PHOTOPHYSICS OF CONJUGATED ORGANOMETALLIC SYSTEMS: PHOTOINDUCED ELECTRON AND ENERGY TRANSFER, TRIplet EXCITON DELocalization, AND PHOSPHORESCENT ORGanoGELATORS

By

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To my family
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We designed and synthesized several series of platinum acetylide oligomers. Their photophysical properties were studied by steady-state and time resolved methods towards the objective of studying exciton and charge transfer. The motivation of this research is to provide a clear understanding of the structure and dynamics of triplet excitons and charged states within conjugated systems that feature organometallic repeats.

First, a series of platinum acetylide oligomers that feature a donor-spacer-acceptor architecture was prepared to investigate photoinduced electron transfer dynamics. The thienylene or bithienylene segments (T1 or T2) were used as electron donors, and naphthalene diimides (NDI) were used as electron acceptors. The donor and the acceptor were connected by several platinum acetylide repeat units. Second, photoinduced energy transfer was studied within anthracene-based platinum acetylide oligomers. Third, triplet exciton delocalization was explored in a series of platinum tetrayne oligomers by varying the carbon chain length. Finally, the properties of triplet excitons and charged states were investigated in supramolecular aggregates (and gels) generated by self-assembly of tailored platinum acetylide oligomers that structurally feature long alkyl chains and amide functional groups.
The most important findings of this research are as follows: (i) Photoinduced electron transfer occurs via a direct or an indirect mechanism depending on the excitation wavelength; (ii) photoinduced energy transfer in the anthracene-based platinum acetylide oligomer occurs via a mechanism that starts from a singlet-triplet energy transfer followed by a triplet-triplet energy transfer; (iii) triplet excitons of the platinum tetracyne oligomers are localized and confined within two repeat units; (iv) in the triplet excited states of the aggregated oligomers, the chromophores interact only weakly and the rate of electron transfer is very rapid likely due to triplet exciton diffusion within closely packed oligomers.
CHAPTER 1
INTRODUCTION

This chapter is divided into two sections. The first section is an overview of basic concepts of photophysics, such as light absorption and emission, and photoinduced electron and energy transfer. The second section introduces platinum acetylides including synthetic methods and photophysical properties.

Basic Concepts of Photophysics

Light Absorption

The understanding of the nature of light started from Newton’s particle theory in the 17th century. Huygens first came up with the wave theory, but it was not accepted until the middle of the 19th century when Maxwell developed a new electromagnetic theory based on a set of equations. To explain his blackbody experiment, in 1900 Planck proposed a new theory in which he suggested that the distribution of energy was not continuous, but was restricted to certain values. Then, Einstein used the principle of quantization that was introduced by Planck to explain the photoelectric effects and concluded that radiation energy was localized in discrete “packets” (photons).

Today, we understand that the nature of light is electromagnetic waves and has wave-particle duality. When an atom or a molecule absorbs light, an electron on the outermost shell of the molecule is promoted to a higher energy level. The light frequency must match the molecular resonant frequency to promote the outmost electron. In other words, the energy of the absorbed light must equal to the energy difference of the two orbital levels involved in this transition. This is because the energy levels of the electrons in an atom or a molecule are not continuous but discrete. The relationship between the photon energy and its frequency is expressed by Equation 1-1.
\[ E = h\nu = \frac{hc}{\lambda} \]  

(1-1)

where \( h \) is Planck’s constant \((6.63 \times 10^{-34} \text{ J.s})\), \( \nu \) is the frequency \((\text{sec}^{-1})\) at which absorption occurs, \( c \) is the speed of light \((3.0 \times 10^8 \text{ m/s})\), and \( \lambda \) is the wavelength \((\text{m})\).

The absorption of light by materials follows Lambert-Beer’s law (Equation 1-2).

\[ A = -\log T = \epsilon l C \]  

(1-2)

where \( A \) is the absorbance (the intensity of light absorbed by molecules at a certain frequency), \( T \) is the transmittance, \( \epsilon \) is the molar absorptivity with units of \( \text{L.mol}^{-1}.\text{cm}^{-1} \), \( l \) is the light pathlength \((\text{cm})\), and \( C \) is the concentration of the absorbing species \((\text{mol.L}^{-1})\). Transmittance is the fraction of incident light at a specific wavelength that passes through a sample (Equation 1-3),

\[ T = \frac{l}{l_0} \]  

(1-3)

where \( I_0 \) is the intensity of the incident light and \( I \) is the intensity of the light coming out of the sample. Lambert-Beer’s law indicates the linear relationship between the absorbance and the concentration of an absorbing species.

From Equation 1-1, only photons with certain frequency can be absorbed by the molecule. Therefore, the absorption spectra should appear as sharp lines. In fact, the absorption bands in molecules usually appear as broad bands. The interpretation for this is given by the Franck-Condon principle.\(^3\)\(^4\) It states that electronic transitions \((10^{-15} \text{ s})\) occur more rapidly than nuclear motion \((10^{-13} \text{ s})\). The nuclear geometry re-adjustment takes place after the electronic transitions have occurred (Figure 1-1). Electronic transitions are vertical with respect to the nuclear geometry, meaning that the electron is excited to the upper state before the nuclei have had a chance to respond to the new electronic structure. As a result, the transition from the lowest vibrational level of the ground state to vibrational levels of the excited state occurs before the nuclei geometry re-equilibrates. The Franck-Condon principle is reflected in absorption spectra
as a series of vibrational bands. However, in solution, in particular in a polar solvent, these vibrational bands are not well resolved due to strong interactions between the excited molecules and solvent molecules, resulting in the loss of the vibronic structure and a broad featureless absorption band seen in the absorption spectrum.

Figure 1-1. Franck-Condon principle. The figure was adopted from Atkins

**Excited States**

The absorption of light by a molecule causes the excitation of the molecule from its ground state to its first excited state. From the excited state, the molecule first relaxes to the lowest vibrational level through thermal relaxation. In the ground state, the electrons are paired and opposite spin. When the electron is promoted to its excited state, its spin does not change due to spin restrictions. Consequently, the excited state formed is called singlet excited state ($S_1$). If the
spin of the excited electron flips, the spin momentum for the excited state becomes three and this process is called intersystem crossing. The resulting state is triplet excited state ($T_1$). Intersystem crossing is a forbidden process due to spin restrictions. However, strong spin-orbit coupling caused by heavy metals in organometallic molecules significantly increases the intersystem crossing yield and results in the increase of the triplet state yield. Platinum acetylide systems that are the focus of the present study are one of the examples.

Several pathways are involved in the excited state relaxation. A singlet excited state decays to the ground state with emission of light and this process is called fluorescence. Similarly, radiative decay of a triplet excited state is called phosphorescence. Non-radiative decay from excited states to the ground state releases energy by the form of heat and this process is called internal conversion. These processes can be illustrated in a Jablonski diagram (Figure 1-2). Moreover, excited state quenching via electron or energy transfer is another pathway of the deactivation of excited states, which will be addressed in detail below.

![Jablonski diagram](image)

**Figure 1-2.** Jablonski diagram showing the photophysical processes
Electron Transfer

Excited states may relax to the ground state by photoinduced electron transfer in the systems that have donor-acceptor characteristic. On the other hand, photoinduced electron transfer reactions are the most fundamental processes in artificial and natural systems. Photosynthesis of the living plant converts the solar energy to chemical energy and produces the oxygen in the Earth’s atmosphere. To mimic photochemical charge separation, synthetic electron donor-acceptor systems have been prepared to study photoinduced electron transfer.⁷

In photoinduced electron transfer, an electron migrates between a photoexcited molecule and a ground state molecule as shown in Figure 1-3. In this figure, D is the electron donor,

![Figure 1-3. Photoinduced electron transfer processes](image)

A is the electron acceptor and * denotes an excited state. The excited state can be an electron donor or acceptor. The energetics of electron transfer are determined by the redox potentials of D and A, as well as the energy of the excited state. Figure 1-4 indicates an energy diagram that describes electron transfer processes and decay pathways. First, either the donor or the acceptor is excited to its singlet excited state followed by rapid electron transfer to form a contact ion pair. The individual spin of the positive ion or negative ion is a doublet, but the overall spin of the ion pair is singlet or triplet. The contact ion pair decays via three pathways: (1) recombination and
return to the ground state; (2) form triplet state \((^3D^* \text{ or } ^3A^*)\); (3) separation to form isolated ion pair. The isolated ion pair eventually recombines again if no chemical reactions take place.\(^8,9\)

![Diagram of decay pathways of photoinduced electron transfer](image)

Figure 1-4. Decay pathways of photoinduced electron transfer\(^8,9\)

**Solution dynamics of photoinduced electron transfer.** Most studies on photoinduced electron transfer have been performed in solution phase. In solution, when either the donor or the acceptor is photoexcited, a series of short-lived ion-pair intermediates is created due to the interaction between an excited state and the ground state. The stability of the ion-pair intermediates depends on electrostatic and solvation effects. If an ion-pair is separated by several solvent molecules, the resulting pair of geminate ions is called a solvent-separated ion pair (SSIP). The driving force of electron transfer resulting in a SSIP is given by Rehm-Weller equation (Equation 1-4).

\[
\Delta G_{SSIP} = E_0^0(D^+/D) - E_0^0(A/A^-) - \Delta G^* + w_P - w_R \tag{1-4}
\]

where \(E_0^0(D^+/D)\) is the oxidation potential of the donor, \(E_0^0(A/A^-)\) is the reduction potential of the acceptor, \(\Delta G^*\) is the free-energy of the equilibrated excited-state, and \(w_P\) and \(w_R\) are the work
terms for electrostatic interaction in the product (P) and in the reactant (R) states, respectively. The work term \( w \) is expressed by Equation 1-5.

\[
w = \frac{Z_D Z_A e^2}{d_{cc} \varepsilon_s}
\]  

(1-5)

where \( Z_D \) and \( Z_A \) are the charges on the donor and the acceptor, \( d_{cc} \) is the centre-centre distance between the donor and the acceptor molecules, and \( \varepsilon_s \) is the static dielectric constant or permittivity of the solvent.

Rehm-Weller equation implies that electrostatic effects are more important in nonpolar solvents. In polar solvents, Coulombic attraction is reduced because the electrostatic attraction of a pair of ions is shielded by solvent molecules. Therefore, polar solvents are more favorable for ion dissociation into free ions.

In the conventional view of photoinduced electron transfer, the collision of neutral reactants within the solvent cage may form a contact ion pair (CIP) or an intimate charge-transfer complex (exciplex) depending on the structure of the reactants and the polarity of the solvent medium. An exciplex displays light emission that can be observed in the emission spectrum. In nonpolar solvents, because of favorable Coulombic and solvent effects, the collision of reactants within the solvent cage is usually favorable exciplex formation.

**Spin Dynamics of photoinduced electron transfer.** Photoinduced electron transfer can occur from both singlet and triplet excited states. The electron spin is usually conserved due to spin restrictions, that is, the overall spin of an ion pair will be singlet if electron transfer occurs from a singlet excited state and a triplet ion pair forms if electron transfer takes place from a triplet excited state. However, in certain cases, the singlet-triplet intersystem crossing of an ion pair can occur. The major factors that contribute to S-T conversion are hyperfine coupling, the Zeeman splitting, and spin-orbit coupling.\(^{10}\)
The energy separation or exchange interaction between singlet and triplet states (J) decreases exponentially with the distance between ions (Figure 1-5). The exchange interaction (J) tends to preserve the original spin orientation. When a force whose energy is stronger than J operates during electron transfer process, electron spin multiplicity changes and intersystem crossing occurs.

![Image of exchange interactions (J). T = Triplet state; S = Singlet state. The figure was adopted from Turro.](image)

| J ~ 60-80 Kcal/mol | J ≤ 0.1 kcal/mol | J < 10⁻⁴ kcal/mol | J << 10⁻⁴ kcal/mol |

Figure 1-5. Exchange interactions (J). T = Triplet state; S = Singlet state. The figure was adopted from Turro.

Hyperfine coupling is an electron-nuclear interaction. Spin-orbit coupling is an interaction that occurs when the magnetic moment changes by a magnetic field that is generated due to the orbital motion of electrons. Spin-orbit coupling becomes very important when the interacting electrons are on a single atomic nucleus. Therefore, spin-orbit coupling is usually not an important mechanism for intersystem crossing of an ion pair. The Zeeman splitting is an interaction due to the strength of an external magnetic field and it can induce a spin flip. With the increase of the strength of an external magnetic field, the Zeeman interaction splits the T⁺ and T⁻ sublevels away from T₀ (Figure 1-6).

When the energy gap between singlet and triplet (J) become smaller, that is, ΔE_{hf} > J, a spin flip takes place by hyperfine coupling. In the cases of solvent-separated ion pair and free ions, the intersystem crossing is operated by hyperfine coupling mechanism because J is
negligible at large distance. In the cases of contact ion pair or exciplexes, J becomes large due to small distance. Thus, spin-orbit coupling is the dominant mechanism for intersystem crossing.

Figure 1-6. Energy diagram of hyperfine coupling and the Zeeman splitting. The figure was adopted from Kavarnos.

With the increase of the strength of an external magnetic field, the Zeeman splitting inhibits intersystem crossing between S and T_+ or T_ and enhances intersystem crossing between S and T_0. The external magnetic effects can be useful in identifying the charged species (SSIPs, CIPs and exciplexes) in photoinduced electron transfer. When hyperfine coupling mechanism dominates intersystem crossing, the quantum yield of the triplet state that is produced by the recombination of the dissociated ion pair decreases with the strength of the external magnetic field. As a consequence, the precursor ion pair must slightly separate, so that ΔE_{hf} > J, such as SSIPs. On the other hand, when the triplet yield has no discernible effects by the change in magnetic-field strength, we can deduce that hyperfine coupling is not an important mechanism for intersystem crossing, that is, ΔE_{hf} < J. Thus, the precursor ion pair must be in close proximity, such as CIPs or exciplexes.
Marcus theory in rigid donor-acceptor molecular systems. The dependence of the rate of electron transfer within rigid donor-acceptor systems on the free energy of reaction and the electronic interaction between the donor and the acceptor are described well by Marcus theory as shown in Equation 1-6.\textsuperscript{12}

\[
\kappa_{ET} = \frac{2\pi}{\hbar} V_{DA}^2 \left( \frac{1}{(4\pi\lambda T)^2} \right) e^{-\frac{\left(\Delta G^0 + \lambda \right)^2}{4\lambda \kappa T}}
\]

where \(\Delta G^0\) is the free energy of reaction, \(V_{DA}\) is the electronic coupling between the donor and acceptor, and \(\lambda\) is the total energy of the nuclear reorganization (structure change) within the donor, acceptor and solvent required for the reaction to occur. Marcus theory predicts that the rate of electron transfer decreases when the driving force \((\Delta G^0)\) for electron transfer becomes very large (i.e., \(-\Delta G^0<<0\)). This is important for maximizing the rate of charge separation, while at the same time minimizing the rate of the energy-wasting charge recombination. Experimental evidence for the so-called Marcus “inverted region” has been obtained in rigid intramolecular systems.\textsuperscript{13}

Energy Transfer

Photoinduced energy transfer is an important pathway for the quenching of molecular emission in a bimolecular system. Unlike electron transfer, the excited state in energy transfer is exclusively an energy donor (Equation 1-7).

\[
D^* + A \rightarrow D + A^* \quad (1-7)
\]

where D is an energy donor, A is an energy acceptor and * denotes the excited state. The energy of D* must be higher than the energy of A* for energy transfer to be thermodynamically favorable. In general, there are four types of energy transfer according to the initial spin multiplicity of D* and final spin multiplicity of A*: singlet-singlet, triplet-triplet, triplet-singlet
and singlet-triplet. Energy transfer can operate by two mechanisms: dipole-dipole (Coulombic) mechanism and electron exchange mechanism.

Coulombic (Förster) energy transfer involves the mutual interaction of electrons and is dominated by long-range dipole-dipole interactions.\(^\text{14}\) The dipole-dipole interactions cause perturbation of the electronic structures of the energy donor and acceptor. Therefore, the oscillating dipole of excited energy donor interacts with the dipole of the acceptor and induces a corresponding dipole oscillation of the acceptor. The oscillation may finally lead to the excitation of the electron on the acceptor and a corresponding de-excitation of the excited electron on the donor (Figure 1-7).

Since mutual contact between the donor and the acceptor is not required, the dipole-dipole mechanism can be operative over large distance, sometimes greater than 50 Å (up to 100 Å). The Coulomionic mechanism of energy transfer does not involve “physical” contact between the donor and the acceptor. Therefore, the change of the spin multiplicity of both the donor and the acceptor is not allowed. Only singlet-singlet energy transfer can be operative under this mechanism.

\[ \text{D}^* \rightarrow \text{A} \rightarrow \text{D} \]

Figure 1-7. Coulombic energy transfer mechanism

Electron exchange (Dexter) energy transfer requires much closer contact between the donor and acceptor to allow for transfer of electrons.\(^\text{15}\) Energy transfer rate is limited by
molecular diffusion of $D^*$ and $A$ to within collision separations. Thus, the rate of energy transfer by electron exchange mechanism is diffusion controlled and is sensitive to the viscosity of the solvent. The mechanism is schematically represented as in Figure 1-8.

![Figure 1-8. Electron exchange energy transfer mechanism](image)

These two mechanisms may be distinguished by comparison of the rate constants for energy transfer ($k_{ET}$) and for diffusion ($k_{diff}$), then measuring the rate constant for energy transfer versus solvent viscosity. If $k_{ET}$ is comparable to or less than $k_{diff}$ and $k_{ET}$ is sensitive to solvent viscosity, then energy transfer is dominated by electron exchange mechanism. On the other hand, if $k_{ET}$ is significantly greater than $k_{diff}$ and $k_{ET}$ is insensitive to solvent viscosity, then a dipole-dipole energy transfer mechanism is applied.

Triplet-triplet energy transfer is forbidden by the dipole-dipole mechanism, but allowed by the electron exchange mechanism.\(^2\) In triplet-triplet energy transfer, an electronically excited donor in its triplet state produces an electronically excited acceptor in its triplet state as shown in Equation 1-8.

$$D^*(T_1) + A(S_0) \rightarrow D(S_0) + A^*(T_1) \quad (1-8)$$

Triplet-triplet energy transfer is the most common and most important type of energy transfer in organic photochemistry. It has been used to generate the triplet excited state of molecules which possess a low quantum yield for triplet formation. The long lifetimes of the triplet excited states
facilitate energy transfer processes. The rate constant for triplet-triplet energy transfer depends on the triplet energy difference between the donor and acceptor ($\Delta E_{T-T}$).

**Photophysical Properties of Molecular Aggregates**

Small molecules self-assemble into supramolecular assemblies by three noncovalent interactions: $\pi-\pi$ stacking, van der Waals interaction and hydrogen bonding. In certain cases, a low mass molecule can form extended structures leading to the gelation of the solvent in which the molecule is dissolved. The process of gelation initiates from self-association of the gelator molecules to form long, polymer-like fibrous aggregates. Then these fibers become entangled to form a matrix that traps the solvent by surface tension.\(^{16}\) Compared with small molecules, molecular aggregates feature very different photophysical properties depending on their aggregation geometries, which can be explained by the molecular exciton model proposed by Kasha and coworkers.\(^{17}\)

According to Kasha’s molecular exciton model, the two most extreme aggregation geometries are the “card pack” H-aggregate and the “head-to-tail” J-aggregate. In the H-aggregate, stacking of transition dipole moments leads to an “allowed” transition shifted to higher energy and a “forbidden” transition shifted to lower energy (Figure 1-9A). In contrast, the allowed transition dipole moments in the J-aggregate are shifted to lower energy and higher energy transition dipole moments are forbidden (Figure 1-9B). The transition dipole moments from $0^\circ$ (H-aggregate) to $180^\circ$ (J-aggregate) lead to the allowed transition shifted from blue to red (Figure 1-9C). The transition dipole moment is in the same energy with the isolated chromophore at $54^\circ$.

