of the most widely employed strategies is the addition of bulky or
functional side chain substituents on the conjugated backbone (Figure 2.7.4). Closely following this strategy is the inclusion of structural variations within the polymer backbone, including modifications where phosphorous is included in the main chain of the polymer.\textsuperscript{11}

\[ \text{Poly(acytylene)} \quad \text{Poly}(\text{p-phenylenvinylene}) \quad \text{Poly}(\text{p-phenyleneethynylene}) \]

\[ \text{Poly(aniline)} \quad \text{Poly(pyrrole)} \quad \text{Poly(thiophene)} \]

\textbf{Figure 2.7.4:} The most common building blocks used in designing conjugated polymers.\textsuperscript{11}

Organophosphorous CPs are notable targets in the continuously growing field of organo-main group CPs. They have proven to be a valuable addition to building blocks for molecular electronics since the 1990s. Organophosphorous additions to CPs can greatly enhance the versatility of electronics from the conjugation ability of the phosphorous lone pair, which can also be functionalized for binding of transition metals, as the most common CP building blocks show in Figure 2.7.4 are not capable of achieving. However, despite the research and developments that have already been carried out, there is still the need for more research in this area to further develop the field of organophosphorous CPs.\textsuperscript{11}
Recent work has shown that phosphorous containing CPs have great potential for developing a variety of applications because of the ease of tuning their band gaps,\textsuperscript{13} increasing the quantum efficiency of electronic devices like OLEDs to nearly 100\% internal quantum efficiency,\textsuperscript{14} facilitating efficient white light emission,\textsuperscript{15} and manipulating photoluminescence characteristics through transition metal complexation.\textsuperscript{16} All of this research shows continued promise for CP containing phosphorous can be applied to electronic devices, and continuing research in this field, through phosphonium polyelectrolyte studies.

2.7.2: DISCUSSION AND RESULTS

FPBipy was synthesized from FP (Section 1.2.1), and 4,10-bis(dibromomethyl)bipyridine by heating in DMF for 24 h (Scheme 2.7.1) with the help of Samantha Kristufek from the 2010 Summer Undergraduate Research Program at Clemson University. The 4,10-bis(dibromomethyl)bipyridine was previously synthesized by Rhett C. Smith.

Scheme 2.7.1: The synthetic scheme of FPBipy.

The $^1$H and $^{31}$P NMR spectra for FPBipy both support the formation of the polymer (Figure A-34, Figure A-35). In the $^1$H NMR spectrum, the aliphatic region of the
spectrum from 0.54 to 2.50 ppm is comparable with that of the proton spectrum for FP, as the signals in that region should not change. Only separation of two peaks that overlap each other is of note. The emergence of a signal at 5.47 ppm that corresponds to the methyl group connecting the bipy unit to the phosphine unit, and the increase in relative integration of protons in the aromatic range of 7.56-8.29 indicate successful polymerization.

The $^{31}$P NMR spectrum indicated a shift from $-5$ ppm to 23.7 ppm also indicates the addition of the bipy unit to the phosphine unit. Unfortunately, the phosphorous spectrum does not provide a signal for the phosphine oxide endcaps like other polymers presented in this work. This makes it impossible to determine important values like $n$, $M_n$, and $p$. All that can be indicated from this result is that the polymer is of high molecular weight, where the repeat units are so high in number that they overshadow and indication of the phosphine oxide endcaps (Figure 2.7.5).

Figure 2.7.5: The $^{31}$P NMR spectrum (DMSO, 121.4 MHz) of FPBipy.
A series of photophysical data were collected using FPBipy are provided in Table 2.7.1. A reasonably high quantum yield was observed.

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<th>Compound</th>
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<th>λ_{emit} (nm)</th>
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</tbody>
</table>

Metal binding effects on UV-Vis spectra of layer-by-layer-deposited films were probed by binding Zn^{2+} with the bipy portion of the monomer and assembling with poly(acrylic acid) (PAA), sodium poly[2-(3-thienyl)ethoxy-4-butyloxysulfonate] (APT), or Poly[5-methoxy-2-(3-sulfopropoxy)-1,4-phenylenevinylene] potassium salt solution (PPV). Metal binding affects on UV-Vis and fluorescence spectra (Figure 2.7.6) indicate an increase or decrease in the absorption spectra depending upon the metal bound, and the fluorescence spectra show a decrease in fluorescence when any metal is bound. Overall, this shows the polymer can be used for indication of metal presence, especially from the fluorescence spectra.
The bilayer studies of FPBipy with and without Zn$^{2+}$ bound before layering with poly (acrylic acid) (PAA), poly[5-methoxy-2-(3-sulfopropoxy)-1,4-phenylenevinylene] potassium salt solution (PPV), and sodium poly[2-(3-thienyl)ethyloxy-4-butylsulfonate] (APT) all show a generally linear, successive increase in the absorption spectra upon each
added layer (Figures 2.7.7-2.7.12). All polymer LBL films were generated by dissolving the polymer in DMSO and diluting with ethanol. DMSO was the only option, as FPBipy has limited solubility outside the reaction solvent, DMF.
Figure 2.7.7: The absorbance spectra (A) and linear plot (B) of LBL studies for FPBipy/PAA without Zn\textsuperscript{2+} bound.
Figure 2.7.8: The absorbance spectra (A) and linear plot (B) of LBL studies for 
FPBipy/PPV without Zn$^{2+}$ bound.
A.

Figure 2.7.9: The absorbance spectra (A) and linear plot (B) of LBL studies for FPBipy/APT without Zn$^{2+}$ bound.
Figure 2.7.10: The absorbance spectra (A) and linear plot (B) of LBL studies for FPBipy/PAA with Zn\textsuperscript{2+} bound.
Figure 2.7.11: The absorbance spectra (A) and linear plot (B) of LBL studies for FPBipy/PPV with Zn$^{2+}$ bound.
Despite the observance of linear increase in absorbance upon each new layer added, the layering does not have a consistent increase in absorbance, especially in the

**Figure 2.7.12:** The absorbance spectra (A) and linear plot (B) of LBL studies for FPBipy/APT with Zn$^{2+}$ bound.
LBL studies without Zn\(^{2+}\) bound, which could be due to imperfections of the substrate or poor layering of the polyelectrolyte within the first ten layers. As the polymer layers are exactly ten with the anionic polyelectrolyte and FFBipy, the observation of inconsistent absorption increase is plausible.\(^{17}\) However, for the LBL studies without Zn\(^{2+}\) bound to FFBipy prior to layering with PAA, PPV, or APT could also be affected by binding the countercation to the anionic polymers.

Nitrogen containing metal ligands tend to be borderline or hard according to hard soft acid base theory, which means these ligands will only bind with borderline or hard metals. Bipyridine is a hard nitrogen-containing ligand, and will therefore bind very well with hard metals. The countercations of sodium and potassium from PPV and APT are both hard metals, and will easily bind with the bipyridine. When these metals are bound, they would prefer an octahedral geometry, which could affect the ability of the polymer to layer in a behaved manner with an anionic polymer. This is due to the octahedral geometry having ligands above and below the x-y plane, which can further the distance of the positive-negative interactions of the polymers for layering. Overall, this could explain why the LBL studies with Zn\(^{2+}\) layer more consistently and with more linear increases in absorbance after the addition of each additional layer. When Zn\(^{2+}\) is coordinated, this \(d^{10}\) metal will prefer a tetrahedral geometry, which may not be as sterically encumbering for LBL assembly. These ideas agree well with the presented data in Figures 2.7.7-2.7.12.

To explain the FFBipy/PAA without Zn\(^{2+}\) bound LBL studies, the bipyridine ligand embedded chromophore could have rotation about single bonds (Figure 2.7.13).
By rotating about the bonds, the ligand will then form two intersecting planes within the polymer, instead of having a flat ligand within one plane. These rotations about the bonds, especially if the nitrogens in the ligand were protonated due to the acidic environment of the PAA solution, could affect layering behaviour of the polymers, and possibly explain why the linearity of the LBL is lower than those with Zn\(^{2+}\) bound.

![Figure 2.7.13: Representation of the bond rotation within the bipyridine ligand, which creates two intersecting planes within the ligand.](image)

Also, no or minimal shifting of absorbance maxima occurred upon layering. This suggests that each layer interacts with the previous layer in the same manner for every addition, and that little conformational change in the \(\pi\)-conjugated segments is occurring (Figures 2.7.7-2.7.12). The uniformity and roughness of the films still needs to be studied, and will be done using atomic force microscopy.

After performing the LBL studies, we also examined 1:1 solutions of **FPBipy** (with and without Zn\(^{2+}\)) with PAA, PPV, or APT to probe energy transfer ability between **FPBipy** and PPV and APT (Figure 2.7.14). The 1:1 **FPBipy**:PAA solution was used as a control as PAA is a nonemissive anionic polymer. The emission spectra for the solutions showed no energy transfer between **FPBipy** and PPV, which was indicated by the lack of an emission band at 525 nm for PPV upon excitation at 420 nm. **FPBipy** and APT,
however, showed significant energy transfer was occurring, as indicated by the emission band at 600 nm in addition to the emission band at 420 nm. Where there are two bands present when the ample is excited at the optimal wavelength for FPBipy (350 nm), this shows partial energy transfer is occurring. The emission band at 600 nm corresponds to the emission band of APT, which has an emission band higher in intensity than the emission band for FPBipy. Overall, this indicated that the majority of the energy is transferred from FPBipy to APT in solution.
Figure 2.7.14: Emission spectra for 1:1 solutions of FPBipy:PAA, FPBipy:PPV (A), and FPBipy:APT (B). Sharp emission bands at 350 nm are the result of exciting the sample.
2.7.3: CONCLUSIONS AND FUTURE WORK

FPBipy has been successfully synthesized and partially characterized. AFM studies of generated polymer films still need to be performed, and will be completed by Naresh Osti from Dr. Perhia’s group at Clemson University.