The absorption spectra in H-aggregates blue-shift because the lowest energy singlet-singlet transition is forbidden according to Kasha’s molecular exciton model. On the other hand, the
absorption spectra in J-aggregates red-shift because the transitions to the ground state from the lowest singlet state are allowed. Correspondingly, the fluorescence emission in H-aggregates may be quenched due to non-radiative decay from the higher singlet state. However, intersystem crossing that competes with other singlet decay processes should be more probable from H-aggregates. In the case of J-aggregates, the fluorescence emission may be enhanced compared to the emission from the monomer.

![Diagram of exciton band structures in dimers with several orientations of transition dipoles. Dotted arrows indicate dipole forbidden transitions. The figure was adopted from Kasha.](image)

Recently, J- and H-aggregates have been investigated in organogel systems. Shinkai and coworkers studied the relationship between the structure and the aggregation mode in an organogel system which consists of a porphyrin moiety bearing the amide groups (Figure 1-10). The UV-Vis absorption band of the gelators with the structures of the amide groups at the 4-position of the meso-phenyl groups is shifted to short wavelength. In contrast, the UV-Vis absorption band of the gelators with the structures of the amide groups at the 3,5-positions and 3-position is shifted to longer wavelength. The shifts of the absorption bands indicate that the gelators 3a and 3b adopt the H-aggregation mode but 2a and 4a adopt J-aggregation mode.
finding reveals that the aggregation modes of porphyrin stacks can be controlled by the peripheral hydrogen-bonding interactions.

Figure 1-10. Molecular structures studied by Shinkai

Platinum Acetylides

Platinum acetylide compounds have attracted recent interest due to their non-linear optical properties and potential applications as materials for the fabrication of high-efficiency organic electroluminescent devices. The general structure of platinum acetylide polymers or oligomers is given in Figure 1-11.

\[
\begin{align*}
\text{PR}_3 & \quad \text{Pt} \quad \text{Ar} \quad \text{PR}_3 \\
\text{PR}_3 & n
\end{align*}
\]

R = Alkyl chain (C$_1$-C$_8$) or phenyl
Ar = Phenyl or thienyl

Figure 1-11. General structure of platinum acetylides

Synthetic Method

The general synthetic method of platinum acetylide complexes is the Hagihara reaction, which was developed by Hagihara and coworkers in 1978 (Figure 1-12). The coupling reaction between the platinum chloride complex and an aryl acetylide is carried out in an alkylamine base (e.g. diethylamine). Copper iodide is used as a catalyst to deprotonate the aryl acetylide. The reaction needs to be carried out under an inert atmosphere to avoid the oxidation of copper iodide.
catalyst. Both cis- and trans- isomers of the platinum chloride complex give trans-platinum acetylide products because the cis-platinum chloride quickly isomerizes in the presence of an amine. The cis- and trans-platinum isomers can be identified by $^{31}$P NMR spectroscopy. The coupling constant ($J_{Pt-P}$) between $^{31}$P and $^{195}$Pt is usually below 2500 Hz for the trans-isomer and higher than 2500 Hz for the cis-isomer.

![Figure 1-12. Hagihara reaction for synthesis of the platinum acetylide monomer or polymer](image)

**Triplet Excited States**

Triplet excited states in conjugated polymers are hard to detect due to the very slow intersystem crossing rate and small phosphorescence quantum yield caused by spin forbidden rule. They can only be investigated by indirect measurements, such as photoinduced absorption, optically detected magnetic resonance, or energy transfer. However, a thorough understanding of triplet photophysics in conjugated polymers is essential for the development of their applications in optical and optoelectronic devices.

On the other hand, heavy metals, such as platinum, induce intersystem crossing due to large spin-orbit coupling. Incorporation of platinum into conjugated polymers significantly increases intersystem crossing and the triplet excited state yield, as well as provides a direct way to study the triplet excited state in conjugated polymers. Due to this reason, platinum acetylide polymers and oligomers have been extensively studied.
Pt(II) adopts a square planar configuration and forms stable bonds with ethynylenes. According to the crystal field model,\(^{25}\) those d orbitals that point towards the ligand groups (d\(_{x^2-y^2}\) in Pt(II)) are destabilized and move to higher energy level, and those that point away from ligand groups (d\(_{xy}\), d\(_z^2\), d\(_{yz}\) and d\(_{xz}\)) are less destabilized. This results in the crystal field splitting as shown in Figure 1-13. Therefore, the HOMO and LUMO orbitals of Pt(II) are d\(_{xy}\) and d\(_{x^2-y^2}\), respectively.

![Diagram of d orbital levels in Pt(II) complexes](image)

Figure 1-13. Splitting of d orbital levels in Pt(II) complexes

In platinum acetylide polymers and oligomers, the HOMO and LUMO involve both platinum d-orbitals and ligand p-orbitals.\(^{26,27}\) The mixing between platinum d-orbitals and the ligands π-system preserves ligand’s conjugation through the metal site. The extent of the mixing depends on the overlap between the ligand and metal orbitals, the size of the spacer and the extent of conjugation in the ligand. Many studies have shown that the fundamental optical transition in platinum acetylide complexes mostly originates from π-π* transition of conjugated ligand with some contributions from metal d-orbitals, but not from intraplatinum d-d transitions.\(^{28}\) This conclusion is consistent with the appearance of vibronic progressions in the emission spectra of platinum acetylidy complex.

The main ground absorption bands of platinum acetylide polymers and oligomers usually appear between 300 and 400 nm. Their emission spectra show strong phosphorescence bands
(T₁-S₀) between 500 and 600 nm, and weak fluorescence bands (S₁-S₀) between 370 and 450 nm. The triplet-triplet absorption bands (T₁-Tₙ) are between 600 and 800 nm. Photophysics of platinum acetylide polymers and oligomers have been extensively studied by several groups. The next section gives an overview of the up-to-date research in this topic.

Wilson and coworkers investigated the evolution of the triplet excited state in a series of platinum acetylide polymers (Figure 1-14).²⁹ They systematically varied the spacer so that the onset of the singlet absorption was tuned from 1.7 to 3.0 eV. They found that the intensities and lifetimes of the triplet state emission are dramatically reduced with decreasing triplet energy as a result of increasing non-radiative decay rate. In a more detailed study,³⁰ they concluded that the non-radiative decay of the triplet states in a series of platinum containing conjugated polymers and monomers obeys the energy gap law. That is, the non-radiative decay rate is sensitive to the triplet energy and increases exponentially as the triplet energy decreases. The simplest form of energy gap law is expressed by Equation 1-9.

\[ \kappa_{nr} \propto \exp(-\gamma \Delta E/\hbar \omega_M) \]  

(1-9)
where $\Delta E$ is the energy gap separation between the potential minima of the states involved, $\gamma$ is a term that can be expressed in terms of molecular parameters, and $\omega_M$ is the maximum and dominant vibrational frequency available in the system.

Another finding of this study is that the singlet-triplet ($S_1$-$T_1$) energy splitting is constant ($\sim0.7$ eV) through the series and independent of the spacer $R$. To further investigate this finding in detail, they extended the study in an extensive series of platinum-containing conjugated polymers and monomers with varying the spacer $R$ (Figure 1-15). They observed that the

Figure 1-15. General structures of platinum containing polymers and monomers studied by Köhler\textsuperscript{31}
singlet state energy is significantly lower in the polymer than in the monomer, indicating that the singlet state is more delocalized in the polymer. In contrast, the triplet energy difference between the polymer and the monomer is very small, demonstrating that the triplet state is more localized in the polymer (Figure 1-16). While the size and the electronic character of the polymer repeat units are variable with varying the spacer R, the singlet-triplet splitting stays constant (~0.7 eV) (Figure 1-17). This finding provides very useful information for estimating singlet-triplet energy gap in the analogous platinum-containing conjugated systems.

Figure 1-16. Photoluminescence spectra at 10 K and absorption spectra at room temperature of thin films of the platinum-containing polymer and monomer with spacer 2. The figure was adopted from Köhler.

Figure 1-17. Energy levels of singlet \( S_1 \) and triplet \( T_1 \) excited states and singlet-triplet splitting energy (\( \Delta E_{S_1-T_1} \)). The figure was adopted from Köhler.
To understand structure-property relationships for platinum acetylide conjugated systems, Rogers and coworkers investigated the effects of the conjugation length of the ligands on photophysical properties of a series of platinum-containing oligomers (Figure 1-18). They found that with increasing conjugation length, both ground state absorption ($S_0-S_1$) and triplet state absorption ($T_1-T_n$) red shift, indicating that spin-orbit coupling effect of platinum is reduced.

![Figure 1-18. Platinum acetylide oligomers studied by Rogers](image)

Liu and Glusac recently reported photophysical studies of a series of platinum acetylide oligomers with varying the oligomer chain length (Figure 1-19). The result of these studies indicates that the singlet excited states red shift with increasing the oligomer chain length, suggesting that the singlet exciton is more delocalized (Figure 1-20). In contrast, the triplet excited states show little or no shift with increasing the oligomer chain length,

![Figure 1-19. Platinum acetylide oligomers studied by Liu](image)
demonstrating that the triplet exciton is more localized. DFT calculations also support the notion that the triplet states of these series of oligomers are restricted within one or two repeat units.

Figure 1-20. UV-Vis absorption (a) and photoluminescence (b) spectra of Pt-n oligomers. Fluorescence (F) intensity scale is magnified 100 × compared to phosphorescence (P). The figure was adopted from Liu.

**Objective of Present Study**

Incorporation of platinum into conjugated organic systems largely enhances the triplet quantum yield due to spin-orbit coupling caused by the heavy metal. Thus, platinum acetylide conjugated polymers and oligomers provide a unique platform for studying triplet excited state properties. Compared with platinum acetylide polymers, platinum acetylide oligomers have precise chemical structure and monodisperse property, which makes them better candidates for investigating structure-property relationships by designing different derivatives.

From previous studies, we conclude that the triplet excited state of platinum acetylide oligomers is more localized and restricted within one or two repeat units. In continuation of our investigation of triplet excited state photophysical properties in platinum acetylide systems, we currently incorporate a donor-acceptor moiety into platinum acetylide oligomers. This design
allows us to investigate photoinduced electron transfer and energy transfer dynamics in platinum acetylide oligomers. On the other hand, the question on how the triplet excited state is influenced by these processes will also be answered. For photoinduced electron transfer study, oligothiophenes were used as electron donors due to their low oxidation potentials and conjugation property. Naphthalene diimides are easily reduced and form stable radical anions, which were used as electron acceptors in this study. For investigating photoinduced energy transfer, we incorporated an anthracene moiety into a platinum acetylide backbone. We expected that triplet-triplet energy transfer from the platinum acetylide segment to the anthracene segment would occur in these systems.

The extended \( \pi \)-conjugated linear carbon-chain oligomers (oligoynes) have attracted increasing interest due to their potential use as molecular wires for transport of charge (polarons) or excitons on the nanoscale.\(^{35}\) Incorporation of platinum into oligoynes increases the stability of linear carbon chain compounds, as well as promotes the formation of the triplet excited state. In the current study, the detailed photophysics of a series of platinum tetrayne oligomers were investigated.

To further extend our study in platinum acetylide oligomers, we designed and synthesized a series of platinum acetylide oligomers with the ability of aggregation in solvents. It is well known that three major non-bonding interactions contribute to molecular aggregation: \( \pi-\pi \) stacking, hydrogen bonding and van der Waals interactions. Our newly designed platinum acetylide oligomer features long alkyl chains (van der Waals interaction) and amide functional groups (H-bonding) that initiate molecular aggregation and even solvent gelation in both nonpolar and polar solvents. We investigated photophysics and molecular morphology of these platinum acetylide aggregates.
CHAPTER 2
PHOTOINDUCED ELECTRON TRANSFER IN TRIBLOCK PLATINUM ACETYLIDE OLIGOMERS

Introduction

Platinum acetylide based conjugated polymers and oligomers have attracted interest due to their possible use in optical and optoelectronic applications. Photophysics of platinum acetylide systems feature dominant long-lived triplet excited states due to strong spin-orbit coupling caused by platinum. Compared to platinum-acetylide polymers, platinum-acetylide oligomers have mono-disperse length and precise chemical structure, which provides a unique platform for investigation of structure-photophysical property relationships in particular how the triplet exciton is influenced by the factors such as conjugation length and energy by designing different derivatives.

We recently reported photophysical studies of a series of platinum acetylide oligomers with the repeat unit [−C≡C−Pt(PBu₃)₂−C≡C−Ph−] (Ph = 1,4-phenylene). This investigation provides very clear experimental and theoretical evidence that the triplet state of these platinum acetylide oligomers is localized on a chromophore consisting approximately of a single [−Pt(PBu₃)₂−C≡C−Ph−C≡C−Pt(PBu₃)₂−] repeat unit. However, their singlet states are delocalized over a chromophore consisting of five or more repeat units.

Charge carriers (polarons or radical ions) are responsible for charge transport in optoelectronic devices, such as light-emitting diodes, field-effect transistors and photovoltaic cells. To investigate radical ion behavior in π-conjugated platinum acetylide systems, we used a pulse radiolysis method to attach ions onto an extended series of platinum acetylide oligomers. The structures of this investigation are shown in Figure 2-1. The study gives insight into the spectroscopy, electronic structure, and delocalization in the ion-radical states of the oligomers.
One of the important key findings of this investigation is that the radical cations are concentrated on a comparatively short oligomer segment, in particular, for Pt4Tn series oligomers (T = 2,5-thienylene, n = 1, 2, 3) radical cations are restricted to near and on the thiophene segments in the core of the oligomers (Figure 2-1).

Figure 2-1. Chemical structures and pulse radiolysis transient absorption spectra for radical cations. The figure was adopted from Cardolaccia.42

In the present investigation, we designed and synthesized a series of platinum acetylide oligomers that are structurally similar to the Pt4Tn series, but feature a donor-spacer-acceptor architecture as shown in Figure 2-2. Pt4T1 and Pt4T2 are also present as reference compounds.
We chose naphthalene-1,8:4,5-tetracarboxydiimide (NDI) as the electron acceptor because it has been widely used as an electron acceptor in many fundamental studies of photoinduced electron transfer.\textsuperscript{43-47} It is also well known that the NDI acceptors undergo reversible one-electron reduction at moderate potentials to form stable radical anions. In addition, the radical anions of the NDI feature intense and characteristic absorption bands in both visible and near-infrared regions, which allows one to spectroscopically identify the formation of charge-separated states.

![Chemical structures of platinum acetylide oligomers](image)

\textbf{Figure 2-2.} Chemical structures of platinum acetylide oligomers

On the other hand, thiophene-based oligomers and polymers have received considerable attention due to their promising optical, electrochemical, and electronic properties.\textsuperscript{48-50} Recently,
organometallic systems consisting of oligothiophenes are gaining increasing interest. In the present investigation, we incorporated oligothiophenes into π-conjugated platinum acetylide systems. The resulting core units of \([-\text{Pt}≡\equiv-T_n≡\equiv\text{Pt}−]\) \((T = 2,5\text{-thiénylene}; n = 1, 2)\) act as electron donors due to their low oxidation potentials according to our previous study. The electron donor and the electron acceptor are linked by several platinum acetylide repeat units that also act as spacers.

The objective of this work is to study photophysical properties and intrachain charge-separation dynamics of the platinum acetylide oligomers that feature a donor-spacer-acceptor architecture.

**Synthesis**

The synthetic strategy we utilized for this series of platinum acetylide oligomers is an iterative-convergent approach according to methods similar to those we have previously reported. Briefly, the structures were assembled from the core outward, where the platinum acetylide segments were constructed iteratively and the NDI end-groups were prepared separately and attached to the oligomers in the final step.

The synthesis of the core units \(6a-b\) is shown in Figure 2-3. It started from the iodination of 2,2′-bithiophene with N-iodosuccinimide (NIS) in a mixed solvent system consisting of methanol and acetic acid. Then the Sonogashira coupling between 5,5′-diiodo-2,2′-bithiophene (or 2,5-dibromothiophene) and trimethylsilyl acetylene (TMS-A) gave the protected diacetylene-oligothiophenes \(2a-b\) in good yields. After deprotection under basic conditions, the resulting compounds \(3a-b\) were reacted with \textit{cis}-dichloro-bis-(tri-n-butylphosphine)platinum(II) in diethylamine to give the platinum complexes \(4a-b\) in ~88% yields. The complexes \(4a-b\) were further coupled with 1-ethynyl-4-(trimethylsilylethynyl)benzene in refluxing diethylamine to
give the TMS-protected platinum complexes 5a-b. Deprotection of the complexes 5a-b in the presence of potassium hydroxide at room temperature gave the core units 6a-b in high yields.

Figure 2-3. Synthesis of the platinum acetylide complexes 6a-b

The synthesis of the cores containing four platinum acetylide repeats is shown in Figure 2-4. First, the TMS-protected platinum complex 8 was synthesized in two steps that started from
the preparation of 1-ethynyl-4-(trimethylsilyl)ethynyl)benzene followed by the coupling reaction with cis-dichloro-bis-(tri-n-butylphosphine)platinum(II). The overall yield of two steps is ~50%. The Hagihara coupling reactions between the complexes 6a-b and the complex 8 in diethylamine with copper iodide as catalyst gave the TMS-protected platinum complexes 9a-b in ~82% yields. After deprotection in basic conditions, the cores containing four platinum acetylide repeats 10a-b were obtained in high yields.

\[
\text{[Reactions and structures]}\]

Figure 2-4. Synthesis of the platinum acetylide complexes 10a-b

The synthesis of the NDI end-groups is shown in Figure 2-5. Condensation of 1,4,5,8-naphthalenetetracarboxylic dianhydride with 1-aminooctane in refluxing DMF gave N-(n-octyl)-naphthalene-1,8-dicarboxyanhydride-4,5-dicarboximide 11 in 36% yield after separation from its disubstituted side product. Then compound 11 was condensed with 4-iodoaniline in refluxing
DMF to yield the corresponding iodide 12. The Sonogashira reaction between 12 and triisopropylsilylacetylene (TIPS-A) gave the TIPS-protected acetylene 13. After deprotection with tetra-n-butyl-ammonium fluoride (TBAF) at room temperature, the resulting acetylene 14 was coupled with cis-dichloro-bis-(tri-n-butylphosphine)platinum(II) to give the NDI end-group 15 in 65% yield.

Figure 2-5. Synthesis of the NDI end-group

For the synthesis of the oligomers Pt4TmA and Pt6TmA (m = 1, 2), the final step was the coupling reactions between the cores and the end-groups as shown in Figure 2-6A. The oligomers Pt2TmA (m = 1, 2) were synthesized by coupling the platinum complex 4a-b with compound 14 (Figure 2-6B). These reactions gave moderate to high yields.
6a-b + 15

\[
\begin{align*}
\text{Pt4T1A} & \quad \text{T1: } \text{Ar} = 2,5\text{-thiophene} \\
\text{Pt4T2A} & \quad \text{T2: } \text{Ar} = 5,5'\text{-2,2'-bithiophene} \\
\end{align*}
\]

10a-b + 15

\[
\begin{align*}
\text{Pt6T1A} & \quad \text{T1: } \text{Ar} = 2,5\text{-thiophene} \\
\text{Pt6T2A} & \quad \text{T2: } \text{Ar} = 5,5'\text{-2,2'-bithiophene} \\
\end{align*}
\]

(A)

4a-b + 14

\[
\begin{align*}
\text{Pt2T1A} & \quad \text{T1: } \text{Ar} = 2,5\text{-thiophene} \\
\text{Pt2T2A} & \quad \text{T2: } \text{Ar} = 5,5'\text{-2,2'-bithiophene} \\
\end{align*}
\]

(B)

i) Cul, Et₂NH, RT; ii) Et₂NH, heat.

Figure 2-6. A) Synthesis of Pt₄TmA and Pt₆TmA (m = 1, 2) oligomers; B) Synthesis of Pt₂TmA oligomers
The oligomers were characterized by $^1$H and $^{31}$P NMR, and elemental analysis. The $J_{\text{Pt-P}}$ coupling constant (2340-2360 Hz) in $^{31}$P NMR is below 2500 Hz, indicating that the platinum centers adopt trans-configuration in this series of oligomers.

**Results**

**Electrochemistry**

In a previous report, $^{42}$ we carried out an extensive electrochemical and pulse radiolysis study of a series of platinum acetylide oligomers which are structurally similar to the complexes that are the focus of this investigation. Some key findings of this work are the following. First, one electron oxidation of oligomers that contain both thienylene and phenylene repeat units exhibits two reversible oxidation waves. The first oxidation is centered on the thienylene segment ($E_{1/2} \approx 0.5 – 0.7$ V) and the second is centered on the phenylene repeats, -(Pt-C≡C-Ph-C≡C-)$_n$ ($E_{1/2} \approx 1.0$ V). Pulse radiolysis was also used to study the absorption spectra of the radical cations, and these data will be described below as we discuss the transient absorption properties of these series of oligomers.

The electrochemical properties of **Pt4T1A** and **Pt4T2A** were investigated by cyclic voltammetry (CV) using nitrogen-degassed methylene chloride solutions with tetra-n-butylammonium hexafluorophosphate (TBAH, 0.1 M) as a supporting electrolyte. The cyclic voltammograms are shown in Figure 2-7. Both complexes feature two reversible waves in the reductive branch of the CV. These waves appear at -0.64 and -1.05 V and they are believed to arise from sequential one-electron reductions centered on the NDI end-groups. This assignment is supported by literature studies of other compounds that contain the NDI unit which show very similar reductive electrochemical response.$^{52,53}$ The oxidative branch of the CV is more complicated, but on the basis of our previous work$^{42}$ we are able to assign the observed waves to
sequential oxidations centered on the thienylene core segment and the -(Pt-C≡C-Ph-C≡C-)n “spacers”. In particular, the first oxidation for Pt4T1A and Pt4T2A appears at 0.63 V and 0.60 V, respectively. These waves are due to one electron oxidation of electrophores that are concentrated on the thienylene “core” units. The oxidation is slightly less positive in Pt4T2A, which reflects the fact that the radical cation is slightly more stable on the bithiophene unit. Sweeping to more positive potentials reveals additional waves. For Pt4T1A the more positive wave is due to oxidation centered on the -(Pt-C≡C-Ph-C≡C-)n segments, and for Pt4T2A several additional waves are observed which are ascribed to further oxidation of the bithiophene core and oxidation of the -(Pt-C≡C-Ph-C≡C-)n segments.42

Figure 2-7. Cyclic voltammograms. A) Pt4T1A B) Pt4T2A (in methylene chloride with 0.1 M TBAH as electrolyte, vs SCE)
**UV-Vis Absorption**

The absorption spectra of all of the oligomers were recorded in THF solutions (Figure 2-8). First, qualitatively the molar absorption coefficients increase with the chain length consistent with the notion that each platinum acetylide repeat unit acts as a chromophore to increase the absorption cross section of the oligomer. There are specific features in the spectra that can be assigned to the individual chromophore units in the oligomers. First, for PtnT1A series (Figure 2-8A, n = 2, 4, 6) the near-UV absorption is dominated by a strong band with several distinct maxima. The origin of these bands is understood by reference to the spectra of the model complex Pt4T1 and a model for the NDI (see Figure A-1 in the appendix A for the structure) chromophore which are shown in the inset to Figure 2-8A. In particular, the near-UV absorption of PtnT1A series arises from a superposition of the $\pi,\pi^*$ transition localized on the platinum-acetylide segments ($\lambda_{\text{max}} \approx 360$ nm) and the $\pi,\pi^*$ transition of the NDI chromophores which appear as a band with $\lambda_{\text{max}} \approx 370$ nm with two well-defined vibronic sub-bands that appear at shorter wavelength. Note that the relative intensity of the structured absorption band due to the NDI chromophores diminishes along the series PtnT1A < PtnT2A < PtnT3A, consistent with the fact that the length of the platinum-acetylide spacer is increasing along the series while the number of NDI end-groups remains constant. A second important feature in the spectra is the distinct shoulder that appears on the long wavelength side of the near-UV band ($\lambda \approx 400$ nm). On the basis of our previous work it is clear that this weak band is due to a transition concentrated on the core thienylene segment, (-Pt-C≡C-T1-C≡C-Pt-).54

The absorption spectra for the PtnT2A (n = 2, 4, 6) series are illustrated in Figure 2-8B. The spectra for these complexes are similar in the near-UV region compared to those of PtnT1A series; however, there is a distinct, broad band that appears in the visible region (400 – 450 nm).
which is clearly due to the bithienylene core segment, (-Pt-C≡C-T2-C≡C-Pt-). The appearance of the distinct long-wavelength band which is due to the core bithienylene segment is significant; as shown below, this allows us to selectively photoexcite this segment of the oligomer in transient absorption experiments.

Figure 2-8. Absorption spectra of platinum acetylide oligomers in THF solution. Inset of A: Pt4T1, NDI (see Figure A-1 in the appendix A for the structure); Inset of B: Pt4T2

Steady-State Photoluminescence

The photoluminescence spectra of all of the oligomers and model compounds were recorded in deoxygenated THF solutions with the excitation wavelength at \( \lambda = 378 \) nm. Figure 2-9 shows the spectra of Pt4T1A, Pt4T2A and their corresponding model compounds. The
photoluminescence spectra of other oligomers are shown in the appendix A as Figure A-2. For the model compound Pt4T1 the spectrum features a broad, dominant band centered at $\lambda = 610$ nm along with a vibronic band. These bands are attributed to the phosphorescence emission arising from the thienylene segment. A relatively weak band centered at $\lambda = 520$ nm arises from the phosphorescence emission of the platinum acetylide segment consistent with our previous report. The relative intensity of this band is smaller than the phosphorescence band of the thienylene segment by over an order of magnitude. A fluorescence emission band of the thienylene segment appears at $\lambda_{\text{max}} = 420$ nm. Compared with its model compound Pt4T1, Pt4T1A only shows a fluorescence emission band centered at $\lambda_{\text{max}} = 420$ nm, which is attributed to the superposition of the fluorescence emission from the thienylene segment and the NDI end-
groups (See Figure A-3 in the appendix A for the emission spectrum of NDI). Both phosphorescence emission bands originating from the thienylene and the platinum acetylide segments are very weak, indicating that the phosphorescence emission is effectively quenched in Pt4T1A. This is also confirmed by the decrease of the quantum yield in Pt4T1A relative to its model compound Pt4T1 (Table 2-1).

For the model compound Pt4T2 the photoluminescence spectrum features a broad, dominant band centered at $\lambda = 460$ nm, which is attributed to the fluorescence emission of the bithienylene segment. Note that a shoulder next to the main emission band arising from the platinum acetylide segment appears at $\lambda = 520$ nm consistent with the moderate emission band in Pt4T1. A weak emission band appears at $\lambda = 720$ nm, which is assigned to the phosphorescence emission of the bithienylene segment according to our previous report.54

Compared with the strong phosphorescence emission of the thienylene segment in Pt4T1, the phosphorescence emission of the bithienylene segment in Pt4T2 is dramatically weak. Based on the previous study by Chawdhury and coworkers in the platinum thienylene-based polymers,55 a possible explanation for the weak phosphorescence emission of the bithienylene segment in Pt4T2 is the reduced intersystem crossing caused by the increase of the number of thiophene rings which reduces the influence of the platinum metal, which is mainly responsible for the intersystem crossing.

For the NDI acceptor end-capped oligomer Pt4T2A the photoluminescence spectrum is dominated by the fluorescence emission of the bithienylene segment centered at $\lambda = 460$ nm. The shoulder of the phosphorescence emission arising from the platinum acetylide segment disappears in Pt4T2A. Note that a band on the left of the main fluorescence emission band centered at $\lambda = 420$ nm is assigned to the fluorescence emission of the NDI end-groups by
comparing with the NDI photoluminescence spectrum (see Figure A-3 in the appendix A). The weak phosphorescence emission of the bithienylene segment decreases and is almost invisible in the Pt4T2A spectrum. Compared with its model compound Pt4T2, the phosphorescence emission is effectively quenched in the Pt4T2A oligomer. The photophysical data are shown in Table 2-1. The detailed quenching mechanism will be analyzed in the discussion section.

| Table 2-1. Photophysical data for oligomers and model compounds |
|-----------------------------|-----------------|-----------------|-----------------|-----------------|
|                            | UV-VIS $\lambda_{\text{max/nm}}$ | $\varepsilon$/ M$^{-1}$cm$^{-1}$ ($\times 10^5$) | PL/ $\lambda_{\text{max/nm}}$ | $\Phi$/% | $\tau$/ ns |
| Pt2T1A                     | 360, 378        | 1.33            | 420 $-$                | 0.058 | $<20$ $-$     |
| Pt4T1A                     | 360, 378        | 1.99            | 420 610               | 0.060 | 47 $-$        |
| Pt6T1A                     | 360, 378        | 2.91            | 420 610               | 0.200 | 65 $-$        |
| Pt4T2A                     | 360, 378, 410   | 0.93            | 460 $-$                | 0.189 | $<20$ $-$     |
| Pt4T2A                     | 360, 378, 410   | 1.47            | 460 720               | 0.280 | 35 1820       |
| Pt6T2A                     | 360, 378, 410   | 2.82            | 460 720               | 0.330 | 191 3690      |
| Pt4T1                      | 369 $-$         | 420 520,610     | 1.640 $-$             | 8818 | $-$          |
| Pt4T2                      | 354, 420        | 460 520,720     | 0.530 $-$             | 4400 | $-$          |

Notes: F: fluorescence; P: phosphorescence; CSS: charge-separated state; TS: triplet state; Charge separated state lifetimes were obtained from transient absorption spectra following 355 nm laser excitation. Triplet state lifetimes of Pt4T2A and Pt6T2A were obtained from transient absorption following 420 nm laser excitation.

**Transient Absorption**

In order to explore detailed electron transfer processes, nanosecond transient absorption spectra of the series of oligomers were recorded in deoxygenated THF solutions.

**PtnT1A series with 355 nm laser excitation.** Several important features can be seen from the transient absorption spectra of PtnT1A series following 355 nm laser excitation (Figure 2-10). The excitation wavelength corresponds to the absorption band of the platinum acetylide segment (-Pt-C≡C-Ph-C≡C-Pt-). First, an intense transient absorption band in the visible region centered at $\lambda= 480$ nm appears on all of the three oligomers. This band is assigned to the characteristic absorption of the NDI radical anion by comparing with the spectra of the NDI
derivatives in the literature reports.\textsuperscript{46,52} Second, a less intense band appears in the red region centered at $\lambda = 610$ nm, which is also attributed to the optical absorption of the NDI radical anion consistent with literature reports.\textsuperscript{46,52} Third, an intense and broad band between 500 and 600 nm superposes with the absorption bands of the NDI radical anion. In order to assign this band, we refer to our recent study in radical ion states of platinum acetylide oligomers.\textsuperscript{42} In this study, a pulse radiolysis method was utilized to produce radical ions in an extended series of platinum acetylide oligomers. The structures of the oligomers and corresponding pulse radiolysis transient absorption spectra of radical cations are shown in Figure 2-1. The radical cation of the model compound $\text{Pt}_4\text{T}_1$ exhibits two absorption bands: one in the visible and the second in the near-IR. The broad visible band with a maximum at $\lambda = 520$ nm appears between 450 and 640 nm. Both visible and near-IR bands were assigned to the radical cation absorption concentrated on the thienylene segment. The other oligomer $\text{Pt}_4$ that structurally consists of all platinum acetylide repeats was also studied by the pulse radiolysis method. The radical cation absorption in $\text{Pt}_4$ features an intense absorption band in the visible and a weak absorption band in the near-IR. The visible band with a maximum at $\lambda \approx 500$ nm appears between 400 and 540 nm. Both visible and near-IR bands in $\text{Pt}_4$ were assigned to the radical cation absorption concentrated on the platinum acetylide segment. By comparing the transient absorption spectrum of $\text{Pt}_4\text{T}_1\text{A}$ in the current study with the radical cation absorption spectra of $\text{Pt}_4\text{T}_1$ and $\text{Pt}_4$, we assigned the absorption band between 500 and 600 nm in $\text{Pt}_4\text{T}_1\text{A}$ to the radical cation absorption of the thienylene segment. It can be seen that both visible absorption bands in $\text{Pt}_4\text{T}_1\text{A}$ and $\text{Pt}_4\text{T}_1$ have similarly broad feature and the absorption regions match very well. The lifetimes recovered from the transient absorption spectra indicate a sufficiently long-lived charge separation in these oligomers (See Table 2-1). Finally, note that the lifetimes increase with the oligomer chain
length, indicating that charge recombination rates decrease with increasing the distance between the radical anion and the radical cation.

Figure 2-10. Transient absorption spectra of PtnT1A series in deoxygenated THF solution. All of the spectra were obtained following 355 nm laser excitation.

**PtnT2A series with 355 nm laser excitation.** The transient absorption spectra for PtnT2A series with 355 nm laser excitation are similar to those of PtnT1A series (Figure 2-11). The characteristic absorption of the NDI radical anion appears as an intense band centered at $\lambda_\text{c} = 480$ nm. However, this band is more distinct and separated from the radical cation absorption. An
intense and broad band centered at $\lambda = 650$ nm can be unambiguously assigned to the absorption of the bithiénylene radical cation. This assignment is confirmed by referring to the radical cation absorption of the model compound $\text{Pt}4\text{T}2$ in our previous study of radical ion states of platinum.

![Figure 2-11. Transient absorption spectra of $\text{Pt}n\text{T}2\text{A}$ series in deoxygenated THF solution. All of the spectra were obtained following 355 nm laser excitation acetylide oligomers that has been described in the introduction part of this chapter.42 The study indicates that the radical cation of $\text{Pt}4\text{T}2$ features an intense absorption band with a maximum at

56
λ = 650 nm in the visible region. The band was assigned to the radical cation absorption centered on the bithienylene segment. The structure and absorption region of this band match very well with the absorption band in Pt4T2A. The red-shift of the radical cation absorption of the bithienylene segment relative to that of the thienylene segment indicates that the radical cations are more stable in PtnT2A series of oligomers. The absorption band of the NDI radical anion at λ = 610 nm is not well resolved due to its superposition with the absorption of the bithienylene radical cation. The lifetimes recovered from transient absorption spectra increase with the oligomer chain length, indicating the same trend as in the PtnT1A series. However, the lifetimes increase more than four times from Pt4T2A (35 ns) to Pt6T2A (191 ns), compared with less than one time increase from Pt4T1A (47 ns) to Pt6T1A (65 ns). The striking long-lived charge-separated state in Pt6T2A indicates that the radical ions are sufficiently stable and the charge recombination rate is largely reduced.

**PtnT2A series with 420 nm laser excitation.** One important feature for PtnT2A series of oligomers is that a distinct absorption band centered at λ = 410 nm arising from the bithienylene segment is separated from the absorption of the platinum acetylide segment. This feature allows us to selectively photoexcite the bithienylene chromophore in the PtnT2A series. We utilized 420 nm laser as an excitation source, and the corresponding transient absorption spectra were obtained as shown in Figure 2-12. For the oligomer Pt2T2A the charge-separated state with same spectroscopic features as excited at 355 nm was observed. However, for Pt4T2A and Pt6T2A the spectra feature broad and dominant bands between 600 and 700 nm. By comparing with the transient absorption spectrum of the model compound Pt4T2, we are able to assigned these bands to the T1-Tn absorption of the bithienylene segment consistent with our previous study.\(^5^4\) The lifetimes recovered from the transient absorption spectra are in the microsecond
range, which are typical triplet state lifetimes (Table 2-1). Note that the lifetime for Pt4T2A is less than that of Pt6T2A, suggesting that there is a quenching process active that depends on the length of the spacer.