The results not only indicated successful synthesis of the polymer, but that the polymer can be used to detect the presence of metals, and can be easily layered with different anionic polyelectrolytes. Both of these qualities can be utilized to detect metals, and in layer-by-layer film studies. The film studies can be performed with layering the same cationic polyelectrolyte, like in the studies performed here, or with other polyelectrolytes. Perhaps this new polymer could even be used in the layer-by-layer study with FPOnxF to promote energy transfer across the visible spectrum.

2.7.4: EXPERIMENTAL

General Considerations

All air-sensitive reactions were performed using standard Schlenk techniques or in an MBraun UNILab glovebox under nitrogen atmosphere. Anhydrous solvents were purchased from Fisher Scientific, and were further dried, degassed, and purified using an MBraun solvent purification system. All other reagents were used as received unless otherwise stated. All NMR spectra were obtained using a Bruker Avance 300 MHz (operating at 300, 75.4, and 121.4 MHz for \(^1\)H, \(^{13}\)C, and \(^{31}\)P nuclei) or a Bruker Avance 500 MHz (operating at 500, 125.7, and 202.4 MHz for \(^1\)H, \(^{13}\)C, and \(^{31}\)P nuclei) NMR spectrometer. NMR spectra are reported in ppm referenced to residual solvent signal (\(^1\)H,
13C) or 85% phosphoric acid (31P). UV-Vis absorption spectra were acquired on a Cary 50 Spectrophotometer, while all photoluminescence spectra were collected on a Varian Eclipse fluorimeter in quartz cuvettes with a pathlength of 1 cm in appropriate solvent. Quantum yields (Φ) for all compounds were calculated relative to quinine bisulfate in 0.1 M H2SO4 (aq) (Φ = 0.546). Lifetime data was collected using an Easylife II Lifetime fluorimeter from Photon Technology International.

**Synthesis of FP-Bipy**

Under an inert atmosphere, a mixture of FP (0.1 g, 0.12 mmol) and 4,10-bis(dibromomethyl) bipyridine (0.31 g, 0.37 mmol) in 5 mL of degassed DMF. The reaction mixture was heated to 80 °C and stirred for 24 h. After such time, the reaction was cooled to room temperature, and 20 mL of ether was added to mixture to precipitate out yellow solid. The precipitate was collected and washed with ether to yield 0.094 g (68% yield, 0.08 mmol). 1H NMR (300 MHz, CDCl3): δ = 0.55-0.57 (m, 10H, hexyl chain, flourene– CH2CH2CH2CH2CH2CH2CH3 × 2), 0.98 (s, 12H, fluorene–CH2CH2CH2CH2CH2CH2CH3 × 2), 2.08 (s, 12H, fluorene– CH2CH2CH2CH2CH2CH2CH3 × 2), 5.47 (m, 4H, bipy-CH2-P × 2), 7.56-8.29 (m, 40H, aromatic fluorene and bipy). 31P NMR (121.4 MHz, CDCl3): δ = 23.7.

**FPBipy and PAA, APT, PPV layer-by-layer studies without Zn2+**

A stock solution of FPBipy containing 50 mg of FP-Bipy in 10 mL of DMSO was made and then diluted to 1.67 × 10^{-4} M with ethanol for the layer-by-layer studies. Three
anionic polyelectrolyte solutions, 0.1% wt% solution of poly(acrylic acid) (PAA), 0.1% wt% solution of sodium poly[2-(3-thienyl)ethyloxy-4-butylsulfonate] (APT) and 0.1% wt% of poly[5-methoxy-2-(3-sulfopropoxy)-1,4-phenylenevinylene] potassium salt solution (PPV) all in water (pH = 6) were also prepared. Glass microscope slides (Fisher Brand) were cleaned with tetrahydrofuran under sonication for 15 mins, followed by sonicating in HPLC grade water for 10 min. The glass slides were air-dried and then placed into a Cary 50 UV-Vis spectrometer for blanking purposes. Subsequent experiments were performed by scanning from 300 to 1100 nm. FPBipy was first deposited on the glass by dipping the microscope slide into the FPBipy solution for a few seconds. After air drying, the absorption spectrum was obtained. The glass slide was then submerged in the desired 0.1% anionic polyelectrolyte solution for a few seconds and air-dried. Once dry, the absorption spectrum was obtained. This process was repeated until the desired number of bilayers had been deposited for each bilayer study with the three different anionic polyelectrolytes.

**FPBipy and PAA, APT, PPV layer-by-layer (LBL) studies with Zn$^{2+}$**

A stock solution of FPBipy containing 20 mg of FP-Bipy and 5.8 mg Zn(ClO$_4$)$_2$ • 6H$_2$O in 10 mL of DMSO was made and then diluted to 1.75 × 10$^{-5}$ M (FPBipy) with ethanol for the LBL studies. Three anionic polyelectrolyte solutions, 0.1% wt% solution of poly(acrylic acid) (PAA), 0.1% wt% solution of sodium poly[2-(3-thienyl)ethyloxy-4-butylsulfonate] (APT), and 0.1% wt% of poly[5-methoxy-2-(3-sulfopropoxy)-1,4-phenylenevinylene] potassium salt solution (PPV) all in water (pH = 6) were also
prepared. Glass microscope slides (Fisher Brand) were cleaned with tetrahydrofuran under sonication for 15 mins, followed by sonicating in HPLC grade water for 10 min. The glass slides were air-dried and then placed into a Cary 50 UV-Vis spectrometer for blanking purposes. Subsequent experiments were performed by scanning from 300 to 1100 nm. **FPBipy** was first deposited on the glass by dipping the microscope slide into the **FPBipy** solution for a few seconds. After air drying, the absorption spectrum was obtained. The glass slide was then submerged in the desired 0.1% anionic polyelectrolyte solution for a few seconds and air-dried. Once dry, the absorption spectrum was obtained. This process was repeated until the desired number of bilayers had been deposited for each bilayer study with the three different anionic polyelectrolytes.

**FPBipy metal binding studies**

A 3.35 x 10⁻⁴ M solutions of **FPBipy** were prepared with 1:4.5 molar ratio of metals to bipy monomer from dissolving 0.094 g Zn(ClO₄)₂ • 6H₂O, 0.093 g Cu(ClO₄)₂ • 6H₂O, 0.078 g, Cd(ClO₄)₂ • 6H₂O, 0.119 g HgCO₂(CF₃)₂, 0.071 g Co(SO₄), 0.065 g EuCl₃ • 6H₂O into each solution. After preparation, each solution was placed in a Cary 50 Spectrophotometer for absorption spectra, and a Varian Eclipse fluorimeter for fluorescence spectra.

**Atomic Force Microscopy (AFM)**
AFM images were acquired using a Digital Instrument Multimode imaging in tapping mode with Olympus cantilevers of 170, spring constant of 42 N/m, and with resonance frequency at 300 kHz.
REFERENCES CITED


Chapter 8: Continued Studies of Light Harvesting Phosphonium Polymers:
Incorporating 9,10- anthryl Units (FPA)

2.8.1: DISCUSSION AND RESULTS

Synthesis of a new phosphonium polyelectrolyte was carried out by reacting FP (Section 1.2.1) with 9,10-bis(chloromethyl)anthracene in DMF for 48 hours (Scheme 2.8.1). As the reaction progressed, the product precipitated from solution as a yellow solid.

![Scheme 2.8.1: The synthetic route to FPA.](image)

Successful synthesis of FPA was assessed initially by $^1$H and $^{31}$P NMR spectroscopy. Some of the few existing impurities are shown in the $^1$H NMR spectrum. The signals at 2.73, 2.89, and 8.02 ppm correspond to DMF, the major impurity. All other peaks in the spectrum, other than the deuterated solvent, are easily explained as being a part of the polymer. The signals at 0.64, 0.94, and 2.06 ppm correspond to the hexyl chain off of the fluorene unit. The signal at 6.31 ppm is the methyl group...
connecting the phosphine to the anthracene linker in the polymer, and all signals occurring after that from 7.00 to 8.14 ppm correspond to the aromatic protons minus the DMF protons at 8.02 ppm (Figure 2.8.1).

The $^{31}$P NMR spectrum shows polymerization was successful, as the peak at –5 ppm has moved to 21.4 ppm (Figure 2.8.2). An interesting observation is that there is not a phosphine oxide endcap present in the spectrum, which is suggestive of a very high molecular weight polymer. As such, the extent of polymerization, average molecular weight, and the number of repeat units of the polymer could not be estimated from the spectrum. The absence of a visible endcap peak does, however, suggest a degree of polymerization greater than 20.

**Figure 2.8.1:** $^1$H NMR spectrum (DMSO, 300 MHz) of FPA.
Photophysical studies were performed on FPA, (Table 2.8.1). The polymer was also used in layer-by-layer assemblies with poly (acrylic acid) (PAA), poly[5-methoxy-2-(3-sulfopropoxy)-1,4-phenylenevinylene] potassium salt solution (PPV), and sodium poly[2-(3-thienyl)ethyloxy-4-butylsulfonate] (APT).

![Figure 2.8.2: The $^{31}$P NMR (DMSO, 121.4 MHz) spectrum of FPA.](image)

Photophysical studies were performed on FPA, (Table 2.8.1). The polymer was also used in layer-by-layer assemblies with poly (acrylic acid) (PAA), poly[5-methoxy-2-(3-sulfopropoxy)-1,4-phenylenevinylene] potassium salt solution (PPV), and sodium poly[2-(3-thienyl)ethyloxy-4-butylsulfonate] (APT).