Figure 2-12. Transient absorption spectra of PtnT2A series in deoxygenated THF solution. All of the spectra were obtained following 420 nm laser excitation

Discussion

Phosphorescence Quenching in Pt4T1A and Pt4T2A

In order to gain insight into the phosphorescence quenching mechanism in Pt4T1A, we first analyze the photophysical processes of the model compound Pt4T1. Note that the model compound Pt4T1 consists of two distinct chromophores: the core thienylene segment, (-Pt-C≡C-
T1-C≡C-Pt-), and the platinum acetylide segment, (-Pt-C≡C-Ph-C≡C-Pt-). The absorption spectrum of Pt4T1 (see inset of Figure 2-8a) features a broad, dominant band centered at $\lambda = 370$ nm which is attributed to the absorption superposition of its two distinct chromophores. According to our previous report, the absorption maximum of the platinum acetylide chromophore is centered at $\lambda_{\text{max}} = 367$ nm. Guo and coworkers reported the absorption maximum ($\lambda_{\text{max}} \approx 385$ nm) of a thienylene-based compound Pt2T1 with the structure of [Ph1≡-Pt(PBu3)2≡-T1≡-Pt(PBu3)2≡-Ph1] (Ph1 = 1-phenylene). This allows us to assign the absorption maximum of the thienylene segment. A thienylene-based platinum acetylide polymer with the absorption maximum $\lambda_{\text{max}} = 406$ nm was also reported by Chawdhury and coworkers. The blue-shift of the absorption maximum of the thienylene chromophore in Pt2T1 is likely due to the singlet exciton destabilization in the oligomer compared with the polymer. In order to avoid the direct excitation of the thienylene segment, the model compound Pt4T1 was first excited at $\lambda = 360$ nm. This wavelength corresponds to the absorption of the platinum acetylide segment. The resulting photoluminescence spectrum is similar to the spectrum obtained with $\lambda_{\text{ex}} = 378$ nm (see Figure 2-9). The spectrum is dominated by the phosphorescence emission of the thienylene segment. According to our previous study, this can be rationalized by effective triplet energy transfer from the platinum acetylide segment to the thienylene segment. With $\lambda = 378$ nm photoexcitation that corresponds to the main absorption of the thienylene segment and a small portion absorption of the platinum acetylide segment, the phosphorescence emission of the platinum acetylide segment still appears in the photoluminescence spectrum. Its intensity does not significantly decrease compared with the phosphorescence with direct excitation of the platinum acetylide segment at $\lambda = 360$ nm. A mechanism involving an equilibrium of energy transfer was proposed as shown in Figure 2-13 according to our previous study.
For the NDI end-capped oligomer **Pt4T1A** more than 95% of the phosphorescence emission from both the platinum acetylide segment and the thienylene segment is quenched and only fluorescence and very weak phosphorescence emission were observed in its photoluminescence spectrum. The phosphorescence quenching can be rationalized by photoinduced electron transfer in this system. The NDI moiety is easily reduced and widely used as an electron acceptor.\(^{43-46,52,57}\) When the NDI moieties are attached to the platinum oligomers, the “donor-spacer-acceptor” system forms, where the donor is the thienylene segment, the spacer is the platinum acetylide segment and the acceptor is the NDI end-group. We observed efficient phosphorescence quenching in **Pt4T1A** with the excitation at both \(\lambda = 360\) and 378 nm. With the excitation at \(\lambda = 360\) nm, first, the platinum acetylide segment is excited to its singlet state.
followed by rapid intersystem crossing to decay to its triplet state. Photoinduced electron transfer occurs from the triplet state of the platinum acetylide segment to the NDI acceptor. While the electron transfer rate was not obtained in our nanosecond transient absorption experiments, the efficient phosphorescence quenching indicates that energy transfer from the platinum acetylide segment to the thienylene segment is significantly suppressed by the electron transfer process. With the excitation at $\lambda = 378$ nm, the thienylene segment is excited to its singlet state. Because the equilibrium mechanism for energy transfer exists in these systems, the final triplet states are independent on the excitation wavelength. Consequently, electron transfer processes are similar to those with the excitation at $\lambda = 360$ nm. Note that direct electron transfer from the triplet state of the thienylene segment to the NDI acceptor may also occur. This assumption is supported by the increasing quantum yield with increasing the oligomer chain length. Direct electron transfer from the thienylene segment to the NDI acceptor is affected by the electronic coupling between the two segments. With increasing the oligomer chain length, the electronic coupling decreases due to the separation by increased platinum acetylide spacers. The efficiency of the phosphorescence quenching for the thienylene segment decreases, and consequently the quantum yield increases along the order of $\text{Pt2T1A} < \text{Pt4T1A} < \text{Pt6T1A}$. The model compound $\text{Pt4T2}$ features weak phosphorescence emission arising from the bithienylene segment. According to our previous study, there is no significant difference for the intensity of the $T_1$-$T_n$ absorption between $\text{Pt4T1}$ and $\text{Pt4T2}$ as shown in their transient absorption spectra, suggesting that the efficiency of the S-T intersystem crossing is similar for the two compounds. Thus, the very low phosphorescence emission in $\text{Pt4T2}$ may be caused by low radiative rate. In addition, the triplet energy level of the bithienylene segment lies ca. 0.3 eV lower than that of the thienylene segment. According to the energy gap law, the non-radiative decay rate increases.
exponentially with decreasing the triplet state energy. The low radiative rate can not compete with the rapid non-radiative decay rate and as a result, the phosphorescence is weak in Pt4T2.

While the phosphorescence quenching in Pt4T2A is not as significant as in Pt4T1A, it is still evident. In particular, the phosphorescence emission of the platinum acetylide segment is almost completely quenched. Partially quenched phosphorescence of the bithiénylene segment was also observed. Once again, the quenching is due to photoinduced electron transfer from the triplet state of the platinum acetylide segment to the NDI acceptor. Chances of direct electron transfer from the bithiénylene segment to the NDI acceptor are small considering the rapid non-radiative decay rate in the triplet state, meaning the triplet relaxation of the bithiénylene segment mainly adopts non-radiative pathway.

**Photoinduced Electron Transfer Mechanism in PtnT1A Series with 355 nm Laser Excitation**

Nanosecond transient absorption spectra clearly show the formation of the charge-separated state upon photoexcitation in the platinum acetylide segment (\( \lambda = 355 \text{ nm} \)). For the PtnT1A series with the thienylene segment in the core, the characteristic absorption of the NDI radical anion appears as an intense band centered at \( \lambda = 480 \text{ nm} \) and a less intense band concentrated at \( \lambda = 610 \text{ nm} \). These absorption bands arising from the NDI radical anion are in excellent agreement with the literature reports of the corresponding NDI derivatives.\(^{46,52} \) The absorption of the thienylene radical cation appears as an intense and broad band between 500 and 600 nm consistent with our previous study of radical ion states of platinum acetylide oligomers.\(^ {42} \) Note that the excitation wavelength (355 nm) is located in the blue edge of absorption of the platinum acetylide segment. The reason for choosing the wavelength is to exclusively excite the platinum acetylide chromophore and to avoid direct excitation of the thienylene chromophore. Thus, with 355 nm laser excitation the platinum acetylide chromophore is excited to its singlet...
excited state. Due to the very efficient S-T intersystem crossing (close to unity because of the efficient spin-orbit coupling caused by platinum metal)\textsuperscript{33} the singlet excited state rapidly decays to its triplet state and the rate of the intersystem crossing is close to \(10^{12} \text{s}^{-1}\) corresponding to 1 ps fluorescence lifetime according to our previous report.\textsuperscript{38,56} The lifetime of the triplet state is long enough to allow electron transfer to the NDI acceptor. Thus, electron transfer becomes the dominant pathway for the triplet state relaxation, and the charge-separated state consisting of the NDI radical anion and the platinum acetylide radical cation is born. Unfortunately, we are not able to detect these processes in our nanosecond transient absorption experiments because these events are too fast and beyond the nanosecond range. The electrochemistry study indicates that the oxidation potential of the thienylene segment is \(~0.2\) V less positive than that of the platinum acetylide segment. This illustrates that the thienylene based radical cation is more stable than the platinum acetylide based radical cation. As a result, a consequent hole shift from the platinum acetylide segment to the thienylene segment follows the initial charge separation to create the second charge-separated state, which is clearly shown in the nanosecond transient absorption spectra.

Taken together, photoinduced electron transfer with 355 nm laser excitation in the \textbf{Pt4T1A} series of oligomers adopts a stepwise mechanism (Figure 2-14A). The initial charge-separated state forms by electron transfer from the triplet state of the platinum acetylide segment to the NDI acceptor followed by consequent hole shift to the thienylene segment to create the final charge-separated state, which relaxes to the ground state by charge recombination. The electron transfer process may suppress the energy transfer process from the platinum acetylide segment to the thienylene segment. However, direct electron transfer from the triplet state of the thienylene segment may also occur, which has been indicated by the efficient phosphorescence quenching
of the thienylene segment in the photoluminescence spectra. Nevertheless, electron transfer from the triplet state of the platinum acetylide segment is the major pathway considering the electronic coupling. Also note that from Pt2T1A to Pt6T1A the lifetimes of the charge separated state increase, which is consistent with the notion that the rate of charge recombination is distance-dependent. The detailed photophysical processes of PtnT1A series are shown in Figure 2-14B.

Figure 2-14. Photophysical processes of PtnT1A series following 355 nm laser excitation. A) Photoinduced electron transfer processes; B) Energy level diagram, energies of charge separated states were estimated from electrochemistry measurements. Blue lines indicate the dominant pathway.
Photoinduced Electron Transfer Mechanism in PtnT2A Series with 355 and 420 nm Laser Excitation

First we analyze the electron transfer processes in the PtnT2A series of oligomers following 355 nm laser excitation. The compound Pt2T2 with the structure of [Cl-Pt≡-T2≡-Pt-Cl] (See Figure A-4 in the appendix A for the structure) was used as a model to locate absorption of the bithienylene segment. The result shows that the absorption maximum of the bithienylene segment is centered at $\lambda = 410$ nm and the red region (from 400-470 nm) is well overlapped with the corresponding absorption region of Pt2T2A (see Figure A-4 in the appendix A). While the bithienylene segment has the minimum absorption at $\lambda = 355$ nm, the absorption of the platinum acetylide segment is close to maximum at $\lambda = 355$ nm, which is about three times more intense than that of the bithienylene segment. Thus, with 355 nm laser excitation the platinum acetylide chromophore is excited to its singlet excited state followed by rapid intersystem crossing to decay to its triplet state. Then, photoinduced electron transfer from the triplet state of the platinum acetylide segment to the NDI acceptor creates the first charge-separated state followed by hole shift to the bithienylene segment to create the second charge-separated state. The processes are similar to the PtnT1A series (Figure 2-14A). Note that direct electron transfer from the bithienylene segment to the NDI acceptor is unlikely to happen considering the deficient electronic coupling between the donor and the acceptor, in particular for the longer chain oligomers, such as Pt4T2A and Pt6T2A. Second, the non-radiative decay is the major pathway for the relaxation of the triplet state of the bithienylene segment in the PtnT2A series oligomers. The photophysical processes in the PtnT2A series are illustrated in Figure 2-15 (blue lines).

For the PtnT2A series oligomers an important feature is that absorption of the bithienylene chromophore is separated from that of the platinum acetylide chromophore in the red region. The bithienylene chromophore absorbs at above 400 nm, while the platinum acetylide chromophore
This feature allows us to selectively excite the bithienylene chromophore without interference from the excitation of the platinum acetylide chromophore.

Figure 2-15. Photophysical processes of PtnT2A series following 355 and 420 nm laser excitation. A) Photoinduced electron transfer with 420 nm laser excitation; B) Energy level diagram, energies of charge separated states were estimated from electrochemistry measurements.
According to our previous study, triplet exciton is more likely to localize in a chromophore consisting of one repeat unit in platinum acetylide oligomers. As shown in Figure 2-16, the electronic coupling between the triplet state of the bithienylene segment and the NDI acceptors in Pt2T2A is sufficient to initiate electron transfer when the bithienylene segment is directly excited. Compared with Pt2T2A, there are one and two platinum acetylide spacers between the bithienylene segment and the NDI acceptor in Pt4T2A and Pt6T2A, respectively. The increasing platinum acetylide spacers interrupt the electronic coupling and consequently electron transfer does not occur in these oligomers when the bithienylene donor is directly photoexcited. The photophysical processes of the PtnT2A series following 420 nm laser excitation are shown in Figure 2-15A and B (red lines). Electron transfer in both series oligomers is strongly exergonic (ΔG < -0.6 eV).

Figure 2-16. Electronic coupling in Pt2T2A.

**Conclusion**

In this investigation, a series of platinum acetylide oligomers that feature a donor-space-acceptor architecture were synthesized. Nanosecond transient absorption spectroscopy was applied to study intrachain electron transfer properties in the oligomers. The formation of the charge-separated states was directly observed in the transient absorption spectra. The radical anion absorption of the NDI acceptor appears as an intense band centered at 480 nm and the radical cation absorption of the \([-\text{Pt}≡\text{N}≡\text{Pt}–]\) donor was also observed in the transient absorption spectra (the absorption band between 500 and 600 nm for the PtnT1A series and the absorption band centred at λ = 650 nm for the PtnT2A series). The most important finding of
this work is that it demonstrates the ability to control a photoinduced charge separation process by photoselection. It also provides a model for investigating the wavelength-dependent behavior of the platinum acetylide systems.

**Experimental**

**Electrochemistry**

Electrochemical measurements were recorded in dry dichloromethane solutions containing 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAH, Aldrich) as the supporting electrolyte. The setup consisted of a platinum microdisk (2 mm²) working electrode, a platinum wire auxiliary electrode and a silver wire quasi-reference electrode. Solutions were degassed with bubbling nitrogen for *ca.* 5 min before measurements and a positive pressure of nitrogen was maintained during the measurements. The concentrations of the oligomers were *ca.* 0.15 mM. All potentials obtained were internally calibrated against the ferrocene/ferricinium couple (E = 0.43 V vs SCE in dichloromethane⁵⁹).

**Photophysical Measurements**

Steady state absorption measurements were recorded on a Varian Cary 100 dual-beam spectrophotometer. Corrected steady state emission measurements were conducted on a SPEX F-112 fluorescence spectrometer. Samples were degassed by argon purging for 30 min and concentrations were adjusted such that the solutions were optically dilute (A<sub>max</sub> < 0.20). Photoluminescence quantum yields were determined according to the “optically dilute” method described by Demas and Crosby, with the quantum yield being computed according to eq. 14 in their paper.⁶⁰ Solutions of Ru(bpy)<sub>3</sub><sup>2+</sup> were used as a reference (Φ = 0.0379 in air-saturated water).
Transient absorption measurements were conducted on a home-built apparatus,\textsuperscript{61} which used a Nd: YAG laser for excitation and PI-Max intensified CCD camera coupled with spectrograph as a detector. Sample concentration were adjusted so that $A \approx 0.8$.

**Synthesis**

**General.** Solvents and chemicals used for synthesis were of reagent grade and used without further purification unless noted. Reactions were carried out under an argon atmosphere. NMR spectra were recorded on Varian VXR, Gemini or Mercury 300 MHz spectrometers. Cis-dichloro-bis-(tri-n-butylphosphine)platinum(II)\textsuperscript{62} and 1,4-diethylbenzene\textsuperscript{33} were prepared according to literature methods.

**5,5'-Diiodo-2,2'-bithiophene (1).** 2,2'-Bithiophene (0.5 g, 3 mmol) and N-iodosuccinimide (1.67 g, 7.4 mmol) were dissolved in methanol (45 mL). To this solution, acetic acid (0.5 mL) was added. After stirring for 2 h, a precipitate formed and the flask was placed in a freezer overnight to ensure complete precipitation of the product. The white solid was then filtered by suction filtration and washed with cold methanol. After drying under vacuum, a white solid was obtained as the product (0.95 g, 76%).\textsuperscript{1}H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.1 (d, 2H), 6.7 (d, 2H).

**2,5-Bis-[{(trimethylsilyl)-ethynyl]-thiophene (2a).** To a solution of 2,5-dibromothiophene (1.41 g, 5.83 mmol) and diisopropylamine (50 mL) in a flask equipped with a magnetic stirrer and a refluxing condenser was added copper iodide (11 mg, 0.058 mmol) and palladium(II) chloride (211 mg, 0.3 mmol) under an argon atmosphere. The solution was degassed for 30 min under a ice-bath. Then trimethylsilylacetylene (2.3 g, 23.40 mmol) was added via syringe. The solution was stirred for 1 h at 0°C, then raised to room temperature and stirred for another 1 h. Then the reaction mixture was allowed to warm to 75°C for 20 h until TLC analysis indicated
that all starting material had disappeared. The solution was allowed to cool to room temperature. Diethyl ether (200 mL) was added to the solution and the produced precipitation was removed by vacuum filtration. The filtrate was washed with 10% HCl solution followed by water twice. The organic phase was dried with anhydrous magnesium sulfate and filtered. The solvent was removed by evaporation under reduced pressure. The crude product was dissolved in hexanes and was purified by column chromatography on silica using hexane as the eluent. The product 2a was obtained (1.13 g, 70%). \( ^1 \)H NMR (CDCl\(_3\), 300 MHz) \( \delta \) 7.02 (s, 2H), 0.22 (s, 18H).

**5,5’-Bis-[(trimethylsilyl-ethynyl)]-2,2’-bithiophene (2b).** 5,5’-Diodo-2,2’-bithophene (1) (0.2 g, 0.48 mmol) and trimethylsilylacetylene (98 mg, 1 mmol) were dissolved in diethylamine (8 mL) and the solution was degassed with argon for 30 min. Then, dichloro-bis-(triphenylphosphine)palladium(II) (0.05 eq, 17 mg, 0.024 mmol) and CuI (0.1 eq, 9 mg, 0.048 mmol) were added and the mixture was stirred at room temperature for 4 h. Methylene chloride (50 mL) was added, and the solution was washed with 10% NH\(_4\)OH (100 mL) and DI water (100 mL), dried with anhydrous sodium sulfate. Chromatography on silica (hexane) gave the desired product 2b as a yellow solid (0.12 g, 70%). \( ^1 \)H NMR (CDCl\(_3\), 300 MHz) \( \delta \) 7.1 (d, 2H), 7.0 (d, 2H), 0.22 (s, 18H).

**2,5-Diethynyl-thiophene (3a).** 2,5-Bis-[(trimethylsilyl)-ethynyl]-thiophene (2a) (0.32 g, 1.16 mmol) was dissolved in methanol (20 mL) and degassed for 15 min with argon. To this solution, potassium hydroxide (0.1 mL, 0.5 M in water) was added and the mixture was stirred at room temperature for 4 h. Then, water (50 mL) was added and the mixture was extracted with pentane. The organic phase was dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure at room temperature. A light yellow oil was obtained as the product (100 mg, 65%). \( ^1 \)H NMR (CDCl\(_3\), 300 MHz) \( \delta \) 7.22 (s, 2H), 3.5 (s, 2H).
5,5'-Diethynyl-2,2'-bithiophene (3b). 5,5'-Bis-[(trimethylsilyl-ethynyl)]-2,2'-bithiophene (2b) (115 mg, 0.32 mmol) was dissolved in THF (6 mL) and the solution was degassed for 15 min with argon. Then, TBAF (1.28 mL of a 1 M solution, 1.28 mmol) was added via syringe and the mixture was stirred at room temperature protected from light for 3 h. Then, the solvent was removed and chromatography on silica (9:1 hexane/CH₂Cl₂) gave a yellow solid as the product (65 mg, 95%). \(^1\)H NMR (CDCl₃, 300 MHz) δ 7.15 (d, 2H), 7.0 (d, 2H), 3.4 (s, 2H).

**Compound 4a.** 2,5-Diethynyl-thiophene (3a) (43 mg, 0.325 mmol) and cis-dichloro-bis-(tri-n-butylphosphine)platinum(II) (0.46 g, 0.686 mmol) were dissolved in diethylamine (15 mL) and the resulting solution was degassed for 15 min with argon. The mixture was stirred under reflux overnight. The solvent was removed and chromatography on silica (7:3 hexane/CH₂Cl₂, then 1:1) gave a yellow solid as the product (0.4 g, 88%). \(^1\)H NMR (CDCl₃, 300 MHz) δ 6.6 (s, 2H), 1.9-2.0 (m, 24H), 1.4-1.6 (m, 48H), 0.9 (t, 36H); \(^{31}\)P NMR (CDCl₃, 121 MHz) δ 8.05 (J_{Pt-P} = 2398.3 Hz).

**Compound 4b.** This compound was synthesized according to the same procedure used for compound 4a, except 5,5’-diethynyl-2,2’-bithiophene (3b) (65 mg, 0.3 mmol) and cis-dichloro-bis-(tri-n-butylphosphine)platinum(II) (423 mg, 0.63 mmol) were used. Chromatography on silica (hexane first, then 9:1, 4:1, 7:3, 3:2 hexane/CH₂Cl₂) gave a yellow green solid as the product (325 mg, 73%). \(^1\)H NMR (CDCl₃, 300 MHz) δ 6.8 (d, 2H), 6.65 (d, 2H), 1.9-2.0 (m, 24H), 1.4-1.6 (m, 48H), 0.9 (t, 36H); \(^{31}\)P NMR (CDCl₃, 121 MHz) δ 8.2 (J_{Pt-P} = 2353.7 Hz).

**Compound 5a.** This compound was synthesized according to the same procedure used for compound 4a, except compound 4a (540 mg, 0.386 mmol) and 1-ethynyl-4-(trimethylsilylethynyl)benzene (191 mg, 0.963 mmol) were used. Chromatography on silica (7:3
hexane/CH$_2$Cl$_2$) gave a yellow green solid as the product (500 mg, 75%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.28 (d, 4H), 7.15 (d, 4H), 6.6 (s, 2H), 1.9-2.0 (m, 24H), 1.4-1.6 (m, 48H), 0.9 (t, 36H), 0.2 (s, 18H); $^{31}$P NMR (CDCl$_3$, 121 MHz) $\delta$ 4.21 ($J_{Pt-P} = 2333.2$ Hz).

**Compound 5b.** This compound was synthesized according to the same procedure used for compound 4a, except compound 4b (400 mg, 0.27 mmol) and 1-ethynyl-4-(trimethylsilylethynyl)benzene (117 mg, 0.59 mmol) were used. Chromatography on silica (7:3 hexane/CH$_2$Cl$_2$) gave a yellow green solid as the product (390 mg, 80%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.3 (d, 4H), 7.15 (d, 4H), 6.8 (d, 2H), 6.6 (d, 2H), 1.9-2.0 (m, 24H), 1.4-1.6 (m, 48H), 0.9 (t, 36H), 0.2 (s, 18H); $^{31}$P NMR (CDCl$_3$, 121 MHz) $\delta$ 4.33 ($J_{Pt-P} = 2340.1$ Hz).

**Compound 6a.** Compound 5a (545 mg, 0.316 mmol) was dissolved in methanol (10 mL) and THF (10 mL). The yellow solution was degassed for 15 min with argon. Then potassium hydroxide (1.6 mL, 2M in water) was added via syringe. The mixture was stirred for 4 h at room temperature. The solvent was removed by vacuum evaporation and the residue was diluted with methylene chloride. The solution was washed with DI water, dried over anhydrous sodium sulfate. After removal of the solvent, a yellow solid was obtained as the product (386 mg, 77%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.28 (d, 4H), 7.15 (d, 4H), 6.6 (s, 2H), 3.1 (s, 2H), 3.1 (s, 2H), 1.9-2.0 (m, 24H), 1.4-1.6 (m, 48H), 0.9 (t, 36H); $^{31}$P NMR (CDCl$_3$, 121 MHz) $\delta$ 4.25 ($J_{Pt-P} = 2344.5$ Hz).

**Compound 6b.** This compound was synthesized according to the same procedure used for compound 6a, except compound 5b (186 mg, 0.1 mmol) and potassium hydroxide (0.5 mL, 2M in water) were used. A yellow green solid was obtained as the product (147 mg, 88%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.3 (d, 4H), 7.15 (d, 4H), 6.8 (d, 2H), 6.6 (d, 2H), 3.1 (s, 2H), 1.9-2.0 (m, 24H), 1.4-1.6 (m, 48H), 0.9 (t, 36H); $^{31}$P NMR (CDCl$_3$, 121 MHz) $\delta$ 4.36 ($J_{Pt-P} = 2338.9$ Hz).
1-Ethynyl-4-(trimethylsilylethynyl)benzene (7). A solution of 1,4-diethynylbenzene (230 mg, 1.82 mmol) in dried THF (30 mL) was cooled to –78 °C. To this solution was added LDA (1.09 mL, 2.73 mmol, 2.5 M in hexanes) via syringe over a period of 1 h. The mixture was stirred at –78 °C for 2 h, and then trimethylsilyl chloride (0.35 mL, 2.73 mmol) was added. The mixture was warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure, and the remaining residue was dissolved in diethyl ether. The ether solution was washed with water, dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified by chromatography using hexanes as an eluent. The product was exposed to high vacuum (25 mtorr) for 12-16 h at room temperature to remove unreacted starting material. The desired product 7 was obtained (280 mg, 78%). 1H NMR (CDCl₃, 300 MHz) δ 7.4 (s, 4H), 3.1 (s, 1H), 0.2 (s, 9H).

Compound 8. Cis-dichloro-bis-(tri-n-butylphosphine)platinum(II) (372 mg, 0.55 mmol) and 1-ethynyl-4-(trimethylsilylethynyl)benzene (7) (110 mg, 0.55 mmol) were dissolved in diethylamine (10 mL), and the solution was degassed for 15 min with argon. The mixture was stirred under reflux for 4 h. Chromatography on silica (7:3 hexane/CH₂Cl₂) gave a yellow solid as the product (330 mg, 72%). 1H NMR (CDCl₃, 300 MHz) δ 7.3 (d, 2H), 7.1 (d, 2H), 1.9-2.0 (m, 12H), 1.4-1.6 (m, 24H), 0.9 (t, 18H), 0.2 (s, 9H); 31P NMR (CDCl₃, 121 MHz) δ 8.04 (J₉-P₉= 2365.0 Hz).

Compound 9a. Compound 6a (100 mg, 0.06 mmol) was dissolved in diethylamine (10 mL) and the solution was degassed for 15 min with argon. Then, compound 8 (126 mg, 0.15 mmol) and CuI (1.1 mg, 0.006 mmol) were added and the mixture was stirred at room temperature overnight. The solvent was removed and the crude product was purified by chromatography on silica (3:2 hexane/CH₂Cl₂) to give a yellow solid as the product (143 mg,
Compound 9b. This compound was synthesized according to the same procedure used for compound 9a, except compound 6b (90 mg, 0.054 mmol), compound 8 (100 mg, 0.12 mmol) and CuI (1.0 mg, 0.005 mmol) were used. Chromatography on silica (7:3, then 3:2 hexane/CH₂Cl₂) gave a yellow solid as the product (144 mg, 82%). ¹H NMR (300 MHz, CDCl₃) δ 7.28 (d, 4H), 7.15 (d, 4H), 7.07 (s, 8H), 6.8 (d, 2H), 6.6 (d, 2H), 1.9-2.0 (m, 48H), 1.4-1.6 (m, 96H), 0.9 (t, 72H), 0.2 (s, 18H); ³¹P NMR (CDCl₃, 121 MHz) δ 4.24, 4.18 (Jₚt-P = 2351.8 Hz).

Compound 10a. This compound was synthesized according to the same procedure used for compound 6a, except compound 9a (94 mg, 0.03 mmol) and potassium hydroxide (0.15 mL, 2 M in water) were used. A yellow solid was obtained as the product (86 mg, 95%). ¹H NMR (300 MHz, CDCl₃) δ 7.28 (d, 4H), 7.15 (d, 4H), 7.07 (s, 8H), 6.6 (s, 2H), 3.1 (s, 2H), 1.9-2.0 (m, 48H), 1.4-1.6 (m, 96H), 0.9 (t, 72H); ³¹P NMR (CDCl₃, 121 MHz) δ 4.12, 4.09 (Jₚt-P = 2352.5 Hz).

Compound 10b. This compound was synthesized according to the same procedure used for compound 6a, except compound 9b (134 mg, 0.04 mmol) and potassium hydroxide (0.2 mL, 2 M in water) were used. A yellow solid was obtained as the product (124 mg, 99%). ¹H NMR (CDCl₃, 300 MHz) δ 7.28 (d, 4H), 7.15 (d, 4H), 7.07 (s, 8H), 6.8 (d, 2H), 6.6 (d, 2H), 3.1 (s, 2H), 1.9-2.0 (m, 48H), 1.4-1.6 (m, 96H), 0.9 (t, 72H); ³¹P NMR (CDCl₃, 121 MHz) δ 4.24, 4.18 (Jₚt-P = 2351.8 Hz).

N-(n-octyl)-naphthalene-1,8-dicarboxyanhydride-4,5-dicarboximide (11). ¹H NMR (CDCl₃, 300 MHz) δ 7.28 (d, 4H), 7.15 (d, 4H), 7.07 (s, 8H), 6.6 (s, 2H), 3.1 (s, 2H), 1.9-2.0 (m, 48H), 1.4-1.6 (m, 96H), 0.9 (t, 72H); ³¹P NMR (CDCl₃, 121 MHz) δ 4.24, 4.18 (Jₚt-P = 2351.8 Hz).

1,4,5,8-Naphthalenetetracarboxyldianhydride (10.0 g, 0.0373 mol) was refluxed under argon with stirring...
in DMF (100 mL). 1-Aminooctane (4.82 g, 0.0373 mol) was added dropwise down a condenser over 5 min. The mixture was refluxed for 15 h, and then cooled in a refrigerator for 2 h. The white precipitate was suction filtered. The filtrate was stripped to near dryness on a rotary evaporator, taken up in p-xylene, and the solvent was evaporated again. The residue was purified by column chromatography on silica (CH$_2$Cl$_2$). A light yellow solid was obtained as the product (5.1 g, 36%). $^1$H NMR (CDCl$_3$, 300 MHz) δ 8.82 (s, 4H), 4.2 (t, 2H), 1.28 (s, 12H), 0.88 (t, 3H).

$N$-(n-octyl)-$N'$-(4-iodo-phenyl)-naphthalene-1,8:4,5-tetracarboxydiimide (12). $N$-(n-octyl)-naphthalene-1,8-dicarboxyhydride-4,5-dicarboximide (11) (0.4 g, 1.05 mmol) was dissolved in DMF. The solution was degassed for 15 min with argon and heated to 80 °C. Then 4-iodoaniline (0.276 g, 1.26 mmol) and CaO (15 mg, 0.266 mmol) were added under an argon atmosphere. The solution was refluxed for 18 h at 150 °C. The hot solution was filtered to remove CaO and the filtrate was cooled in an ice bath. The residue yellow precipitate was filtered again and washed with hot hexane to afford a pale yellow powder as the product (0.4 g, 66%). $^1$H NMR (CDCl$_3$, 300 MHz) δ 8.8 (s, 4H), 7.9 (d, 2H), 7.0 (d, 2H), 4.2 (t, 2H), 1.28 (s, 12H), 0.85 (t, 3H).

$N$-(n-octyl)-$N'$-(4-triisopropylsilyl-ethynylphenyl)-naphthalene-1,8:4,5-tetracarboxydiimide (13). $N$-(n-octyl)-$N'$-(4-iodo-phenyl)-naphthalene-1,8:4,5-tetracarboxydiimide (12) (130 mg, 0.224 mmol) was dissolved in a mixed solvent system (1:1:1, THF/i-Pr$_2$NH/CH$_3$CN, 20 mL) and the mixture was degassed for 30 min with argon. Pd(PPh$_3$)$_4$ (0.02 eq, 0.0045 mmol, 5.2 mg) and CuI (0.04 eq, 0.009 mmol, 1.71 mg) were added under an argon atmosphere. Then triisopropylsilyl acetylene (1.5 eq, 0.334 mmol, 61 mg) was added dropwise and the reaction solution was heated to 40 °C for 20 h. The solution was cooled to room temperature and diluted with chloroform (75 mL), washed with saturated NH$_4$Cl (50 mL),
DI water (50 mL) and saturated NaCl (50 mL), and dried over anhydrous sodium sulfate. After removal of the solvents under a rotary evaporator, a yellow solid was obtained as the product (97 mg, 68%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 8.8 (s, 4H), 7.6 (d, 2H), 7.25 (d, 2H), 4.2 (t, 2H), 1.26 (s, 12H), 1.1 (s, 21H), 0.86 (t, 3H).

N-(n-octyl)-N’-(4-ethynylphenyl)-naphthalene-1,8:4,5-tetracarboxydiimide (14). N-(n-octyl)-N’-(4-triisopropylsilylacetylenylphenyl)-naphthalene-1,8:4,5-tetracarboxydiimide (13) (232 mg, 0.365 mmol) was dissolved in THF and the solution was degassed for 15 min with argon. Then TBAF (3 eq, 1.1 mmol, 1.1 mL, 1 M in THF) was added. After stirring at room temperature for 3 h, the mixture was diluted with methylene chloride (100 mL), washed with saturated NaCl (100 mL) and DI water (100 mL), and dried over anhydrous sodium sulfate. The solvent was removed under a rotary evaporator and the residue was purified by chromatography on silica (CH$_2$Cl$_2$). A dark brown solid was obtained as the product (140 mg, 80%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 8.8 (s, 4H), 7.6 (d, 2H), 7.25 (d, 2H), 4.2 (t, 2H), 3.15 (s, 1H), 1.26 (s, 12H), 0.86 (t, 3H).

Compound (15). N-(n-octyl)-N’-(4-acetylenylphenyl)-naphthalene-1,8:4,5-tetracarboxydiimide (14) (0.2 g, 0.418 mmol) and cis-dichloro-bis-(tri-n-butylphosphine)platinum(II) (0.34 g, 0.507 mmol) were dissolved in THF (12 mL) and diethylamine (15 mL), and the solution was degassed for 15 min with argon. Then the mixture was stirred under reflux overnight. The solvents were removed and chromatography on silica (4:1 CH$_2$Cl$_2$/hexane) gave a brown solid as the product (0.3 g, 65%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 8.8 (s, 4H), 7.4 (d, 2H), 7.1 (d, 2H), 4.2 (t, 2H), 2.09 (m, 12H), 1.55 (m, 12H), 1.42 (m, 12H), 1.26 (s, 12H), 0.87 (m, 21H); $^{31}$P NMR (CDCl$_3$, 121 MHz) $\delta$ 8.17 (J$_{Pt-P}$ = 2362.0 Hz).
Pt2T1A. Compound 14 (38 mg, 0.079 mmol) and compound 4a (50 mg, 0.036 mmol) were added to diethylamine (10 mL) to form a yellow suspension. The suspension was degassed for 15 min with argon. Then, the mixture was stirred under reflux overnight. The solvent was removed and chromatography on silica (1:4, then 1:9 hexane/CH₂Cl₂) gave a green solid as the product (60 mg, 73%). ¹H NMR (CDCl₃, 300 MHz) δ 8.8 (s, 8H), 7.4(d, 4H), 7.1 (d, 4H), 6.6 (s, 2H), 4.2 (t, 4H), 2.1 (broad singlet, 24H), 1.26-1.75 (m, 72H), 0.8-0.9 (m, 42H); ³¹P NMR (CDCl₃, 121 MHz) δ 4.38 (J_{Pt-P} = 2345.1 Hz); Elemental anal. calc’d C: 60.98, H: 7.06, N: 2.45; Found C: 60.79, H: 7.33, N: 2.39.

Pt2T2A. This compound was synthesized according to the same procedure used for Pt2T1A, except compound 14 (57 mg, 0.12 mmol) and compound 4b (80 mg, 0.054 mmol) were used. Chromatography on silica (3:7, then 1:4 hexane/CH₂Cl₂) gave a green solid as the product (77 mg, 60%). ¹H NMR (300 MHz, CDCl₃) δ 8.8 (s, 8H), 7.4(d, 4H), 7.1 (d, 4H), 6.8 (d, 2H), 6.6 (d, 2H), 4.2 (t, 4H), 2.1 (broad singlet, 24H), 1.26-1.75 (m, 72H), 0.8-0.9 (m, 42H); ³¹P NMR (CDCl₃, 121 MHz) δ 4.50 (J_{Pt-P} = 2339.6 Hz); Elemental anal. calc’d C: 60.90, H: 6.90, N: 2.37; Found C: 60.80, H: 6.72, N: 2.33.

Pt4T1A. Compound 6a (30 mg, 0.019 mmol) was dissolved in THF (10 mL) and diethylamine (10 mL), and the solution was degassed for 15 min with argon. Then, compound 15 (50 mg, 0.045 mmol) and CuI (0.36 mg, 0.0019 mmol) were added, and the mixture stirred at room temperature overnight. The solvents were removed and the crude product was purified by chromatography on silica (2:3, 3:7, 1:4, then 1:9 hexane/CH₂Cl₂) to give a gray dark solid as the product (43 mg, 61%) ¹H NMR (CDCl₃, 300 MHz) δ 8.8 (s, 8H), 7.4(d, 4H), 7.1 (m, 12H), 6.6 (s, 2H), 4.2 (t, 4H), 2.1 (broad singlet, 48H), 1.26-1.75 (m, 120H), 0.8-0.9 (m, 78H); ³¹P NMR
Pt4T2A. This compound was synthesized according to the same procedure used for Pt4T1A, except compound 6b (106 mg, 0.064 mmol), compound 15 (145 mg, 0.130 mmol) and CuI (1.2 mg, 0.0063 mmol) were used. Chromatography on silica (2:3, then 1:4 hexane/CH$_2$Cl$_2$) gave a gray dark solid as the product (146 mg, 60%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 8.8 (s, 8H), 7.4 (d, 4H), 7.1 (m, 12H), 6.8 (d, 2H), 6.6 (d, 2H), 4.2 (t, 4H), 2.1 (broad singlet, 48H), 1.26-1.75 (m, 120H), 0.8-0.9 (m, 78H); $^{31}$P NMR (CDCl$_3$, 121 MHz) $\delta$ 4.26, 4.22 (J$_{Pt-P}$ = 2351.6 Hz); Elemental anal. calc’d C: 59.20, H: 7.35, N: 1.47; Found C: 59.34, H: 7.10, N: 1.40.

Pt6T1A. This compound was synthesized according to the same procedure used for Pt4T1A, except compound 10a (82 mg, 0.027 mmol), compound 15 (62 mg, 0.056 mmol) and CuI (0.52 mg, 0.0027 mmol) were used. Chromatography on silica (1:4, then 1:9 hexane/CH$_2$Cl$_2$) gave a gray dark solid as the product (67 mg, 48%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 8.8 (s, 8H), 7.4 (d, 4H), 7.1 (m, 20H), 6.6 (s, 2H), 4.2 (t, 4H), 2.1 (broad singlet, 72H), 1.26-1.75 (m, 168H), 0.8-0.9 (m, 114H); $^{31}$P NMR (CDCl$_3$, 121 MHz) $\delta$ 4.26, 4.10, 4.00 (J$_{Pt-P}$ = 2355.0 Hz); Elemental anal. calc’d C: 58.43, H: 7.63, N: 1.08; Found C: 58.61, H: 7.38, N: 1.06.