Table 2.8.1: Photophysical Data of FPA

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\pi-\pi^*}$ (nm)</th>
<th>log $\varepsilon$</th>
<th>$E_{opt}$ (eV)</th>
<th>Stokes Shift (nm)</th>
<th>$\lambda_{emit}$ (nm)</th>
<th>$\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FPA</td>
<td>355</td>
<td>4.13</td>
<td>3.09</td>
<td>65</td>
<td>420</td>
<td>0.202</td>
</tr>
</tbody>
</table>

The absorbance and emission spectra showed unexpected results for containing an anthracene chromophore within the polymer (Figure 2.8.3). Both of the spectra show large, broad emission and absorption bands, which is different from known spectra of anthracene. A possible explanation for these results in the absorption and emission
spectra are from the anthracene chromophore being embedded in a polymer. This can cause a broad band from all of the repeated chromophores being in slightly different environments to blur the spectrum into seeing a large average of the emission or absorption area.

The LBL studies showed that FPA could be easily layered with anionic polymers like PAA, PPV, and APT (Figures 2.8.4-2.8.6). With the addition of each additional layer, the absorbance increases in a linear fashion, indicating that there is an increase in FPA with each bilayer addition with the anionic polymers. However, the increase in absorbance is not perfectly linear. This could be because of poor layering ability within the first ten layers of polymer, or substrate imperfections. Negligible shift of absorbance maxima occurred, indicating that the top layer is interacting with the previous layer in the

Figure 2.8.3: Absorption and emission spectra for FPA (DMSO). The sharp emission peak at 350 is due to the excitation peak.
same manner each time, and that there are not any conformational $\pi$-system distorting conformational changes of the polyelectrolyte occurring. The uniformity and roughness of the films still needs to be investigated, and will be done using atomic force microscopy (AFM).

Fluorescent spectra were also obtained for the bilayer study, however, the films’ emission intensity was too low to be observed by our equipment. Hence, the fluorescent data was not fully investigated for this study.
Figure 2.8.4: The absorbance spectra (A) and the linear plot (B) of the FPA/PAA LBL study.
Figure 2.8.5: The absorbance spectra (A) and the linear plot (B) of the FPA/PPV LBL study.
Figure 2.8.6: The absorbance spectra (A) and the linear plot (B) of the FPA/APT LBL study.
After completing the LBL studies of FPA with PAA, PPV, and APT, 1:1 ratio solutions of FPA with the respective anionic polymers were made to probe for energy transfer ability between FPA and PPV and APT. The 1:1 FPA:PAA solution was used as a control for comparison (Figure 2.8.7). When comparing the three solutions it is clear that energy transfer between FPA and APT is not occurring. This is shown by the emission band occurring at 415 nm with no emission bands present near 575 nm for APT when excited at 355 nm. However, the FPA:PPV solution could potentially have weak energy transfer occurring, but it is difficult to see as the emission band for FPA is broad and slightly extends over 525 nm, which is the emission wavelength of PPV.

These observations can be explained further through considering Marcus Theory, as absorbance and emission bands need to be aligned between two species for energy transfer to occur. In this case, the absorbance and emission of FPA and the anionic polyelectrolytes may not be well aligned for energy transfer, which is rather surprising as the absorbance of FPA is similar to other phosphonium polyelectrolytes presented in Section 2. Perhaps there are other interchain interactions occurring that are preventing efficient energy transfer.
Figure 2.8.7: The emission spectra for 1:1 FPA:APT (A), FPA:PPV (B), and FPA:PAA (B) solutions.
2.8.2: CONCLUSIONS AND FUTURE WORK

**FPA** has been synthesized, and partial characterization was presented. AFM studies, and determination of polymer characteristics such as extent of polymerization, average molecular weight, and number of repeat units still needs to be determined due to the polymer being of such high molecular weight no estimation could be made from the phosphorus-31 NMR spectrum.

Overall **FPA** presents as a well-behaved polymer with a simple synthesis. Although the polymer can be readily be utilized in LBL deposited films, **FPA** does not show energy transfer between the polymer and APT in solution compared to the other three phosphonium polyelectrolytes presented in Chapters 8-10, which was an interesting result. Perhaps if the LBL studies were repeated using an appropriate layering counterpart with overlap of the **FPA** absorbance with the new counterpart’s fluorescence range, more efficient energy transfer could be achieved between the layering polymers in solution and film form.

2.8.3: EXPERIMENTAL

**General Considerations**

All air-sensitive reactions were performed using standard Schlenk techniques or in an MBraun UNILab glovebox under nitrogen atmosphere. Anhydrous solvents were purchased from Fisher Scientific, and were further dried, degassed, and purified using an MBraun solvent purification system. All other reagents were used as received unless otherwise stated. All NMR spectra were obtained using a Bruker Avance 300 MHz
(operating at 300, 75.4, and 121.4 MHz for $^1$H, $^{13}$C, and $^{31}$P nuclei) or a Bruker Avance
500 MHz (operating at 500, 125.7, and 202.4 MHz for $^1$H, $^{13}$C, and $^{31}$P nuclei) NMR
spectrometer. NMR spectra are reported in ppm referenced to residual solvent signal ($^1$H,
$^{13}$C) or 85% phosphoric acid ($^{31}$P). UV-Vis absorption spectra were acquired on a Cary
50 Spectrophotometer, while all photoluminescence spectra were collected on a Varian
Eclipse fluorimeter in quartz cuvettes with a pathlength of 1 cm in appropriate solvent.
Quantum yields ($\Phi$) for all compounds were calculated relative to quinine bisulfate in 0.1
M $\text{H}_2\text{SO}_4$ (aq) ($\Phi = 0.546$). Lifetime data was collected using an Easylife II Lifetime
fluorimeter from Photon Technology International.

**Synthesis FPA**

A reaction vessel was charged with 0.1 g (0.12 mmol) of Fp, 0.27 g of 9,10-
bis(chloromethyl)anthracene, and 5 mL of degassed DMF. The reaction was then heated
to 100 °C, and stirred for 48 hrs. At which time, the reaction was allowed to cool to
room temperature, and the yellow precipitate that had formed during the reaction was
filtered from solution. The yellow solid was purified by triturating in chloroform to yield
0.103 g (78%) of bright yellow polymer powder. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 0.64$
(m, 10H, hexyl chain, flourene–CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$ x2), 0.94 (s, 12H, fluorene–
CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$ x2), 2.06 (s, 12H, fluorene–CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$ x2),
6.35 (m, 4H, anthracene–CH$_2$-P- x2), 7.00-8.14 (m, 57 H, aromatic flourene and
anthracene). $^{31}$P NMR (121.4 MHz, CDCl$_3$): $\delta = 21.4$. 

150
Layer-by-layer study of FPA and poly(acrylic acid)

A $1.75 \times 10^{-5}$ M solution of FPA in DMSO/ethanol solution and a 1% wt% solution of poly(acrylic acid) (PAA) in water (pH = 4) were prepared. The solution of FPA was prepared from first dissolving 50 mg of FPA in 10 mL of DMSO, followed by diluting with ethanol to the desired concentration. Glass microscope slides (Fisher Brand) were cleaned by sonicating in DCM for 15 min, followed by sonicating in HPLC grade water for 10 min. The microscope slide was allowed to air dry, then placed in a Cary UV-Vis spectrometer for blanking purposes. All experiments from this point forward were collected from 285 to 800 nm. FPA was first deposited on the microscope slide by dipping the glass into the FPA solution with a deposition time of a few seconds. The glass was air dried, and then an absorption spectrum was obtained. The microscope slide was then dipped into the 0.1% wt% solution of PAA for a few seconds, air dried, then an absorption spectrum was obtained. This process was repeated until the desired number of bilayers were deposited.

Layer-by-layer study of FPA and polythiophene (APT)

A $1.75 \times 10^{-5}$ M solution of FPA in DMSO/ethanol solution and a 1% wt% solution of polythiophene (PT) in water (pH = 4) were prepared. The solution of FPA was prepared from first dissolving 50 mg of FPA in 10 mL of DMSO, followed by diluting with ethanol to the desired concentration. Glass microscope slides (Fisher Brand) were cleaned by sonicating in DCM for 15 min, followed by sonicating in HPLC grade water for 10 min. The microscope slide was allowed to air dry, then placed in a Cary UV-Vis
spectrometer for blanking purposes. All experiments from this point forward were collected from 285 to 800 nm. **FPA** was first deposited on the microscope slide by dipping the glass into the **FPA** solution with a deposition time of a few seconds. The glass was air dried, and then an absorption spectrum was obtained. The microscope slide was then dipped into the 0.1% wt% solution of PT for a few seconds, air dried, then an absorption spectrum was obtained. This process was repeated until the desired number of bilayers were deposited.