Pt6T2A. This compound was synthesized according to the same procedure used for Pt4T1A, except compound 10b (114 mg, 0.037 mmol), compound 15 (82 mg, 0.0735 mmol) and CuI (0.67 mg, 0.0035 mmol) were used. Chromatography on silica (3:7, hexane/CH$_2$Cl$_2$, then 100% CH$_2$Cl$_2$) gave a gray dark solid as the product (160 mg, 82%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 8.8 (s, 8H), 7.4(d, 4H), 7.1 (m, 20H), 6.8 (d, 2H), 6.6 (d, 2H), 4.2 (t, 4H), 2.1 (broad singlet, 72H), 1.26-1.75 (m, 168H), 0.8-0.9 (m, 114H); $^{31}$P NMR (CDCl$_3$, 121 MHz) $\delta$ 4.26, 4.22 (J$_{Pt-P}$ = 2351.6 Hz); Elemental anal. calc’d C: 59.21, H: 7.45, N: 1.50; Found C: 58.95, H: 7.19, N: 1.40.
4.25, 4.04 (J_{P-P} = 2351.2 \text{ Hz}); \text{ Elemental anal. calc'd C: 58.43, H: 7.55, N: 1.06; Found C: 58.29, H: 7.27, N: 1.09.}
CHAPTER 3
PHOTOINDUCED ENERGY TRANSFER IN BIBLOCK PLATINUM ACETYLIDE Oligomers

Introduction

Triplet-triplet energy transfer is the most common and most important type of energy transfer in chemical and biochemical processes. The mechanism for triplet energy transfer is usually described by Dexter electron-exchange interaction and may be visualized in terms of two electron transfer processes. Triplet-triplet energy transfer has been studied in many donor-acceptor systems. Eng and coworkers designed a series of porphyrin-based donor-bridge-acceptor systems with varying bridge length to investigate triplet excitation energy transfer. They found that triplet-triplet energy transfer rates decrease exponentially with increasing the distance between the donor and the acceptor. Both their experimental and theoretical results indicate that energy transfer adopts an electron superexchange mechanism. In the other study, Danilov and coworkers reported ultrafast energy migration in platinum(II) diimine complexes bearing pyrenylacetylide chromophores. They found that triplet-triplet energy transfer (from $^{3}$MLCT [metal to ligand charge transfer] to ligand $^{3}(\pi,\pi^*)$) occurs with a few hundred femtoseconds because of highly electronically coupled structures. In our group, we recently reported intrachain triplet energy transfer in platinum acetylide copolymers. These copolymers consist of major repeat units of the type $[trans$-$Pt(PBu_3)_2(-C\equivC-Ph-C\equivC-)]$, where Ph = 1,4-phenylene, with randomly incorporating repeat units of the type $[trans$-$Pt(PBu_3)_2(-C\equivC-T-C\equivC-)]$, where T = 2,5-thienylene. Photoluminescence and transient absorption spectroscopy indicate that at room temperature intrachain triplet transfer from 1,4-phenylene to the 2,5-thienylene repeats occurs rapidly and efficiently in the copolymer with a low content of 2,5-thienylene repeats. The rate constant for energy transfer is greater than $10^8$ s$^{-1}$. At low temperature, triplet energy transfer is
much less efficient and a fraction of the triplet excitations is trapped on the high-energy 1,4-phenylene units.

In continuation of our investigation of intrachain triplet energy transfer in $\pi$-conjugated platinum acetylide systems, we designed and synthesized donor-acceptor systems by incorporating an anthracene moiety into the platinum acetylide backbone. The anthracene-based conjugated systems have been extensively studied due to their high yield fluorescence.\textsuperscript{76-87} Kashiwagi and coworker\textsuperscript{85} recently reported fluorine-containing biethynylanthracene derivatives, which they utilized to fabricate organic field-effect transistors. Zhao and coworkers\textsuperscript{87} reported synthesis and characterization of a series of conjugated anthracene/fluorene oligomers. They found that these oligomers emit a high yield yellow fluorescence due to the 9,10-biethynylanthracene incorporated into the oligomer backbone. However, little work has been done to explore phosphorescence and triplet excited states of anthracene-based derivatives due to low intersystem crossing yield in these systems.

Triplet-triplet energy transfer provides a good way to sensitize a triplet excited state that is not efficiently populated by intersystem crossing. It requires that the lowest triplet energy level of the donor must lie above that of the acceptor. According to literature reports,\textsuperscript{88} the first singlet excited state energy of 9,10-bis(phenylethynyl)anthracene (\textbf{BPEA}) lies at $\sim$2.4 eV, which is lower than that of the platinum acetylide chromophore ($\sim$3.0 eV). Our studies in platinum acetylide oligomers indicate that the first triplet excited state energy of the platinum acetylide chromophore is $\sim$2.38 eV.\textsuperscript{33} The first triplet excited state energy of \textbf{BPEA} or its derivatives has not been reported to our best knowledge. However, according to the DFT calculations in our newly designed compounds (refer to the discussion section), the first triplet excited state energy
of the anthracene moiety lies at ~1.31 eV, which is much lower than that of the platinum acetylide chromophore.

Because of the difference in energy levels between the anthracene moiety and the platinum acetylide moiety, it allows us to study the influences of the low energy trap on the triplet exciton in the platinum acetylide systems. The structures of the focus of the current study are shown in Figure 3-1. **Pt2An** and **Pt4An** consist of the core segment of anthracene and one and two repeat units of the type [-C≡C-trans-Pt(PBu3)2-C≡C-Ph1], where Ph1 = 1-phenylene, respectively. Our previously studied platinum complexes **Pt2** and **Pt4** are also shown as references.

![Chemical structures of anthracene-based platinum acetylide oligomers and reference complexes](image)

**Synthesis**

The oligomer **Pt2An** was synthesized according to Figure 3-2. It started from the Sonogashira coupling reaction between 9,10-dibromoanthracene and trimethylsilyl acetylene. The resulting TMS-protected compound **1** was deprotected with potassium hydroxide in a
THF/methanol solvent system to give 9,10-bis(ethynyl)anthracene (2). The Hagihara coupling reaction between compound 2 and cis-dichloro-bis-(tri-n-butylphosphine)platinum(II) gave the platinum complex 3 in 77% yield. The complex 3 was further reacted with phenylacetylene with CuI as catalyst in diethylamine to give the oligomer Pt2An in 80% yield.

\[ \text{Br} \quad \text{Br} \quad \xrightarrow{i} \quad \text{TMS} \quad \xrightarrow{98\%} \quad \text{Br} \quad \text{TMS} \quad \xrightarrow{98\%} \quad \text{TMS} \]

i) TMSA, Pd(PPh3)2Cl2, CuI, 1Pr2NH/THF, heat; ii) KOH, THF/MeOH; iii) Pt(PBu3)2Cl2, Et2NH; iv) Phenylacetylene, CuI, Et2NH.

Figure 3-2. Synthesis of Pt2An

The oligomer Pt4An was prepared following steps listed in Figure 3-3. First, the coupling reaction between phenylacetylene and cis-dichloro-bis-(tri-n-butylphosphine)platinum(II) gave the platinum complex 4 that was further reacted with 1-ethynyl-4-(trimethylsilylethynyl)benzene to give the TMS-protected platinum complex 5. After deprotection of the complex 5 under basic conditions, the resulting complex 6 was coupled with the complex 3 to give the final product Pt4An in moderate yield. The oligomers were characterized with 1H and 31P NMR, and elemental analysis. The coupling constant (JPt-Pt) in 31P NMR is below 2500 Hz, indicating that platinum centers adopt trans-configuration in the oligomers.
Results and Discussion

UV-Vis Absorption

The absorption spectra of Pt2An and Pt4An were recorded in dilute THF solutions (Figure 3-4). Both spectra feature two primary transitions. The low energy bands with two absorption maxima ($\lambda_{\text{max}} = 450$ and $480$ nm), which are attributed to $\pi,\pi^*$ transition of the anthracene segment. This is consistent with a literature report in an anthracene-based platinum containing...
compound that is structurally similar to Pt2An.\textsuperscript{89} According to a polarized electronic spectroscopy study of BPEA by Levitus and coworkers,\textsuperscript{88} the lower energy absorption band ($\lambda_{\text{max}} = 480$ nm) is attributed to the long axis $\pi,\pi^*$ transition (the short axis of anthracene) and the higher energy absorption band ($\lambda_{\text{max}} = 450$ nm) arises from the overlap of the long and short axis $\pi,\pi^*$ transition of the anthracene segment. Compared with the absorption spectrum of BPEA, two features can be seen with respect to the anthracene absorption in Pt2An and Pt4An. First, both anthracene absorption bands in Pt2An and Pt4An red shift ca. 30 nm, which is caused by the longer conjugation length in Pt2An and Pt4An. However, the shift from Pt2An to Pt4An is small (~3 nm), indicating that the effective oligomer chain length is confined within one repeat unit. Second, the two absorption bands ($\lambda = 450$ and 480 nm) are better resolved in Pt2An and Pt4An likely due to the rigid confirmation in these molecules that freezes the free rotation of the anthracene segment. The absorption bands near UV region are very different for the two complexes. For Pt2An a narrow absorption band centered at $\lambda = 317$ nm arises from the platinum acetylide segment that features the type of [-C≡C-Pt≡C-Ph1]. For Pt4An a broad and intense band concentrated at $\lambda = 355$ nm is assigned to $\pi,\pi^*$ transition of the platinum acetylide segment that features the type of [-Pt-C≡C-Ph-C≡C-Pt-]. Due to the longer conjugation length, the absorption band of the platinum acetylide segment in Pt4An red shifts ca. 25 nm relative to the absorption band in Pt2An. To explore influences of the conjugation length of the platinum acetylide segment on the absorption spectra, we used our previously studied platinum acetylide oligomers Pt2 and Pt4 as references for Pt2An and Pt4An, respectively (see Figure 3-1 for structures). The absorption spectra of the complexes Pt2 and Pt4 exhibit the dominant bands at UV region (355 nm for Pt2 and 367 nm for Pt4) according to our previous report.\textsuperscript{33} The absorption bands of the platinum acetylide segments in both Pt2An and Pt4An blue shift
compared with their corresponding references, indicating that the effective conjugation length is confined within the platinum acetylide segment, in particular, the unit of the type [Ph₁-C≡C-Pt-C≡C-] for Pt₂An and the unit of the type [-Pt-C≡C-Ph-C≡C-Pt-] for Pt₄An.

**Steady State Photoluminescence**

The photoluminescence spectra of Pt₂An and Pt₄An were recorded in dilute THF solutions with several different excitation wavelengths (Figure 3-5). The photoluminescence spectra of Pt₂An exhibit an intense emission band centered at $\lambda_{\text{max}} = 505$ nm along with a vibronic band concentrated at $\lambda = 550$ nm. The band intensity increases with increasing excitation wavelength and reaches the maximum with $\lambda_{\text{ex}} = 480$ nm. We assigned these bands to the fluorescence emission that arises from the anthracene segment. Compared with BPEA, the emission band red shifts *ca.* 40 nm due to the increased conjugation length in Pt₂An (Figure 3-6). In addition, the vibronic band becomes broader and less resolved, indicating that different conformers of Pt₂An may exist in its excited state. Phosphorescence emission originating from the platinum acetylide segment was not observed. The fluorescence quantum yield measured with BPEA as standard is ~0.96 for Pt₂An.

For Pt₄An the intense fluorescence bands originating from the anthracene segment are also shown when the anthracene segment was directly excited ($\lambda_{\text{ex}} = 450$ and 480 nm). With direct excitation of the platinum acetylide segment at $\lambda = 355$ nm, the spectrum features the dominant fluorescence arising from the anthracene segment, as well as a weak band centered at $\lambda \approx 400$ nm that is assigned to fluorescence originating from the platinum acetylide segment. The fluorescence quantum yield of Pt₄An measured with Ru(bpy)₃²⁺ in air-saturated water as standard is ~0.014. Compared with Pt₂An, fluorescence in Pt₄An is dramatically quenched.

Photophysical data of both complexes are shown in Table 3-1.
Figure 3-5. Photoluminescence spectra of A) Pt2An and B) Pt4An in THF solution

Figure 3-6. Normalized photoluminescence spectra of Pt2An and Pt4An in THF solution with $\lambda_{ex} = 450$ nm. For BPEA $\lambda_{ex} = 440$ nm.
Table 3-1. Photophysical data of Pt2An and Pt4An

<table>
<thead>
<tr>
<th></th>
<th>Absorption $\lambda_{\text{max}}$/nm</th>
<th>Emission $\lambda_{\text{max}}$/nm</th>
<th>Quantum yield (F) (Φ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt2An</td>
<td>317, 450, 480</td>
<td>504</td>
<td>0.96</td>
</tr>
<tr>
<td>Pt4An</td>
<td>355, 453, 483</td>
<td>504</td>
<td>0.014</td>
</tr>
</tbody>
</table>

Note: F = Fluorescence.

To further confirm the origin of the bands in the photoluminescence spectra, the excitation spectra of Pt2An and Pt4An were measured in THF solutions (Figure 3-7). The absorption spectra are also shown for comparison purposes. The fluorescence band at $\lambda = 536$ nm was monitored when scanning for excitation. The resulting excitation spectra are in the same shape with their corresponding absorption spectra. However, the bands at 450 and 480 nm are almost...
twice as strong as their absorption bands, indicating that the emission bands arise from the anthracene segment.

To explore effects of temperature on the spectroscopy of Pt4An, variable-temperature photoluminescence were carried out in 4-methyltetrahydrofuran (Me-THF) solution with the excitation wavelength at $\lambda = 450$ nm (Figure 3-8). Below the solvent glass temperature, the vibronic band is more resolved. This is believed due to the rigid conformation of Pt4An in the frozen glass. In this case, only one conformation exists compared with the coexistence of several conformations in the solution state, which is consistent with literature reports.\(^8\) Low temperature emission spectra were also recorded with $\lambda_{ex} = 355$ nm. The spectra are similar to the one that was obtained with $\lambda_{ex} = 450$ nm. Note that the weak peak at ca. 610 nm is a scanning peak.

![Figure 3-8. Low temperature emission spectra of Pt4An in Me-THF solution](image)

According to our DFT calculations (see later section for detail), the energy level of the first triplet state of the anthracene segment in Pt2An and Pt4An is $\sim 1.31$ eV (946 nm). To detect the corresponding phosphorescence emission, the near-IR photoluminescence was carried out in deoxygenated THF solution. We monitored the spectra ranging from 850 to 1400 nm. The phosphorescence emission was not observed with excitation at $\lambda = 355, 450$ and 480 nm.
Time-Resolved Photoluminescence

To further gain insight into the dynamics and decays of singlet and triplet excited states, time-resolved emission measurements were carried out in deoxygenated THF solutions for Pt2An and Pt4An. The spectra were obtained following 355 nm laser excitation (Figure 3-9).

For Pt2An the fluorescence decay is fast and the lifetime recovered from time-resolved spectra is less than 10 ns. For Pt4An in the early time (less than 20 ns) following laser pulses, the fluorescence emission of the anthracene segment appears and it decays rapidly. A slow decay band centred at $\lambda = 517$ nm along with a vibronic band shows up at ~60 ns after laser pulses, which is assigned to the phosphorescence decay of the platinum acetylide segment consistent with our previous study. The lifetime of this decay band is ~1.6 $\mu$s, which is much shorter.
compared with the lifetime of its corresponding reference compound \textbf{Pt4} (\( \tau = 18.6 \, \mu s \)), indicating that the phosphorescence emission of the platinum acetylide segment in \textbf{Pt4An} is dramatically quenched.

\textbf{Transient Absorption}

In order to gain insight into the dynamics of the triplet excited states, transient absorption spectra of \textbf{Pt2An} and \textbf{Pt4An} were recorded in deoxygenated THF solutions following 355 nm laser excitation (Figure 3-10). Both complexes exhibit intense excited state absorption bands centered at \( \lambda_{\text{max}} = 530 \, \text{nm} \) along with the ground state bleaching bands (450-500 nm). In order to assign the origin of these bands, we compare the spectra with the triplet-triplet absorption spectra of the reference compound \textbf{Pt4}. The triplet absorption band of \textbf{Pt4} is centered at \( \lambda = 660 \, \text{nm} \), which arises from the platinum acetylide segment according to our previous study.\textsuperscript{33} A ca. 130 nm blue shift and the completely different band shape in \textbf{Pt4An} transient absorption spectra indicate that the excited state absorption band of \textbf{Pt4An} does not arise from the platinum acetylide segment. It is therefore reasonable to assign this band to the triplet-triplet absorption originating from the anthracene segment. It may also contain some contributions of triplet-triplet absorption of the platinum acetylide segment, which is shown as the broad tail between 600 and 700 nm. The triplet lifetimes recovered from transient absorption spectra are 3.7 \( \mu s \) for \textbf{Pt2An} and 4.2 \( \mu s \) for \textbf{Pt4An}. Compared with their reference compounds, the lifetimes are much shorter in \textbf{Pt2An} and \textbf{Pt4An}, suggesting that the triplet decay is fast likely due to the low triplet energy level in \textbf{Pt2An} and \textbf{Pt4An} that results in rapid non-radiative decay. This is consistent with the energy gap law which states that non-radiative decay rates decrease exponentially with decreasing triplet energy.
Density Functional Theory Calculations

Density functional theory (DFT) calculations were applied to provide insight concerning the energies of the singlet and triplet states of $\text{Pt}2\text{An}$ and $\text{Pt}4\text{An}$. Both calculation and spectroscopic energies of the singlet and triplet states are shown in Table 3-2. It is important to note that the calculation results are very consistent with spectroscopic study. The calculations indicate that two different conformers exist in the triplet state of the platinum acetylide segment in $\text{Pt}4\text{An}$: one is defined “twisted” (t) as the conformation in which the planes defined by the square-planar $\text{trans}-\text{Pt}(\text{PBU}_3)_2(\text{C})_2$ and phenylene units are perpendicular and the other one is defined “planar” (p) as the conformation in which these two units are coplanar (Figure 3-11).
The twisted conformer in the triplet state lies ca. 0.2 eV lower in energy (Table 3-2). This is consistent with our previous DFT calculations in platinum acetylide oligomers.\textsuperscript{34} DFT calculations indicate that the energy level of the first triplet excited state of the anthracene segment is \( \sim 1.31 \) eV. Khan and coworkers observed a weak phosphorescence shoulder at the energy of \( \sim 1.50 \) eV in a platinum(II) di-yne complex that consists of an anthracene spacer inserted into a platinum acetylide backbone that is structurally similar to \textbf{Pt2An}. Considering the calculation errors, our DFT calculations are in good agreement with the literature report.\textsuperscript{89} The orbital diagram of DFT calculations is shown in Figure 3-11.

Figure 3-11. Energies of \textbf{Pt2An} and \textbf{Pt4An} by DFT calculations
Table 3-2. Energies of Pt2An and Pt4An

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<tr>
<td>Pt2An</td>
<td>2.54</td>
<td>-</td>
<td>1.31</td>
</tr>
<tr>
<td>Pt4An</td>
<td>2.52</td>
<td>2.61(p)</td>
<td>1.31</td>
</tr>
</tbody>
</table>

Note: An = Anthracene segment; Pt = Platinum acetylide segment; Ca. = Calculation; Sp. = Spectroscopy (calculated from the emission spectra); S1 = First singlet excited state; T1 = First triplet excited state; p = planar conformer; t = twisted conformer.

Energy Transfer Dynamics

Prior to further discussion of the energy transfer dynamics in the anthracene-based platinum acetylide systems, we first summarize the photophysical results of Pt4An based on the above spectroscopic and DFT studies: (1) The fluorescence emission originating from the anthracene segment is present and the phosphorescence emission arising from the platinum acetylide segment is strongly quenched in the photoluminescence spectra; (2) in contrary with Pt2An whose fluorescence quantum yield is close to unity, the fluorescence quantum yield of Pt4An is very low (0.014); (3) the phosphorescence lifetime of the platinum acetylide segment (1.6 µs) recovered from time-resolved emission is much shorter compared with its reference compound Pt4 (τ = 18.6 µs); (4) the phosphorescence emission of the anthracene segment is not present in near-IR photoluminescence spectra; (5) DFT calculations indicate that the triplet energy gap between the platinum acetylide segment and the anthracene segment is large (~1.1 eV); (6) triplet-triplet absorption of the anthracene segment dominates the transient absorption spectra along with small contributions of triplet-triplet absorption of the platinum acetylide segment.

In order to explain the above observations, we proposed an energy transfer mechanism as shown in Figure 3-12. Two important energy transfer processes are involved in this mechanism: singlet to triplet energy transfer from the anthracene segment to the platinum acetylide segment; triplet to triplet energy transfer from the platinum acetylide segment to the anthracene segment.
Singlet to triplet energy transfer is rare because it is a spin-forbidden process. But it can occur in certain systems if a number of conditions are fulfilled. First, the singlet excited state of the acceptor must lie above the singlet state of the donor to avoid singlet-singlet energy transfer. In Pt4An, the singlet excited state of the platinum acetylide segment (3.1 eV) is ~0.65 eV higher than that of the anthracene segment. Second, the donor triplet level must be considerable lower than the acceptor triplet level. The larger the energy difference between the donor and acceptor triplet states, the higher the probability of appearance of acceptor molecules in the triplet state at the expense of S-T energy transfer relative to the probability of T-T energy transfer from the donor to acceptor. Some studies indicate that the triplet-triplet energy gap between the donor and acceptor must be more than 0.12 eV. In Pt4An, the triplet state of the anthracene segment lies ~1.1 eV lower than the triplet state of platinum acetylide segment. The dramatic fluorescence quenching in Pt4An demonstrates that singlet to triplet energy transfer is very efficient in this system.

![Energy diagram of photophysical processes in Pt4An](image)

**Figure 3-12.** Energy diagram of photophysical processes in Pt4An. An = the anthracene segment; Pt = the platinum acetylide segment; NR = non-radiative decay
Following singlet-triplet energy transfer, triplet-triplet energy transfer from the platinum acetylide segment to the anthracene segment occurs. The significant phosphorescence quenching of the platinum acetylide segment and the dominant triplet-triplet absorption of the anthracene segment provide experimental evidence for efficient triplet-triplet energy transfer. The phosphorescence emission originating from the anthracene segment was not observed in the near-IR spectroscopy, indicating that the decay of its triplet state adopts non-radiative pathway because of the energy gap law, which states that non-radiative decay rate increases exponentially with decreasing triplet energy level. This is consistent with previous studies which have been concluded that non-radiative decay rate of platinum containing oligomers and polymers obeys the energy gap law. In addition, from our DFT calculations the first triplet state level of the anthracene segment lies at ~1.31 eV, which is considerably lower than that of most $\pi$-conjugated platinum oligomers, indicating that non-radiative decay rate must be extremely rapid in this system.

The other pathway of triplet-triplet energy transfer called direct energy transfer is also involved, in particular, when the platinum acetylide segment is directly excited ($\lambda = 355$ nm). First, the singlet excited state of the platinum acetylide segment is created followed by rapid intersystem crossing to give corresponding triplet excited state, then energy transfer to the triplet state of the anthracene segment. These two pathways do not occur separately and they both contribute to the triplet excited state of the anthracene segment.

For Pt2An, it lacks the triplet state of the platinum acetylide segment according to both spectroscopic study and DFT calculations. The triplet-triplet absorption of the anthracene segment may be explained by the increasing intersystem crossing when platinum metal is incorporated into the anthracene segment. The singlet excited state of the platinum acetylide
segment is well mixed with that of the anthracene segment in \textbf{Pt2An}. A singlet-singlet energy transfer equilibrium therefore exists, which enhances intersystem crossing. A diagram concerning photophysical processes in \textbf{Pt2An} is shown in Figure 3-13.

![Energy diagram of photophysical processes in Pt2An](image)

Figure 3-13. Energy diagram of photophysical processes in \textbf{Pt2An}. An = the anthracene segment; Pt = the platinum acetylide segment; NR = non-radiative decay

\section*{Conclusion}

We designed and synthesized two platinum acetylide oligomers that incorporate an anthracene moiety into a platinum acetylide backbone to study energy transfer dynamics. Both spectroscopic study and DFT calculations support an indirect energy transfer mechanism — a rare singlet-triplet energy transfer process followed by a triplet-triplet energy transfer process. This system provides a unique platform for studying singlet-triplet energy transfer because of its fulfillment of energies required. Future studies of these systems with fast timescale spectroscopic techniques are suggested.
Experimental

Photophysical Measurements

Steady-state absorption spectra were recorded on a Varian Cary 100 dual-beam spectrophotometer. Corrected steady-state emission measurements were conducted on a SPEX F-112 fluorescence spectrometer. Samples were degassed by argon purging for 30 min and concentrations were adjusted such that the solutions were optically dilute ($A_{\text{max}} < 0.20$). Low-temperature emission measurements were conducted in 1-cm diameter borosilicate glass tubes in a liquid-nitrogen-cooled Oxford Instruments DN-1704 optical cryostat connected to an Omega CYC3200 autotuning temperature controller. Samples were degassed by three consecutive freeze-pump-thaw cycles on a high-vacuum ($10^{-5}$ Torr) line.

Photoluminescence quantum yields were determined by relative actinometry. BPEA ($\Phi_F = 1$ in THF) and Ru(bpy)$_3^{2+}$ ($\Phi_F = 0.0379$ in air-saturated H$_2$O) were used as actinometers for Pt$2\text{An}$ and Pt$4\text{An}$, respectively. Time-resolved emission measurements were conducted on a previously described home-built apparatus.$^{92}$ Optically dilute solutions were used.

Transient absorption measurements were carried out on a home-built apparatus consisting of a Continuum Surelite series Nd:YAG laser as the excitation source ($\lambda = 355$ nm, 10 ns fwhm). Typical excitation energies were 5 mJ/pulse. The source for monitoring optical transients was a Hamamatsu Super-Quiet series xenon flashlamp, and the monitoring light was detected by a Princeton Instruments PI-MAX intensified CCD camera detector coupled to an Acton SpectroPro 150 spectrograph. Samples were contained in a cell with a total volume of 10 mL and the contents were continuously circulated through the pump-probe region of the cell. Solutions were degassed by argon purging for 30 min. Sample concentrations were adjusted so that $A_{355} \approx 0.8$. 

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DFT Calculations

DFT calculations were carried out by Dr. Erkan M. Kose in National Renewable Energy Laboratory using the Gaussian 03 program.

Synthesis

General. Solvents and chemicals used for synthesis were of reagent grade and used without purification unless noted. Reactions were carried out under an argon atmosphere. NMR spectra were recorded on Varian VXR, Gemini or Mercury 300 MHz spectrometers. *Cis-*dichloro-bis-(tri-n-butylphosphine)platinum(II) and 1-ethynyl-4-(trimethylsilylethynyl)benzene were prepared by literature methods.

9,10-Bis(trimethylsilylethynyl)anthracene (1). 9,10-Dibromoanthracene (0.5 g, 1.5 mmol), Pd(II) (53 mg, 0.075 mmol) and CuI (29 mg, 0.15 mmol) were added to THF/i-Pr₂NH and the solution was degassed for 15 min. Then the temperature was increased to 50 °C, at which time TMSA (0.59 g, 6 mmol) was added. The mixture was stirred at 80 °C overnight. Solvents were removed under vacuum and the crude product was further purified by column chromatography with hexane as an eluent. A deep red solid was obtained as the product (0.55 g, 98%). ¹H NMR (CDCl₃, 300 MHz) δ 8.55 (q, 4H), 7.6 (q, 4H), 0.4 (t, 18 H).

9,10-Bis(ethynyl)anthracene (2). Compound 1 (50 mg, 0.135 mmol) was dissolved in THF and the solution was degassed for 15 min. Then KOH (15 mg, 0.27 mmol, in methanol) was added via syringe. After TLC analysis showed that all starting material was consumed, MeCl₂ (50 mL) was added. The solution was washed with water and dried over anhydrous Na₂SO₄. A brown solid was obtained as the product after removal of the solvents under vacuum (30 mg, 98%). ¹H NMR (CDCl₃, 300 MHz) δ 8.60 (q, 4H), 7.60 (q, 4H), 4.05 (s, 2H).
**Compound 3.** 9,10-Bis(ethynyl)anthracene (2) (45 mg, 0.2 mmol) and cis-dichloro-bis-(tri-n-butylphosphine)platinum(II) (0.27 g, 0.4 mmol) were dissolved in diethylamine (10 mL) and the solution was degassed for 15 min, then refluxed overnight. The solvent was removed under vacuum. Column chromatography on silica (3:2 hexane/MeCl₂) gave an orange solid as the product (0.23 g, 77%). ¹H NMR (CDCl₃, 300 MHz) δ 8.60 (q, 4H), 7.38 (q, 4H), 1.90 (m, 24H), 1.60 (m, 24H), 1.40 (m, 24H), 0.90 (t, 36 H). ³¹P NMR (CDCl₃, 121 MHz) δ 8.50 (J_{Pt-P} = 2370.1 Hz).

**Pt₂An.** Compound 3 (42 mg, 0.028 mmol), phenylacetylene (6 mg, 0.06 mmol) and CuI (3 mg) were added to diethylamine. The solution was degassed for 15 min and stirred at room temperature overnight. The solvent was removed under vacuum. Column chromatography on silica (4:1, then 3:2 hexane/MeCl₂) gave an orange solid as the product (36 mg, 80%). ¹H NMR (CDCl₃, 300 MHz) δ 8.70 (bs, 4H), 7.1-7.3 (m, 14H), 2.10 (m, 24H), 1.65 (m, 24H), 1.40 (m, 24H), 0.90 (t, 36 H). ³¹P NMR (CDCl₃, 121 MHz) δ 4.75 (J_{Pt-P} = 2356.7 Hz); Elemental anal. calc’d C 60.57, H 7.81, found C 60.29, H 8.09.

**Compound 4.** This compound was synthesized according to the same procedure used for compound 3, except phenylacetylene (36 mg, 0.35 mmol) and cis-dichloro-bis-(tri-n-butylphosphine)platinum(II) (0.23 g, 0.34 mmol) were used. Column chromatography on silica (7:3 hexane/MeCl₂) gave a light yellow solid as the product (0.24 g, 96%). ¹H NMR (CDCl₃, 300 MHz) δ 7.20 (m, 5H), 2.10 (m, 12H), 1.61 (m, 12H), 1.45 (m, 12H), 0.90 (t, 18 H). ³¹P NMR (CDCl₃, 121 MHz) δ 7.94 (J_{Pt-P} = 2365.0 Hz).

**Compound 5.** This compound was synthesized according to the same procedure used for compound 3, except compound 4 (0.35 g, 0.475 mmol) and 1-ethynyl-4-(trimethylsilyl)ethynyl)benzene (0.1 g, 0.5 mmol) were used. Column chromatography on silica
(4:1 hexane/MeCl₂) gave a yellow solid as the product (0.26 g, 61%). $^1$H NMR (CDCl₃, 300 MHz) δ 7.20 (m, 5H), 6.9 (m, 4H), 2.10 (m, 12H), 1.61 (m, 12H), 1.45 (m, 12H), 0.90 (t, 18 H), 0.24 (t, 9H). $^{31}$P NMR (CDCl₃, 121 MHz) δ 4.21 (J_{Pt-P} = 2347.0 Hz).

**Compound 6.** This compound was synthesized according to the same procedure used for compound 2, except compound 5 (0.25 g, 0.278 mmol) and KOH (0.16 g, 2.78 mmol, in methanol) were used. A yellow solid was obtained as the product (0.2 g, 87%). $^1$H NMR (CDCl₃, 300 MHz) δ 7.20 (m, 5H), 6.9 (m, 4H) 3.10 (s, 1H), 2.10 (m, 12H), 1.61 (m, 12H), 1.45 (m, 12H), 0.90 (t, 18 H). $^{31}$P NMR (CDCl₃, 121 MHz) δ 4.21 (J_{Pt-P} = 2347.0 Hz).

**Pt4An.** This compound was synthesized according to the same procedure used for Pt2An, except compound 6 (0.2 g, 0.24 mmol), compound 3 (0.17 g, 0.114 mmol) and CuI (5 mg) were used. Column chromatography on silica (1:1 hexane/MeCl₂) gave a red solid as the product (0.2 g, 57%). $^1$H NMR (CDCl₃, 300 MHz) δ 8.71 (bs, 4H), 7.36 (bs, 4H), 7.10-7.3 (m, 18 H), 2.10 (m, 48H), 1.61 (m, 48H), 1.45 (m, 48H), 0.90 (t, 72H). $^{31}$P NMR (CDCl₃, 121 MHz) δ 4.90, 4.12 (J_{Pt-P} = 2363.0 Hz). Elemental anal. calc’d C 58.61, H 7.94, found C 58.38, H 8.22.
CHAPTER 4
PHOTOPHYSICS OF PLATINUM TETRAYNE OLIGOMERS: DELOCALIZATION OF TRIPLET EXCITATION

Introduction

Organic and organometallic oligomers that feature extended sp carbon chains, e.g., R-(C≡C)_n-R and L_yM-(C≡C)_n-ML_y have attracted recent interest due to their potential use as electronic and optoelectronic materials.⁹³-⁹⁹ Oligoynes feature rigid rod structures and extended π-electron delocalization, which makes them attractive building blocks for the construction of linear carbon-rich materials which may possess potential applications as molecular electronic wires for studying exciton or charge transport on the nanoscale.³⁵

To increase the stability of linear carbon chain compounds, transition metals, such as rhenium, iron, ruthenium, platinum, manganese and gold, have been incorporated as end-caps to the oligoyne chains.⁹⁴,⁹⁷,⁹⁸,¹⁰⁰-¹⁰⁴ Most studies of these transition metal-containing carbon chain compounds have focused on synthesis, structural properties and optical absorption spectroscopy. However, an important feature of these compounds is that their triplet excited states are produced in relatively high yield due to the strong spin-orbit coupling induced by the transition metals. There are only a few reports concerning this aspect. Yam and coworkers¹⁰⁴ reported a spectroscopic study of a series of platinum (II)-terpyridyl-capped carbon chains. They found that low temperature photoluminescence of these complexes features the phosphorescence emission originating from carbon chain ³(π,π*) transition with a vibrational progressional spacing of ca. 2052 cm⁻¹. Che and coworkers⁹⁹ investigated a series of gold end-capped carbon chain compounds. Their spectroscopic results indicate that the lowest-energy electronic excited states are dominated by the acetylenic ³(π,π*) transition and a well-defined vibronic progression with spacing of ca. 2000 cm⁻¹ corresponds to the ν (C≡C) stretch in the ³(π→π*) excited state.
We recently reported a photophysical study of a series of platinum end-capped polyyne oligomers that features increasing sp carbon chain length (Figure 4-1).\textsuperscript{92} The results of this study indicate that low temperature photoluminescence spectra exhibit moderately efficient phosphorescence appearing as a series of narrow vibronic bands separated by \textit{ca.} 2100 cm\textsuperscript{-1}. The emission originates from the sp carbon chain $^3(\pi,\pi^*)$ transition and the vibronic progression arises from coupling of the excitation to the $\nu (C\equiv C)$ stretch. With increasing sp carbon chain length, the 0-0 energy of the phosphorescence decreases across the series. Moreover, a quantitative energy gap law correlation has been revealed with the analysis of the triplet non-radiative decay rates in these compounds.

![Figure 4-1. Platinum end-capped polyynes studied by Farley\textsuperscript{92}](image)

While there have been a number of studies of transition metal end-capped linear carbon chain molecules, little work has been done on metal-carbon chain alternant constructed compounds, e.g., M-$\{\text{C=C}_n\text{-M}\}_{\text{m}}$. In particular, the type of the molecule with $n > 2$ and $m > 1$ is unknown according to our best knowledge. However, the molecule with this type of structure is very important, as it provides a unique platform to study triplet exciton delocalization. To extend our photophysical study of this type of molecule, one of our groups have recently synthesized and structurally characterized a series of platinum-containing tetrayne oligomers of the type Cl-Pt(P$_2$)-$\{\text{C=C}_n\text{-Pt(P$_2$)}\}_{\text{m}}$-Cl, where P = a phosphine ligand and $n = 1$-3.\textsuperscript{105}
We now report a detailed study of the photophysics of the series of platinum tetrayne oligomers, \((\text{PtC}_8)_n\) \((n = 1, 2, 3; \text{Figure 4-2})\). The properties of the triplet excited states have been probed by variable-temperature luminescence and transient absorption spectroscopy.

Figure 4-2. Platinum tetrayne oligomers of the current study

**Results**

**UV-Vis Absorption**

The absorption spectra of the series of \((\text{PtC}_8)_n\) oligomers were recorded in Me-THF solutions. As shown in Figure 4-3, all of three oligomers feature two electronic primary transitions which each appear as a manifold of vibronic bands. In general, the high energy transition occurs between 300 and 380 nm and the low energy transition occurs between 380 and 450 nm. Both transitions red-shift with increasing carbon chain length. However, the red-shift is small from \((\text{PtC}_8)_2\) to \((\text{PtC}_8)_3\), indicating that the effective conjugation length for absorption is \(\sim 2\) repeat units. The low energy transition is relatively weak, whereas the higher energy transition is very intense. For \((\text{PtC}_8)_2\) and \((\text{PtC}_8)_3\) a well-defined vibronic progression appears in both transitions. For \((\text{PtC}_8)_1\) the high energy transition features a broad absorption band along
with a weak vibronic shoulder. According to our previous study, both of these bands originate from the -(C≡C)₄- carbon chain π,π* transitions.

![Figure 4-3. Absorption spectra of *(PtC₈)ᵢ* complexes in Me-THF solution](image)

**Steady-State Photoluminescence**

Photoluminescence spectra for all of the *(PtC₈)ᵢ* complexes were recorded in Me-THF solution at temperature ranging from 300 to 80 K. Several features can be seen from the spectra at 100 K in the Me-THF solvent glass (Figure 4-4). First, all of complexes exhibit an intense and narrow 0-0 emission band followed by two vibronic progression sub-bands. The 0-0 bands are assigned to phosphorescence from $^{3}\pi,\pi^*$ excited states and the vibronic sub-bands in each spectrum arise due to coupling of the triplet excitation to the C≡C stretch of the carbon chain. Second, the 0-0 phosphorescence bands red-shifts *ca.* 20 nm from *(PtC₈)₁* to *(PtC₈)₂*, whereas there is little or no shift from *(PtC₈)₂* to *(PtC₈)₃*. This indicates that the triplet exciton is localized, which is consistent with our previous reports. Third, the ratio of the intensity of 0-1 to 0-0 bands ($I_{0-1}/I_{0-0}$) decreases with increasing chain length. Interestingly, the ratio drops sharply from 0.5 to 0.25 between *(PtC₈)₁* and *(PtC₈)₂*, but it is then approximately the same for *(PtC₈)₂* and
(PtC₈)₃. This observation is consistent with the trends in the absorption and phosphorescence maxima, which imply that the triplet state is localized over ~2 repeat units.

Figure 4-4. Photoluminescence spectra of (PtC₈)ₙ complexes in Me-THF solvent glass at 100 K. A) (PtC₈)₁, $\lambda_{\text{ex}} = 327$ nm. B) (PtC₈)₂, $\lambda_{\text{ex}} = 368$ nm. C) (PtC₈)₃, $\lambda_{\text{ex}} = 371$ nm
With increasing temperature, the phosphorescence intensity steadily decreases, whereas the spectra red-shifts only ca. 4 nm (80 → 300 K) and the band shape are not changed. Temperature dependent spectra of \( (\text{PtC}_8)_2 \) are shown in Figure 4-5 and the spectra of the other two complexes indicate similar trend. The quantum yields measured at ambient temperature are in the range of 0.001 to 0.004, and increase with increasing chain length (Table 4-2). Excitation spectra were obtained for all of the complexes monitored at 0-0 emission peak at 100 K in Me-THF glass. As shown in Figure 4-6, the spectra are similar to the absorption spectra, except that the bands are better resolved. This is likely due to the frozen glass matrix.