**Layer-by-layer study of FPA and PPV**

A $1.75 \times 10^{-5}$ M solution of **FPA** in DMSO/ethanol solution and a 1% wt% solution of **PPV** in water (pH = 4) were prepared. The solution of **FPA** was prepared from first dissolving 50 mg of **FPA** in 10 mL of DMSO, followed by diluting with ethanol to the desired concentration. Glass microscope slides (Fisher Brand) were cleaned by sonicating in DCM for 15 min, followed by sonicating in HPLC grade water for 10 min. The microscope slide was allowed to air dry, then placed in a Cary UV-Vis spectrometer for blanking purposes. All experiments from this point forward were collected from 285 to 800 nm. **FPA** was first deposited on the microscope slide by dipping the glass into the **FPA** solution with a deposition time of a few seconds. The glass was air dried, and then an absorption spectrum was obtained. The microscope slide was then dipped into the 0.1% wt% solution of **PPV** for a few seconds, air dried, then an absorption spectrum was obtained. This process was repeated until the desired number of bilayers were deposited.
**Atomic Force Microscopy (AFM)**

AFM images were acquired using a Digital Instrument Multimode imaging in tapping mode with Olympus cantilevers of 170, spring constant of 42 N/m, and with resonance frequency at 300 kHz.
APPENDICES
Appendix A:

NMR SPECTRA
(1,4-iodophenyl)diphenyl phosphine oxide (IPO1) TRM-1-20; 02/11/10

Structure:

![Structure Diagram]

Figure A-1: $^1$H NMR spectrum (CDCl$_3$, 300 MHz) of IPO1. Solvent peak is marked with an asterisk.
(1,4-iodophenyl)diphenyl phosphine oxide (IPO1) TRM-1-20; 02/11/10

Structure:

![Structure of IPO1](image)

Figure A-2: $^{13}$C NMR spectrum (CDCl$_3$, 75 MHz) of IPO1. Solvent peaks are marked with an asterisk.
(1,4-iodophenyl)diphenyl phosphine oxide (IPO1) TRM-1-20; 02/11/10

Structure:

![Chemical Structure](image)

**Figure A-3:** $^{13}$C NMR spectrum (CDCl$_3$, 75 MHz) of IPO1 focused on the aromatic region.
(1,4-iodophenyl)diphenyl phosphine oxide (IPO1) TRM-1-20; 02/11/10

Structure:

![Structure Diagram]

**Figure A-4:** $^{31}$P NMR spectrum (CDCl$_3$, 121.4 MHz) of IPO1.
9,9-dihexyl-2,7-bis(4-(diphenylphosphino))-fluorene oxide (FPO) TRM-1-33; 03/12/10

Structure:

![Structure Diagram](image_url)

**Figure A-5:** $^1$H NMR spectrum (CDCl$_3$, 300 MHz) of FPO. Solvent peak is marked with an asterisk.
9,9-dihexyl-2,7-bis(4-(diphenylphosphino))-fluorene oxide (FPO) TRM-1-33; 03/12/10

Structure:

![Structure diagram]

**Figure A-6:** $^{13}$C NMR spectrum (CDCl$_3$, 125 MHz) of FPO. Solvent peaks are marked with an asterisk.
9,9-dihexyl-2,7-bis(4-(diphenylphosphino))-fluorene oxide (FPO) TRM-1-33; 03/12/10

Structure:

![Chemical Structure Image]

**Figure A-7:** $^{13}$C NMR spectrum (CDCl$_3$, 125 MHz) of FPO focused on the aromatic region.
9,9-dihexyl-2,7-bis(4-(diphenylphosphino))-fluorene oxide (FPO) TRM-1-33; 03/12/10

Structure:

Figure A-8: $^{31}$P NMR spectrum (CDCl$_3$, 121.4 MHz) of FPO.
9,9-dihexyl-2,7-bis(4-(diphenylphosphino))-fluorene (FP) TRM-1-89; 05/05/10

Structure:

![Chemical Structure](image)

Figure A-9: $^1$H NMR spectrum (CDCl$_3$, 300 MHz) of FP. Solvent peak is marked with asterisk.
9,9-dihexyl-2,7-bis(4-(diphenylphosphino))-fluorene (FP) TRM-1-33; 03/12/10

Structure:

![Structure Diagram]

Figure A-11: $^{31}$P NMR spectrum (CDCl$_3$, 121.4 MHz) of FP.
Platinum(II) based starting polymer (FPPtCl) TRM-1-35; 03/12/10

Structure:

![Structure diagram](image)

**Figure A-12**: $^1$H NMR spectrum (CDCl$_3$, 300 MHz) of FPPtCl. Solvent peak is marked with an asterisk.
Platinum(II) based starting polymer (FP\textsubscript{PPtCl}) TRM-1-35; 03/12/10

Structure:

![Chemical structure of FP\textsubscript{PPtCl}](image)

Figure A-13: \textsuperscript{31}P NMR spectrum (CDCl\textsubscript{3}, 121.4 MHz) of FP\textsubscript{PPtCl}. 
Platinum(II) based starting polymer (FPPtCl) TRM-1-35; 03/12/10

Structure:

![Structure Diagram]

**Figure A-14:** $^{31}$P NMR spectrum (CDCl$_3$, 121.4 MHz) of FPPtCl focused on peaks of interest.
Platinum(II) based starting polymer (cis FPPtCl) TRM-1-41; 03/19/10

Structure:

Figure A-15: $^1$H NMR spectrum (CDCl$_3$, 300 MHz) of cis FPPtCl. Solvent peak is marked with an asterisk.
Platinum(II) based starting polymer (*cis* FPPtCl) TRM-1-41; 03/19/10

Structure:

![Structure Diagram]

**Figure A-16:** $^{31}$P NMR spectrum (CDCl$_3$, 121.4 MHz) of *cis* FPPtCl.
Platinum(II) based starting polymer (cis FPPtCl) TRM-1-41; 03/19/10

Structure:

Figure A-17: $^{31}$P NMR spectrum (CDCl$_3$, 121.4 MHz) of cis FPPtCl focused on peaks of interest.
Platinum(II) based starting polymer (\textbf{FP}Pt\textbf{Cl}) TRM-1-63; 04/10/10

Structure:

![Chemical Structure Image]

**Figure A-18:** $^{31}$P NMR spectra (CDCl$_3$, 121.4 MHz) of FP\textbf{P}t\textbf{Cl} \textit{trans} and \textit{cis} formation over time.
Platinum(II) based starting polymer (trans FPPtCl) TRM-1-75; 04/16/10

Structure:

![Chemical Structure Image](image)

Figure A-19: $^1$H NMR spectrum (CDCl$_3$, 300 MHz) of trans FPPtCl. Solvent peak is marked with an asterisk.
Platinum(II) based starting polymer (*trans* FPPtCl) TRM-1-75; 04/16/10

Structure:

![Chemical Structure](image)

**Figure A-20:** $^{31}$P NMR spectrum (CDCl$_3$, 121.4 MHz) of *trans* FPPtCl.
Platinum(II) based starting polymer (trans FPPtCl) TRM-1-75; 04/16/10

Structure:

Figure A-21: $^{31}$P NMR spectrum (CDCl$_3$, 121.4 MHz) of trans FPPtCl focused on peaks of interest.
Platinum(II) acetylide polymer with butyl group (FPPtCC-C(CH₃)₃) TRM-1-81; 04/28/10

Structures:

Figure A-22: $^{31}$P NMR spectrum (CDCl₃, 121.4 MHz) of FPPtCC$^t$Bu polymer with phosphonium byproduct.
Platinum(II) acetylde polymer with NO$_2$ group (FPtCCNO$_2$) TRM-1-150; 06/21/10

Structure:

![Structure Diagram]

Figure A-23: $^1$H NMR spectrum (CDCl$_3$, 300 MHz) of FPtCCNO$_2$. No solvent peak was observable.
Platinum(II) acetylide polymer with NO$_2$ group (FP$\text{PtCC}$) TRM-1-150; 06/21/10

Structure:

Figure A-24: $^{31}$P NMR spectrum (CDCl$_3$, 121.4 MHz) of FP$\text{PtCCNO}_2$. 

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Platinum(II) acetylide polymer with NO$_2$ group (FPtCCNO$_2$) TRM-1-150; 06/21/10

Structure:

![Chemical Structure Diagram]

Figure A-25: $^{31}$P NMR spectrum (CDCl$_3$, 121.4 MHz) of FPtCCNO$_2$ focused on peaks of interest.
Platinum(II) acetylide polymer with NO₂ group (FPPTCl) TRM-1-154; 06/18/10

Structure:

Figure A-26: $^{31}$P NMR spectrum (CDCl₃, 121.4 MHz) of FPPTCl prior to chloride exchange to form FPPTCCNO₂.
Platinum(II) acetylide polymer with NO$_2$ group (FPPtCl) TRM-1-154; 06/18/10

Structure:

![Structure Diagram]

**Figure A-27:** $^{31}$P NMR spectrum (CDCl$_3$, 121.4 MHz) of FPPtCl prior to chloride exchange to form FPPtCCNO$_2$ focused on peaks of interest.
Platinum(II) acetylide polymer with NMe₂ group (FPPtCCNMe₂) TRM-1-160; 06/22/10

Structure:

Figure A-28: ¹H NMR spectrum (CDCl₃, 300 MHz) of FPPtCCNMe₂.
Platinum(II) acetylide polymer with NMe₂ group (FPtCCNMe₂) TRM-1-160; 06/22/10

Structure:

![Structure Diagram]

Figure A-29: $^{31}$P NMR spectrum (CDCl₃, 121.4 MHz) of FPtCCNMe₂.
Platinum(II) acetylide polymer with NMe\(_2\) group (FPPtCCNMe\(_2\)) TRM-1-154; 06/22/10

Structure:

![Structure diagram]

**Figure A-30:** \(^{31}\)P NMR spectrum (CDCl\(_3\), 121.4 MHz) of FPPtCCNMe\(_2\) focused on peaks of interest.
Platinum(II) acetylide polymer with NMe$_2$ group (FPtCCNMe$_2$) TRM-2-90; 11/18/10

Structure:

Figure A-31: $^{31}$P NMR spectrum (CDCl$_3$, 121.4 MHz) of FPtCCNMe$_2$. 
Platinum(II) acetylide polymer with NMe₂ group (\textbf{FPPtCCNMe₂}) TRM-2-90; 11/18/10

Structure:

![Structure diagram]

\textbf{Figure A-32:} \textsuperscript{31}P NMR spectrum (CDCl\textsubscript{3}, 121.4 MHz) of \textbf{FPPtCCNMe₂} focused on peaks of interest.
Platinum(II) acetylide polymer with Ph group (FPtCCPh) TRM-2-85; 11/10/10

Structure:

Figure A-33: $^1$H NMR spectrum (CDCl$_3$, 300 MHz) of FPtCCPh.
Platinum(II) acetylide polymer with Ph group (FPtCCPh) TRM-2-85; 11/10/10

Structure:

![Structure Diagram]

Figure A-34: $^{31}$P NMR spectrum (CDCl$_3$, 121.4 MHz) of FPtCCPh focused on peaks of interest.
Platinum(II) acetylide polymer with \(^t\)Bu group (FPPtCC\(^t\)Bu) TRM-2-72; 09/30/10

Structure:

![Structure Diagram]

Figure A-35: \(^1\)H NMR spectrum (CDCl\(_3\), 300 MHz) of FPPtCC\(^t\)Bu.
Platinum(II) acetylide polymer with $^t$Bu group (FPtCC$^t$Bu) TRM-2-72; 09/30/10

Structure:

![Structural diagram]

**Figure A-36:** $^{31}$P NMR spectrum (CDCl$_3$, 121.4 MHz) of FPtCC$^t$Bu.
Platinum(II) acetylide polymer with $^t$Bu group ($\text{FPPtCC}^t\text{Bu}$) TRM-2-72; 09/30/10

Structure:

![Chemical Structure](image)

**Figure A-37:** $^{31}$P NMR spectrum (CDCl$_3$, 121.4 MHz) of $\text{FPPtCC}^t\text{Bu}$ focused on peaks of interest.
Platinum(II) acetylide polymer with H (FPtCC-H) TRM-2-74; 09/30/10

Structure:

![Structure Diagram]

Figure A-38: $^1$H NMR spectrum (CDCl$_3$, 300 MHz) of FPtCC-H.
Light Harvesting Phosphonium Polymer 1 (FPOHx) TRM-1-87; 05/03/10

Structure:

![Structure Diagram](image)

Figure A-39: $^1$H NMR spectrum (CDCl$_3$, 300 MHz) of FPOHx. Solvent peak is marked with asterisk.
Light Harvesting Phosphonium Polymer 1 (FPOHx) TRM-1-87; 05/03/10

Structure:

![Structure diagram](image)

Figure A-40: $^{31}$P NMR spectrum (CDCl$_3$, 121.4 MHz) of FPOHx.
Light Harvesting Phosphonium Polymer 1 (\textbf{FPOHx}) TRM-1-87; 05/03/10

Structure:

\begin{center}
\includegraphics[width=\textwidth]{structure.png}
\end{center}

\textbf{Figure A-41}: $^{31}$P NMR spectrum (CDCl$_3$, 121.4 MHz) of \textbf{FPOHx} focused on peaks of interest.
Light Harvesting Phosphonium Polymer 1 (FPOHx) TRM-1-143; 06/07/10

Structure:

Figure A-42: $^{31}$P NMR spectrum (CDCl$_3$, 121.4 MHz) of FPOHx before exchanging the counteranion to fluorescein.
Light Harvesting Phosphonium Polymer 1 (FPOHx) TRM-1-143; 06/07/10

Structure:

![Structure Diagram]

**Figure A-43**: $^{31}\text{P}$ NMR spectrum (CDCl$_3$, 121.4 MHz) of FPOHx before exchanging the counterion to fluorescein focused on peaks of interest.
Light Harvesting Phosphonium Polymer 2 (FPOHx-F) TRM-1-156; 06/21/10

Structure:

Figure A-44: $^1$H NMR spectrum (EtOD, 300 MHz) of FPOHx-F. Solvent and water peaks are marked with asterisk.
Light Harvesting Phosphonium Polymer 2 (FPOHx-F) TRM-1-156; 06/21/10

Structure:

![Structure of FPOHx-F](image)

Figure A-45: $^{31}$P NMR spectrum (EtOD, 121.4 MHz) of FPOHx-F.
Light Harvesting Phosphonium Polymer 2 (FPOHx-F) TRM-1-156; 06/21/10

Structure:

Figure A-46: $^{31}$P NMR spectrum (EtOD, 121.4 MHz) of FPOHx-F focused on peaks of interest.
Light Harvesting Phosphonium Polymer 3 (FPBipy) SLK-1-21; 06/29/10

Structure:

![Chemical Structure Diagram]

**Figure A-47:** H NMR spectrum (DMSO, 300 MHz) of FPBipy. Solvent and water peaks are marked with asterisk.
Light Harvesting Phosphonium Polymer 3 (FPBipy) SLK-1-21; 06/29/10

Structure:

![Structure Diagram]

Figure A-48: $^{31}$P NMR spectrum (DMSO, 121.4 MHz) of FPBipy.
Light Harvesting Phosphonium Polymer 3 (FPBipy) SLK-1-21; 06/29/10

Structure:

![Structure diagram](image)

**Figure A-49:** $^{31}$P NMR spectrum (DMSO, 121.4 MHz) of FPBipy focused on peak of interest.
Light Harvesting Phosphonium Polymer 4 (FPA) TRM-1-181; 07/13/10

Structure:

Figure A-50: $^1$H NMR spectrum (DMSO, 300 MHz) of FPA.
Light Harvesting Phosphonium Polymer 4 (FPA) TRM-1-181; 07/13/10

Structure:

Figure A-51: $^{31}$P NMR spectrum (DMSO, 121.4 MHz) of FPA focused on peaks of interest.
Appendix B:

UV-VIS AND PHOTOLUMINESCENCE SPECTRA
9,9-dihexyl-2,7-bis(4-(diphenylphosphino))-fluorene oxide (FPO) TRM-1-33, 94; 03/12/10, 05/06/10

Structure:

![Structure of FPO](image)

**Figure B-1:** Normalized absorbance spectrum for FPO (CH$_2$Cl$_2$, 9 x 10$^{-6}$ M) showing a maximum absorbance at 338.9 nm.
9,9-dihexyl-2,7-bis(4-(diphenylphosphino))-fluorene oxide (FPO) TRM-1-33, 94; 03/12/10, 05/06/10

Structure:

![Structure Diagram]

Figure B-2: Normalized fluorescence spectrum for FPO (CH$_2$Cl$_2$) showing a maximum emission at 395.8 nm.
9,9-dihexyl-2,7-bis(4-(diphenylphosphino))-fluorene oxide (FPO) TRM-1-33, 94; 03/12/10, 05/06/10

Structure:

![Structure of FPO]

**Figure B-3:** Lifetime spectrum for FPO (CH$_2$Cl$_2$) showing data necessary for $\tau$ calculation.
9,9-dihexyl-2,7-bis(4-(diphenylphosphino))-fluorene (FP) TRM-1-89, 96; 05/05/10, 05/06/10

Structure:

Figure B-4: Normalized absorbance spectrum for FP (CH$_2$Cl$_2$, $2.92 \times 10^{-7}$ M) showing a maximum absorbance at 400 nm.
9,9-dihexyl-2,7-bis(4-(diphenylphosphino))-fluorene (FP) TRM-1-89, 96; 05/05/10, 05/06/10

Structure:

Figure B-5: Normalized fluorescence spectrum for FP (CH\textsubscript{2}Cl\textsubscript{2}) showing a maximum emission at 340 nm.
9,9-dihexyl-2,7-bis(4-(diphenylphosphino))-fluorene (FP) TRM-1-89, 96; 05/05/10, 05/06/10

Structure:

![Structure diagram]

**Figure B-6:** Lifetime spectrum for FP (CH₂Cl₂) showing data necessary for \( \tau \) calculation.
Platinum(II) based starting polymer (cis FPPtCl) TRM-1-35, 93; 03/12/10, 05/06/10

Structure:

![Structure Diagram]

**Figure B-7:** Normalized absorbance spectrum for cis FPPtCl (CH$_2$Cl$_2$, $9 \times 10^{-6}$ M) showing a maximum absorbance at 345 nm.
Platinum(II) based starting polymer (*cis FPPtCl*) TRM-1-35, 93; 03/12/10, 05/06/10

Structure:

![Structure of cis FPPtCl](image)

**Figure B-8:** Normalized fluorescence spectrum for *cis FPPtCl* (CH₂Cl₂) showing a maximum emission at 379 nm.
Platinum(II) based starting polymer *(cis FPPtCl)* TRM-1-35, 93; 03/12/10, 05/06/10

Structure:

![Structure diagram](image)

**Figure B-9**: Lifetime spectrum for *(cis FPPtCl) (CH₂Cl₂)* showing data necessary for τ calculation.
Platinum(II) based starting polymer (*trans* FPPtCl) TRM-1-75, 94; 04/16/10, 05/6/10

Structure:

![Structure Image](image)

**Figure B-10:** Normalized absorbance spectrum for *trans* FPPtCl (CH\(_2\)Cl\(_2\), 8.44 \times 10^{-7} \text{ M}\) showing a maximum absorbance at 343 nm.
Platinum(II) based starting polymer (trans FPPtCl) TRM-1-75, 94; 04/16/10, 05/06/10

Structure:

![Structure diagram](image)

**Figure B-11:** Normalized fluorescence spectrum for *trans FPPtCl* (CH₂Cl₂) showing a maximum emission at 399 nm.
Platinum(II) based starting polymer (trans FPPtCl) TRM-1-75, 94; 04/16/10, 05/06/10

Structure:

![Structure Diagram](image)

**Figure B-12:** Lifetime spectrum for trans FPPtCl (CH₂Cl₂) showing data necessary for τ calculation.
Platinum(II) based starting polymer (*trans FPPtCl*) TRM-1-75; 04/16/10; TRM-2-8; 07-10-10

Structure:

![Structure](image)

**Figure B13:** Normalized phosphorescence spectrum for *trans FPPtCl* (2-methyl THF) showing a maximum emission of 400 nm at 298 K.
Platinum(II) based starting polymer (*trans* **FPPtCl**) TRM-1-75; 04/16/10; TRM-2-8; 07-10-10

Structure:

![Structure diagram](image)

**Figure B-14:** Normalized phosphorescence spectrum for *trans* **FPPtCl** (2-methyl THF) showing a maximum emission at 395 nm at 77 K.
Platinum(II) acetylide polymer with NO$_2$ group ($\text{FPtCCNO}_2$) TRM-1-150,186; 06/21/10, 07/20/10

Structure:

Figure B-15: Normalized absorbance spectrum for FPtCCNO$_2$ (toluene, $8 \times 10^{-6}$ M) showing a maximum absorbance at 343 nm.
Platinum(II) acetylide polymer with NO$_2$ group (FPtCCNO$_2$) TRM-1-150,186; 06/21/10, 07/20/10

Structure:

Figure B-16: Normalized fluorescence spectrum for FPtCCNO$_2$ (toluene) showing a maximum emission at 400 nm.
Platinum(II) acetylide polymer with NO$_2$ group (FP$\text{PtCCNO}_2$) TRM-1-150,186; 06/21/10, 07/20/10

Structure:

Figure B-17: Lifetime spectrum for FP$\text{PtCCNO}_2$ (toluene) showing data necessary for $\tau$ calculation.
Platinum(II) acetylide polymer with NO$_2$ group (FPtCCNO$_2$) TRM-1-158 06/21/10; TRM-2-8 07-10-10

Structure:

![Structure Diagram]

**Figure B-18:** Normalized phosphorescence spectrum for FPtCCNO$_2$ (2-methyl THF) showing a maximum emission at 385 nm at 298 K.
Platinum(II) acetylide polymer with NO$_2$ group (FPPtCCNO$_2$) TRM-1-158 06/21/10; TRM-2-8 07-10-10

Structure:

Figure B-19: Normalized phosphorescence spectrum for FPPtCCNO$_2$ (2-methyl THF) showing a maximum emission at 535 nm at 77 K.
START INSERTING CHAPTER 3 SPECTRA
Phosphonium Polymer 1 (FPOHx) TRM-1-87; 06/21/10SLK-1-15; 06/15/10

Structure:

![Structure of FPOHx](image)

**Figure B-20:** Normalized absorbance spectrum for FPOHx (toluene, $1.17 \times 10^{-5}$ M) showing a maximum absorbance at 361 nm.
Phosphonium Polymer 1 (FPOHx) TRM-1-87; 06/21/10SLK-1-15; 06/15/10

Structure:

Figure B-20: Normalized fluorescence spectrum for FPOHx (toluene, $1.17 \times 10^{-5}$ M) showing a maximum absorbance at 361 nm.
Phosphonium Polymer 1 (FPOHx) TRM-1-87; 06/21/10  SLK-1-15; 06/15/10

Structure:

![Structure Diagram]

Figure B-21: Normalized absorbance spectrum for FPOHx (CH$_3$CN, $1.17 \times 10^{-5}$ M) showing a maximum absorbance at 349 nm.
Phosphonium Polymer 1 \textbf{(FPOHx)} TRM-1-87; 06/21/10 SLK-1-15; 06/15/10

Structure:

![Structure Diagram]

**Figure B-22:** Normalized fluorescence spectrum for \textbf{FPOHx} (CH$_3$CN, $1.17 \times 10^{-5}$ M) showing a maximum emission at 420 nm.
Phosphonium Polymer 1 (FPOHx) TRM-1-87; 06/21/10  SLK-1-15; 06/15/10

Structure:

![Structure Diagram]

**Figure B-23:** Normalized absorbance spectrum for FPOHx (CH$_2$Cl$_2$, 1.17 × 10$^{-5}$ M) showing a maximum absorbance at 352 nm.
Phosphonium Polymer 1 (FPOHx) TRM-1-87; 06/21/10  SLK-1-15; 06/15/10

Structure:

Figure B-24: Normalized fluorescence spectrum for FPOHx (CH₂Cl₂, 1.17 × 10⁻⁵ M) showing a maximum emission at 420 nm.
Phosphonium Polymer 1 (**FPOHx**) TRM-1-87; 06/21/10  SLK-1-15; 06/15/10

Structure:

![Structure Diagram]

**Figure B-25:** Normalized absorbance spectrum for **FPOHx** (THF, $1.17 \times 10^{-5}$ M) showing a maximum absorbance at 351 nm.
Phosphonium Polymer 1 (FPOHx) TRM-1-87; 06/21/10 SLK-1-15; 06/15/10

Structure:

![Structural formula of FPOHx](image)

**Figure B-26:** Normalized fluorescence spectrum for FPOHx (THF, $1.17 \times 10^{-5}$ M) showing a maximum emission at 405 nm.
Phosphonium Polymer 1 (FPOHx) TRM-1-87; 06/21/10 SLK-1-15; 06/15/10

Structure:

Figure B-27: Normalized absorbance spectrum for FPOHx (water, $1.17 \times 10^{-5}$ M) showing a maximum absorbance at 346 nm.
Phosphonium Polymer 1 (FPOHx) TRM-1-87; 06/21/10 SLK-1-15; 06/15/10

Structure:

![Phosphonium Polymer 1 Structure](image)

**Figure B-28:** Normalized fluorescence spectrum for FPOHx (water, $1.17 \times 10^{-5}$ M) showing a maximum emission at 396 nm.
Phosphonium Polymer 1 (FPOHx) TRM-1-170, 182; 07/1/10 , 07/09/10

Structure:

![Structure Image]

**Figure B-29**: Absorbance spectrum for FPOHx (ethanol, $2.8 \times 10^{-5}$ M) showing a maximum absorbance at 350 nm.
Phosphonium Polymer 1 (FPOHx) TRM-1-170, 182; 07/1/10, 07/09/10

Structure:

![Structure Diagram]

**Figure B-30:** Fluorescence spectrum for FPOHx (ethanol) showing a maximum emission at 418 nm.
Phosphonium Polymer 1 (**FPOHx**) TRM-1-87; 06/21/10  SLK-1-15; 06/15/10

Structure:

![Structure Diagram]

**Figure B-31**: Absorbance spectrum for the LBL of **FPOHx** and poly(acrylic acid) (1.75 × 10⁻⁵: 0.1% wt%) at a pH of 4.
Phosphonium Polymer 1 (FPOHx) TRM-1-87; 06/21/10 SLK-1-15; 06/15/10

Structure:

![Chemical structure of FPOHx](image)

**Figure B-32:** Absorbance spectrum for the LBL of FPOHx and sodium poly[2-(3-thienyl)ethyloxy-4-butylsulfonate] (APT) \((1.75 \times 10^{-5}; 0.1\% \text{ wt})\) at a pH of 10.
Phosphonium Polymer 1 (FPOHx) TRM-1-87; 06/21/10  SLK-1-15; 06/15/10

Structure:

Figure B-33: Absorbance spectrum for the 1:1 FPOHx:PAA (9.0 × 10^{-6}: 0.05% wt%) solution dropcast at pH 4 showing a maximum at 350 nm.
Phosphonium Polymer 1 (FPOHx) TRM-1-87; 06/21/10 SLK-1-15; 06/15/10

Structure:

![Structure diagram]

Figure B-34: Absorbance spectrum for the 1:1 FPOHx:PAA (9.0 × 10^{-6}; 0.05% wt%) solution at pH 4 showing a maximum at 350 nm.
Phosphonium Polymer 1 (FPOHx) TRM-1-87; 06/21/10  SLK-1-15; 06/15/10

Structure:

![Chemical Structure](image)

**Figure B-35:** Fluorescence spectrum for the 1:1 FPOHx:PAA solution at pH 4 showing a maximum at 420 nm.
Structure:

![Structure Diagram](image)

**Figure B-36:** Absorbance spectrum for the 1:1 FPOHx:APT (4.5 × 10^{-6}; 0.025% wt%) solution at pH 10 showing a maximum at 360 nm.
Phosphonium Polymer 1 (FPOHx) TRM-1-87; 06/21/10  SLK-1-15; 06/15/10

Structure:

![Chemical Structure](image)

**Figure B-37:** Absorbance spectrum for the 1:1 FPOHx:APT (4.5 × 10⁻⁶; 0.025% wt%) solution dropcast at pH 10 showing a maximum at 355 nm.
Phosphonium Polymer 1 *(FPOH)* TRM-1-87; 06/21/10  SLK-1-15; 06/15/10

Structure:

![Chemical structure of Phosphonium Polymer 1](image)

**Figure B-38:** Fluorescence spectrum for the 1:1 *FPOH*:APT solution at pH 10 showing a maximum at 605 nm from an excitation wavelength of 350 nm.
Phosphonium Polymer 1 (FPOHx) TRM-1-87; 06/21/10 SLK-1-15; 06/15/10

Structure:

Figure B-39: Fluorescence spectrum for the 1:1 FPOHx:APT solution at pH 10 showing a maximum at 615 nm from an excitation wavelength of 435 nm.
Phosphonium Polymer 2 (FPOHx-F) TRM-1-170, 182; 07/1/10, 07/09/10

Structure:

![Structure Diagram]

Figure B-40: Normalized absorbance spectrum for FPOHx-F (EtOH, 5.2 × 10⁻⁵ M) showing a maximum absorbance at 349 nm.
Structure:

Figure B-41: Fluorescence spectrum for FPOHx-F (EtOH) showing a maximum emission at 420 nm from excitation wavelength of 349 nm.
Phosphonium Polymer 2 (FPOHx-F) TRM-1-170, 182; 07/1/10, 07/09/10

Structure:

![Structure Image]

Figure B-42: Fluorescence spectrum for FPOHx-F (EtOH) showing a maximum emission at 518 nm from excitation wavelength of 400 nm.
Phosphonium Polymer 2 (FPOHx-F) TRM-1-170, 182; 07/1/10, 07/09/10

Structure:

![Structure Diagram]

**Figure B-43:** Fluorescence spectrum for FPOHx-F (EtOH) showing a maximum emission at 520 nm from excitation wavelength of 496 nm.
Fluorescein disodium salt TRM-1-182; 07/09/10

Structure:

![Fluorescein Disodium Salt Structure](image)

Figure B-44: Normalized absorbance spectrum for fluorescein disodium salt (EtOH, 5.2 \times 10^{-5} M) showing a maximum absorbance at 496 nm.
Fluorescein disodium salt TRM-1-182; 07/09/10

Structure:

![Structure Diagram](image)

**Figure B-45:** Fluorescence spectrum for fluorescein disodium salt (EtOH) showing a maximum emission at 520 nm from excitation wavelength of 349 nm.
Fluorescein disodium salt TRM-1-182; 07/09/10

Structure:

![Structure diagram](image)

**Figure B-46**: Fluorescence spectrum for fluorescein disodium salt (EtOH) showing a maximum emission at 520 nm from excitation wavelength of 400 nm.
Figure B-47: Fluorescence spectrum for fluorescein disodium salt (EtOH) showing a maximum emission at 520 nm from excitation wavelength of 496 nm.
Phosphonium Polymer 2 (FPOHx-F) TRM-1-170, 182; 07/1/10, 07/09/10

Structure:

![Structure diagram]

**Figure B-48:** Absorbance spectrum for LBL of FPOHx-F:PAA ($1.9 \times 10^{-5}$; 0.1% wt%) at pH 4.
Phosphonium Polymer 2 (FPOHx-F) TRM-1-170, 182; 07/1/10, 07/09/10

Structure:

![Structure of FPOHx-F](image)

Figure B-49: Absorbance spectrum for LBL of FPOHx-F:PAA (1.9 \times 10^{-5}; 0.1\% wt\%) at pH 10.
Phosphonium Polymer 2 (FPOHx-F) TRM-1-170, 182; 07/1/10, 07/09/10

Structure:

![Structure Diagram]

**Figure B-50**: Absorbance spectrum for LBL of FPOHx:F:APT (1.9 x 10^{-5}; 0.1% wt%) at pH 10.
Phosphonium Polymer 2 (FPOHx-F) TRM-1-170, 182; 07/1/10, 07/09/10

Structure:

Figure B-51: Absorption spectrum of the FPOHx-F dropcast film showing a maximum at 350 nm.
Phosphonium Polymer 2 (FPOHx-F) TRM-1-170, 182; 07/1/10 , 07/09/10

Structure:

![Structure Diagram]

**Figure B-52:** Absorption spectrum of the 1:1 FPOHx-F:PA (1 × 10^{-5}: 0.05% wt%) solution at pH 4 showing a maximum absorbance at 355 nm.
Phosphonium Polymer 2 (FPOHx-F) TRM-1-170, 182; 07/1/10, 07/09/10

Structure:

Figure B-53: Emission spectrum of the 1:1 FPOHx-F:PAA (1 × 10^{-5}; 0.05% wt%) solution at pH 4 showing a maximum emission at 525 nm from an excitation wavelength of 350 nm.
Phosphonium Polymer 2 (FPOHx-F) TRM-1-170, 182; 07/1/10, 07/09/10

Structure:

![Structure diagram]

**Figure B-54**: Absorbance spectrum of the 1:1 FPOHxF:PAA ($1 \times 10^{-5}$; 0.05% wt%) solution at pH 10 showing a maximum absorbance at 500 nm.
Phosphonium Polymer 2 (FPOHx-F) TRM-1-170, 182; 07/1/10 , 07/09/10

Structure:

![Structure diagram]

Figure B-55: Emission spectrum of the 1:1 FPOHxF:PAA (1 x 10^{-5}; 0.05% wt%) solution at pH 10 showing a maximum emission at 525 nm from an excitation wavelength of 350 nm.
Phosphonium Polymer 2 (FPOHx-F) TRM-1-170, 182; 07/1/10, 07/09/10

Structure:

![Structure Diagram]

Figure B-56: Absorption spectrum of the 1:1 FPOHxF:APT solution dropcast at pH 10 showing a maximum absorbance at 360 nm.
Phosphonium Polymer 2 (FPOHx-F) TRM-1-170, 182; 07/1/10, 07/09/10

Structure:

![Structure Diagram]

**Figure B-57:** Absorbance spectrum of the 1:1 FPOHxF:APT (1 $\times$ $10^{-5}$; 0.05% wt%) solution at pH 10 showing a maximum absorbance at 440 nm.
Phosphonium Polymer 2 (FPOHx-F) TRM-1-170, 182; 07/1/10, 07/09/10

Structure:

Figure B-58: Emission of spectrum the 1:1 FPOHxF:APT ($1 \times 10^{-5}$; 0.05% wt%) solution at pH 10 showing a maximum emission at 575 nm from an excitation wavelength of 350 nm.
Phosphonium Polymer 2 (FPOHx-F) TRM-1-170, 182; 07/1/10 , 07/09/10

Structure:

![Phosphonium Polymer 2 Structure](image)

**Figure B-59:** Emission of spectrum the 1:1 FPOHxF:APT (1 × 10^{-5}; 0.05% wt%) solution at pH 10 showing a maximum emission at 575 nm from an excitation wavelength of 435 nm.
Phosphonium Polymer 3 (FPBipy) SLK-1-15; 06/17/10

Structure:

![Structure Diagram](image)

**Figure B-60:** Absorbance spectrum for FPBipy (DMSO, 3.35 \times 10^{-5} M) showing a maximum absorbance at 353 nm.
Phosphonium Polymer 3 (FPBipy) SLK-1-15; 06/17/10

Structure:

![Chemical Structure](image)

Figure B-61: Emission spectrum for FPBipy (DMSO) showing a maximum emission at 415 nm.
Figure B-62: Absorbance spectrum for FPBipy and Zn$^{2+}$ (DMSO, $3.35 \times 10^{-5}$ M) showing a maximum absorbance at 353 nm.
Phosphonium Polymer 3 (FPBipy) SLK-1-15; 06/17/10

Structure:

![Structure diagram](image)

**Figure B-63:** Emission spectrum for FPBipy and Zn$^{2+}$ (DMSO) showing a maximum emission from an excitation wavelength of 353 nm.
Phosphonium Polymer 3 (FPBipy) SLK-1-15; 06/17/10

Structure:

![Structure Diagram](image)

**Figure B-64:** Absorbance spectrum for FPBipy and Hg$^{2+}$ (DMSO, $3.35 \times 10^{-5}$ M) showing a maximum absorbance at 353 nm.
Phosphonium Polymer 3 (**FPBipy**) SLK-1-15; 06/17/10

Structure:

![Structure Image]

**Figure B-65:** Emission spectrum for **FPBipy** and Hg$^{2+}$ (DMSO) showing a lack of maximum emission from exciting at 353 nm.
Phosphonium Polymer 3 (FPBipy) SLK-1-15; 06/17/10

Structure:

![Structure Diagram](image)

Figure B-66: Absorbance spectrum for FPBipy and Cd$^{2+}$ (DMSO, $3.35 \times 10^{-5}$ M) showing a maximum absorbance at 353 nm.
Figure B-67: Emission spectrum for FPBipy and Cd$^{2+}$ (DMSO) showing a maximum emission at 420 nm from an excitation wavelength of 353 nm.
Phosphonium Polymer 3 (FPBipy) SLK-1-15; 06/17/10

Structure:

![Structure diagram](image)

**Figure B-68:** Absorbance spectrum for FPBipy and Cu$^{2+}$ (DMSO, 3.35 x 10$^{-5}$ M) showing a maximum absorbance at 353 nm.
Phosphonium Polymer 3 (FPBipy) SLK-1-15; 06/17/10

Structure:

![Structure Diagram]

Figure B-69: Emission spectrum for FPBipy and Cu$^{2+}$ (DMSO) showing a maximum emission at 415 nm from an excitation wavelength of 353 nm.
Phosphonium Polymer 3 (FPBipy) SLK-1-15; 06/17/10

Structure:

![Structure Diagram]

**Figure B-70:** Absorbance spectrum for FPBipy and Co$^{2+}$ (DMSO, 3.35 × 10$^{-5}$ M) showing a maximum absorbance at 353 nm.
Phosphonium Polymer 3 (FPBipy) SLK-1-15; 06/17/10

Structure:

Figure B-71: Emission spectrum for FPBipy and Co$^{2+}$ (DMSO, $3.35 \times 10^{-5}$ M) showing a maximum emission at 415 nm from an excitation wavelength of 353 nm.
Phosphonium Polymer 3 (FPBipy) SLK-1-15; 06/17/10

Structure:

![Structure Diagram]

**Figure B-72:** Absorbance spectrum for FPBipy and Eu$^{3+}$ (DMSO, $3.35 \times 10^{-5}$ M) showing a maximum absorbance at 353 nm.
Phosphonium Polymer 3 (FPBipy) SLK-1-15; 06/17/10

Structure:

![Structure Diagram]

**Figure B-73:** Emission spectrum for FPBipy and Eu³⁺ (DMSO) showing a maximum emission at 418 nm from an excitation wavelength of 353 nm.
Phosphonium Polymer 3 (FPBipy) SLK-1-15; 06/17/10

Structure:

![Structure of FPBipy](image)

**Figure B-74:** Absorbance spectra for FPBipy-PAA bilayer study with Zn$^{2+}$ bound to FPBipy.
Structure:

![Structure Diagram]

**Figure B-75:** Absorbance spectra for **FPBipy**-APT bilayer study with Zn$^{2+}$ bound to **FPBipy**.
Phosphonium Polymer 3 (FPBipy) SLK-1-15; 06/17/10

Structure:

![Chemical Structure Diagram]

Figure B-76: Absorbance spectra for FPBipy-PPV bilayer study with Zn\(^{2+}\) bound to FPBipy.
Phosphonium Polymer 3 (FPBipy) SLK-1-15; 06/17/10

Structure:

![Structure Diagram]

Figure B-77: Absorbance spectra for FPBipy-PAA LBL study.
Figure B-78: Absorbance spectra for FPBipy-PPV LBL study.
Phosphonium Polymer 3 (FPBipy) SLK-1-15; 06/17/10

Structure:

Figure B-79: Absorbance spectra for FPBipy-APT LBL study.
Phosphonium Polymer 3 (FPBipy) SLK-1-15; 06/17/10

Structure:

![Structure Image]

**Figure B-80:** Absorbance spectrum for 1:1 FPBipy + Zn:PAA solution dropcast showing a maximum absorbance at 360 nm.
Phosphonium Polymer 3 (FPBipy) SLK-1-15; 06/17/10

Structure:

![Chemical Structure of Phosphonium Polymer 3 (FPBipy)](image_url)

**Figure B-81:** Absorbance spectrum for 1:1 FPBipy + Zn:PAA solution (8.75 × 10⁻⁶ M: 0.05%) showing a maximum absorbance at 355 nm.
Phosphonium Polymer 3 (**FPBipy**) SLK-1-15; 06/17/10

Structure:

![Chemical structure of Phosphonium Polymer 3 (**FPBipy**)](image.png)

**Figure B-82**: Emission spectrum for 1:1 **FPBipy** + Zn:PAA solution ($8.75 \times 10^{-6}$ M: 0.05%) showing a maximum emission at 420 nm from an excitation wavelength of 350 nm.
Phosphonium Polymer 3 (FPBipy) SLK-1-15; 06/17/10

Structure:

Figure B-83: Absorbance spectrum for 1:1 FPBipy + Zn:PPV solution dropcast showing a maximum absorbance at 350 nm.
Figure B-84: Absorbance spectra for 1:1 FPBipy + Zn:PPV solution (8.75 × 10⁻⁶ M: 0.05%) showing a maximum absorbance at 355 nm.
Structure:

Figure B-85: Emission spectrum for 1:1 FPBipy + Zn:PPV solution (8.75 × 10⁻⁶ M: 0.05%) showing a maximum emission at 415 nm from an excitation wavelength of 350 nm.
Phosphonium Polymer 3 (FPBipy) SLK-1-15; 06/17/10

Structure:

![Chemical Structure](image)

**Figure B-86:** Absorbance spectrum for 1:1 FPBipy + Zn:APT solution dropcast showing a maximum absorbance at 459 nm.
Phosphonium Polymer 3 (FPBipy) SLK-1-15; 06/17/10

Structure:

![Structure Diagram]

Figure B-87: Absorbance spectra for 1:1 FPBipy + Zn:APT solution (8.75 × 10⁻⁶ M: 0.05%) showing a maximum absorbance at 435 nm.
Phosphonium Polymer 3 (FPBipy) SLK-1-15; 06/17/10

Structure:

![Structure Diagram](image)

Figure B-88: Emission spectrum for 1:1 FPBipy + Zn:APT solution (8.75 × 10^{-6} M: 0.05%) showing a maximum emission at 355 nm from an excitation wavelength of 350 nm.
Phosphonium Polymer 3 (FPA) TRM-2-12; 09/03/10

Structure:

![Structure Diagram]

**Figure B-89:** Absorbance spectrum for FPA (DMSO, $4.4 \times 10^{-5}$ M) showing a maximum absorbance at 350 nm.
Phosphonium Polymer 3 (FPA) TRM-2-12; 09/03/10

Structure:

![Structure of Phosphonium Polymer 3 (FPA)](image)

Figure B-90: Emission spectrum for FPA (DMSO) showing a maximum emission at 420 nm from an excitation wavelength of 350 nm.
Phosphonium Polymer 3 (FPA) TRM-2-12; 09/03/10

Structure:

![Structure Diagram]

Figure B-91: Absorbance spectra for FPA:PAA (pH = 6) LBL study.
Phosphonium Polymer 3 (FPA) TRM-2-12; 09/03/10

Structure:

![Structure Diagram]

**Figure B-92:** Absorbance spectra for FPA:PPV (pH = 6) LBL study.
Phosphonium Polymer 3 (**FPA**) TRM-2-12; 09/03/10

Structure:

![Chemical Structure](image)

**Figure B-93**: Absorbance spectra for **FPA**:APT (pH = 6) LBL study.
Phosphonium Polymer 3 (FPA) TRM-2-12; 09/03/10

Structure:

Figure B-94: Absorbance spectrum for FPA (DMSO) dropcast showing a maximum absorbance at 355 nm.
Phosphonium Polymer 3 (FPA) TRM-2-12; 09/03/10

Structure:

![Chemical Structure](image)

Figure B-95: Absorbance spectrum for 1:1 FPA:PAA solution dropcast showing a maximum absorbance at 355 nm.
Structure:

![Structure Image]

**Figure B-96:** Absorbance spectrum for 1:1 FPA:PAA solution (8.75 × 10^{-6} M: 0.05%) showing a maximum absorbance at 355 nm.
Phosphonium Polymer 3 (FPA) TRM-2-12; 09/03/10

Structure:

Figure B-97: Emission spectrum for 1:1 FPA:PAA solution (8.75 × 10^{-6} M: 0.05%) showing a maximum emission at 425 nm from an excitation wavelength of 350 nm.
Structure:

![Structure Image]

**Figure B-98:** Absorbance spectrum for 1:1 FPA:PPV solution dropcast showing a maximum absorbance at 350 nm.
Phosphonium Polymer 3 (FPA) TRM-2-12; 09/03/10

Structure:

![Structure Diagram]

**Figure B-99:** Absorbance spectrum for 1:1 FPA:PPV solution (8.75 × 10^{-6} M: 0.05%) showing a maximum absorbance at 350 nm.
Phosphonium Polymer 3 (FPA) TRM-2-12; 09/03/10

Structure:

Figure B-100: Emission spectrum for 1:1 FPA:PPV solution (8.75 × 10^{-6} M; 0.05%) showing a maximum emission at 420 nm from an excitation wavelength of 350 nm.
Figure B-101: Absorbance spectrum for 1:1 FPA:APT solution dropcast showing a maximum absorbance at 355 nm.
Structure:

Figure B-102: Absorbance spectrum for 1:1 FPA:APT solution ($8.75 \times 10^{-6}$ M: 0.05%) showing a maximum absorbance at 345 nm.
Phosphonium Polymer 3 (FPA) TRM-2-12; 09/03/10

Structure:

![Structure Diagram]

Figure B-103: Emission spectrum for 1:1 FPA:APT solution (8.75 × 10^{-6} M: 0.05%) showing a maximum emission at 395 nm from an excitation wavelength of 350 nm.
Appendix C:

INFRARED SPECTRA
Platinum(II) based starting polymer (trans FPPtCl) TRM-1-75; 04/16/10

Structure:

Figure C-1: ATR IR spectrum of trans FPPtCl using a one-bounce diamond crystal.
Platinum(II) based starting polymer (*trans FPPtCl*) TRM-1-75; 04/16/10

Structure:

![Structure Diagram](image)

**Figure C-2:** ATR IR spectrum of *trans FPPtCl* using a one-bounce diamond crystal focused on region of interest.
Platinum(II) based starting polymer (cis FPPtCl) TRM-1-41; 03/19/10

Structure:

![Structure diagram]

**Figure C-3:** ATR IR spectrum of trans FPPtCl using a one-bounce diamond crystal.
Platinum(II) based starting polymer (*cis* FP*PtCl*) TRM-1-41; 03/19/10

Structure:

![Structure Diagram]

**Figure C-4**: ATR IR spectrum of *cis* FP*PtCl* using a one-bounce diamond crystal focused on region of interest.
Platinum(II) acetylide polymer with NO$_2$ group (FPtCCNO$_2$) TRM-1-150; 06/21/10

Structure:

Figure C-5: ATR IR spectrum of FPtCC-NO$_2$ using a one-bounce diamond crystal.
Platinum(II) acetylide polymer with NO$_2$ group (FPtCCNO$_2$) TRM-1-150; 06/21/10

Structure:

![Chemical Structure](image)

**Figure C-6:** Focused ATR IR spectrum of FPtCC-NO$_2$ using a one-bounce diamond crystal.