![Variable-temperature photoluminescence spectra of \( (\text{PtC}_8)_2 \) in Me-THF](image)

Figure 4-5. Variable-temperature photoluminescence spectra of \( (\text{PtC}_8)_2 \) in Me-THF

The photoluminescence spectra of all of three complexes appear as a narrow 0-0 bands with two vibronic sub-bands separated by approximately 2100 cm\(^{-1}\). The vibronic progression originates from the stretching mode of the \((\text{C}≡\text{C})_4\) chains. In order to gain further insight into the nature of the triplet state, utilizing methods described in previous papers,\(^{92,106}\) the photoluminescence spectra of \( (\text{PtC}_8)_1 \), \( (\text{PtC}_8)_2 \) and \( (\text{PtC}_8)_3 \) at 100 K were analyzed by a single-mode Franck-Condon expression as shown in Equation 4-1.
Figure 4-6. Excitation spectra of A) (PtC₈)₁, B) (PtC₈)₂ and C) (PtC₈)₃. The corresponding absorption spectra are also shown for comparison. Excitation spectra were monitored at 0-0 emission peaks in Me-THF solvent glass at 100 K.
\[ I(\nu) = \sum_{\nu_m=0}^{S_m} \left( \frac{E_{00} - \nu_m \hbar \omega_m}{E_{00}} \right)^3 \frac{(S_m)^{v_m}}{v_m!} \exp \left[ -4 \ln 2 \left( \frac{\nu - E_{00} + \nu_m \hbar \omega_m}{\Delta \nu_{0,1/2}} \right)^2 \right] \]  \hspace{1cm} (4-1)

where \( I(\nu) \) is the relative emission intensity at energy \( \nu \), \( E_{00} \) is the energy of the 0-0 transition, \( \nu_m \) is the quantum number of the average medium-frequency vibrational mode, \( \hbar \omega_m \) is the average medium-frequency acceptor modes coupled to the triplet-excited-state to ground-state transition, \( S_m \) is the Huang-Rhys factor, and \( \Delta \nu_{0,1/2} \) is the half-width of the individual vibronic bands. The experimental emission spectra were fitted using a Visual Basic macro in Microsoft Excel. The fitted spectra are shown in the appendix B as Figure B-1. A summary of the parameters recovered from the spectra fitting is provided in Table 4-1.

### Table 4-1. Emission spectra fitting parameters for (PtC₈)ₙ complexes at 100 K

<table>
<thead>
<tr>
<th></th>
<th>( \lambda_{\text{max,em}} ) /nm</th>
<th>( E_{00} ) /cm(^{-1} )</th>
<th>( \hbar \omega ) /cm(^{-1} )</th>
<th>( \Delta \nu_{0,1/2} ) /cm(^{-1} )</th>
<th>( S_m )</th>
<th>( \Delta E_{\text{ST}} ) /eV</th>
<th>( \Delta E_{\text{ST}} ) /eV(^a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PtC₈)₀₁</td>
<td>584</td>
<td>17 123</td>
<td>2100</td>
<td>230</td>
<td>0.9</td>
<td>0.64</td>
<td>0.92(Pt-1)</td>
</tr>
<tr>
<td>(PtC₈)₀₂</td>
<td>595</td>
<td>16 778</td>
<td>2045</td>
<td>250</td>
<td>0.5</td>
<td>0.50</td>
<td>0.82(Pt-2)</td>
</tr>
<tr>
<td>(PtC₈)₀₃</td>
<td>595</td>
<td>16 806</td>
<td>2085</td>
<td>235</td>
<td>0.4</td>
<td>0.50</td>
<td>0.79(Pt-3)</td>
</tr>
</tbody>
</table>

\(^a\) singlet-triplet energy splitting of reference compounds (see Figure 4-10 for structures).

Several interesting features emerge from Table 4-1 with respect to the parameters recovered from the spectral fits. First, while the 0-0 emission energy for (PtC₈)₀₁ is ca. 350 cm\(^{-1} \) higher than that for (PtC₈)₀₂, the energy difference between (PtC₈)₀₂ and (PtC₈)₀₃ is only ca. 30 cm\(^{-1} \). Second, the Huang-Rhys parameter for (PtC₈)₀₂ is noticeably smaller than that for (PtC₈)₀₁ but is close to that for (PtC₈)₀₃. Both of these features indicate that the triplet exciton delocalization is restricted within two to three repeat units.

**Transient Absorption**

In order to provide additional information regarding the properties of the triplet state of the oligomers, nanosecond transient absorption spectra were recorded at room temperature in deoxygenated THF solution. As shown in Figure 4-7, all three oligomers feature strong triplet-triplet absorption bands following near-UV ground state bleachings. Interestingly, the triplet
absorption for each oligomer consists of two distinct bands: the first stronger band which appears in the near-UV region and the second relatively weaker band that is concentrated on middle and red of the visible. The first band is believed to be the overlap of the triplet absorption and the ground state bleachings, and the second band is broad. The ratio of the second and first bands

![Image of absorption spectra](image)

Figure 4-7. Triplet absorption spectra of (PtC₈)ₙ complexes following 355 nm laser excitation: A) (PtC₈)₁, 80 ns delay increment; B) (PtC₈)₂, 160 ns delay increment; C) (PtC₈)₃, 160 ns delay increment
(ΔA₂/ΔA₁) increases about one times from (PtC₈)₁ (0.3) to (PtC₈)₂ (0.6) and then stay constant for (PtC₈)₃ (0.6). Both absorption bands red-shift with increasing oligomer chain length. However, no noticeable shift was observed from (PtC₈)₂ to (PtC₈)₃ (Figure 4-8A). Lifetimes recovered from transient absorption spectra are in a time scale of a few hundred nanoseconds and increase with the oligomer chain length (the decay profiles are shown in Figure 4-8B and lifetimes are shown in Table 4-2).

![Figure 4-8. A) Transient absorption spectra at t = 0 μs; B) Decay profiles](image)

While assignment of the triplet absorption bands will require further investigation, several conclusions can be drawn from the transient absorption study. First, intersystem crossing for all
of three oligomers is very efficient, which is consistent with strong phosphorescence in photoluminescence spectra. Second, the triplet-triplet absorption of the carbon chains is strongly allowed, which is indicated by the large ΔA value (> 0.1). Third, the triplet exciton is localized and restricted to two repeat units.

**Phosphorescence Decay Kinetics**

In order to gain insight concerning phosphorescence decay kinetics for the \((\text{PtC}_8)_n\) series, temperature-dependent time-resolved emission were carried out in deoxygenated Me-THF solution (glass) over the 100-300 K temperature range. The lifetimes recovered from time-resolved emission by spectra decay fitting are plotted versus temperature as shown in Figure 4-9. Several interesting features emerge from Figure 4-9. First, for all three oligomers, the emission lifetimes decrease with increasing temperature. In particular, the lifetimes decrease slightly more rapidly in the temperature region corresponding to the glass-to-fluid transition of Me-THF (120-140 K). Second, the emission lifetimes increase with the oligomer chain length in the whole temperature region.

![Figure 4-9. Temperature dependence of photoluminescence lifetimes for \((\text{PtC}_8)_n\) complexes in Me-THF solution (glass)](image-url)
The radiative and non-radiative decay rates \((k_r \text{ and } k_{nr})\) can be calculated using Equations 4-4 and 4-5, which were obtained by rearrangement of Equations 4-2 and 4-3.

\[
\tau_T = \frac{1}{k_r + k_{nr}} \quad \text{(4-2)}
\]

\[
\Phi_p = \Phi_{isc} k_r \tau_T \quad \text{(4-3)}
\]

\[
k_{nr} = \left[1 - \left(\frac{\Phi_p}{\Phi_{isc}}\right)\right] \frac{1}{\tau_T} \quad \text{(4-4)}
\]

\[
k_r = \left(\frac{\Phi_p}{\Phi_{isc}}\right) \frac{1}{\tau_T} \quad \text{(4-5)}
\]

where \(\tau_T\) is the triplet lifetime, \(\Phi_p\) is phosphorescence quantum yield, \(\Phi_{isc}\) is intersystem crossing efficiency. The values of \(\tau_T, \Phi_p\) and \(\Phi_{isc}\) are needed in order to compute \(k_r\) and \(k_{nr}\). Here \(\tau_T, \Phi_p\) are known and \(\Phi_{isc}\) is unknown. However, according to previous studies on platinum-containing compounds, and the fact that the fluorescence is very weak for the compounds of the current investigation, it is safe to conclude that intersystem crossing efficiency \((\Phi_{isc} \approx 1)\). Furthermore, since \(\Phi_p\) is small, \(\Phi_p \ll \Phi_{isc}\) and under these conditions Equations 4-4 and 4-5 can be further rearranged to Equations 4-6 and 4-7.

\[
k_{nr} \approx \frac{1}{\tau_T} \quad \text{(4-6)}
\]

\[
k_r \approx \frac{\Phi_p}{\tau_T} \quad \text{(4-7)}
\]

The values of \(k_r\) and \(k_{nr}\) computed from the experimental data are listed in Table 4-2.

Several features are shown regarding these data. First, for all of three oligomers, the values of \(k_{nr}\) exceed \(k_r\) by about 1000-fold, indicating that non-radiative decay is the dominant pathway for these oligomers. Also note that non-radiative decay rates decrease by approximately a factor of 10 at 100 K. Second, there is a slightly decrease in \(k_{nr}\) with increasing the oligomer chain length, which is consistent with our previous study.\(^{33}\)
Table 4-2. Photophysical parameters for \((\text{PtC}_8)_n\) complexes

<table>
<thead>
<tr>
<th>((\text{PtC}_8)_1)</th>
<th>((\text{PtC}_8)_2)</th>
<th>((\text{PtC}_8)_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\tau_p/10^6\text{s}^a)</td>
<td>(\Phi_p^a)</td>
<td>(k_{nr}/10^6\text{s}^{-1}a)</td>
</tr>
<tr>
<td>0.26</td>
<td>0.0011</td>
<td>3.8</td>
</tr>
<tr>
<td>0.49</td>
<td>0.0025</td>
<td>2.1</td>
</tr>
<tr>
<td>0.70</td>
<td>0.0031</td>
<td>1.4</td>
</tr>
</tbody>
</table>

\(^a\) Phosphorescence decay measured at room temperature. \(^b\) Measured at 100 K. \(^c\) Extracted from room temperature transient absorption.

**Discussion**

**Effect of Spacer on Delocalization of Triplet Exciton**

These results provide evidence that triplet exciton in the platinum tetrayne oligomers is localized to two repeat units. First, the phosphorescence energy shifts ca. 20 nm from \((\text{PtC}_8)_1\) to \((\text{PtC}_8)_2\) and then stays constant for \((\text{PtC}_8)_3\). Second, the transient absorption spectroscopy presented in this study further supports the notion of triplet localization.

A number of recent studies have explored the variation of the singlet and triplet energies with oligomer length for \(\pi\)-conjugated platinum containing oligomers or polymers. The initial work was done by Beljonne and coworkers. They investigated the spatial extent of the singlet and triplet exciton in platinum acetylide monomers and polymers. The key finding of their study is that while the singlet exciton is delocalized over a few repeat units, the triplet exciton is strongly localized on a single phenylene ring.\(^{27}\) A more systematic study of the delocalization of singlet and triplet excitons in platinum acetylide oligomers was conducted by our group.\(^{33,34}\)

Here we carry out a detailed comparison between our former and current studies.

The structures of the oligomers from our previous study chosen for comparison are shown in Figure 4-10. Note that the main structural difference between the two series oligomers is that the phenylene units (spacers) are replaced by the butadiynyl segment in the oligomers of the current study. According to our previous study,\(^{34}\) the phenylene unit adopts two different configurations with respect to the plane defined by the square planar platinum center: twisted (t) and planar (p) conformation. DFT calculations indicate that in the ground state the “all-t”
conformation is energetically preferred over conformers in which terminal or internal phenylenes are rotated into the p conformation, while in the triplet state the lowest-energy conformation is “p”, where the central phenylene ring is rotated planar. This investigation shows that the geometry of the triplet state differs from that of the ground state in phenyl-based platinum oligomers. The geometry distortion is confined within only one phenylene unit and thus the triplet state in these series oligomers is confined to one repeat unit. The oligomers of the current study consist of all ethynylemic units, which appear to be slight rigid with respect to photoexcitation. It is reasonable to conclude that there is little geometry distortion between the excited state and the ground state. As a result, triplet excitons in these oligomers are a little more delocalized (two repeat units according to the spectroscopic study).

![Pt-n](n = 1-5, 7)

Figure 4-10. Platinum acetylide oligomers studied by Liu

The delocalization of the triplet exciton also depends on the binding energy which is defined as the singlet-triplet energy difference; the larger the binding energy, the stronger the confinement of the excited state wavefunction. Since significant fluorescence was not observed for the current studied oligomers, we estimate the singlet energy based on the onset of the absorption bands. The values of computed estimated singlet-triplet splitting (ΔE_{S-T}) for the (PtC₈)_n series are listed in Table 4-1. The ΔE_{S-T} values of the corresponding reference compounds are also listed in Table 4-1. It is evident that the binding energy in Pt-n oligomers is approximate 0.3 eV larger than that in (PtC₈)_n series. This further supports the idea that the triplet exciton is more confined in Pt-n oligomers.
Effect of Platinum on Delocalization of Triplet Exciton

It is well known that incorporation of transition metals, such as platinum, into \( \pi \)-conjugated organic systems enhances intersystem crossing due to spin-orbit coupling induced by the heavy metal. The triplet exciton delocalization is also affected by the platinum metal in \( \pi \)-conjugated metal-organic systems. Studies of both platinum phenyl-based and platinum tetrayne-based oligomers conclude that the triplet exciton is more localized and confined to one or two repeat units in these systems. We recently reported a photophysical study of platinum end-capped oligoynes (see Figure 4-1).\(^9\) One key result of this study is that the triplet exciton is delocalized across the entire \( \pi \)-conjugated system defined by the carbon chain for all oligomers. The effective conjugation length for the triplet state has not been reached in the longest carbon chain \(-(C=\text{C})_6-\) oligomer. In contrast with the current study, the platinum metal has no significant influence on triplet excitons of \( \pi \)-conjugated organic systems. Rogers and coworkers\(^{32}\) also reported photophysical studies of a series of platinum-containing pheny-ethynyl oligomers with varying the ligand chain length. The results indicate that the triplet exciton is delocalized with respect to the ligand chain length. With increasing the ligand chain length, the spin-orbit coupling effect of platinum on the ground and excited state properties is reduced. By comparison these studies with our current study, it is safe to conclude that the triplet exciton in \( \pi \)-conjugated platinum-containing oligomers is more likely affected by the platinum metal if \( \pi \)-conjugated organic units are more proximate to the platinum metal. With increasing \( \pi \)-conjugated organic chain length, influences by the platinum metal is less effective and thus the triplet exciton delocalization shows \( \pi \)-conjugated organic system features.
Conclusion

A detailed photophysical investigation of a series of platinum tetrayne oligomers has been carried out. The photophysics of these oligomers is dominated by a $^3\pi,\pi^*$ state that is concentrated on the -(C≡C)$_4$- chain. The low temperature emission spectrum of each oligomer shows an intense and narrow phosphorescence band followed by a vibronic progression of sub-bands separated by *ca.* 2100 cm$^{-1}$ which corresponds to the stretch of the -(C≡C)$_4$- chain. Both absorption and emission bands red-shift from (PtC$_8$)$_1$ to (PtC$_8$)$_2$ and then are not changed for (PtC$_8$)$_3$, indicating that the triplet exciton is localized on two repeat units in the oligomers. Room temperature transient absorption measurements also support the notion of triplet localization. The slightly rigid nature of the -(C≡C)$_4$- units more likely induces little geometry distortion upon photoexcitation, which causes the triplet exciton to be slightly delocalized (two repeat units) compared with platinum phenyl-based oligomers (one repeat unit). The effect of the platinum centers on triplet exciton delocalization is less effective when the conjugated organic units are not close to platinum centers and as a consequence, the corresponding triplet state features the properties of $\pi$-conjugated organic systems.

Experimental

Materials

The platinum tetrayne oligomers were provided by Dr. John A. Gladysz’s lab in the Texas A&M University. The synthesis and characterization of the oligomers were described in the literature.$^{105}$

Photophysical Measurements

Steady-state absorption, and low-temperature and time-resolved photoluminescence measurements were carried out by procedures similar to those described in Chapter 3.
Photoluminescence quantum yields were determined by relative actionmetry, with Ru(bpy)$_3^{2+}$ as an actinometer ($\Phi_p = 0.0379$ in air saturated H$_2$O). Transient absorption measurements were carried out by procedures similar to those described in Chapter 2.

**Photoluminescence Spectral Fitting**

The spectral fitting was carried out according to the method described by Farley.$^{92}$
CHAPTER 5
PHOSPHORESCENT ORGANOGELATORS

Introduction

The \( \pi \)-conjugated oligomers and polymers have been widely used in fabrication of organic electronic devices such as light emitting diodes, photovoltaic cells and field effect transistors.\(^{107,108}\) The performance of these devices depends on the intrinsic optical and electronic properties as well as intermolecular interactions and morphology of the constituent materials. While molecular modification and functionalization in order to improve their optical and electronic properties have attracted the most attention, intermolecular interactions and material morphology are among the most important factors in determining the performance of an organic material in device applications. Supramolecular architectures or molecular aggregates have been achieved through controlling self-assembly of \( \pi \)-conjugated polymers or oligomers.\(^{109}\) Three non-bonding intermolecular interactions are responsible for self-assembly of \( \pi \)-conjugated systems: \( \pi-\pi \) interaction, hydrogen-bonding and van der Waals interactions.\(^{110-113}\)

Self-assembly of suitably functionalized derivatives of oligo(phenylene vinylene) and oligo(phenylene ethynylene) in solution has produced helical or lamellar supramolecular structures.\(^{114-120}\) Ajayaghosh and coworkers\(^{121,122}\) recently discovered that well-designed oligo(phenylene vinylene)-based derivatives have the ability to form organogels in hydrocarbon solvents such as hexane, cyclohexane and benzene, which is induced by intermolecular hydrogen-bonding interaction.

While considerable studies have been carried out on supramolecular structures consisting of organic \( \pi \)-conjugated systems, relatively little work has been done on self-assembling properties comprised of transition metal-organic or organometallic \( \pi \)-conjugated oligomers or polymers.\(^{123-128}\) However, these systems are of interest for several reasons. First, introduction of
transition metal centers into $\pi$-conjugated systems has a profound influence on their optical and electronic properties. Second, these systems provide a unique platform for the study of triplet excited state in aggregates or gels due to high intersystem crossing yield induced by a transition metal center.

Inspired by the discovery of gelation of oligo(phenylene vinylene) derivatives by Ajayagosh and coworkers, we designed and synthesized a series of platinum acetylide oligomers decorated with long alkyl chains and their gelation and photophysical properties were recently reported. Several important findings with respect to this study are as follows. First, these platinum acetylide oligomers gel hydrocarbon solvents and form fiber structures as shown in TEM images. Second, the blue shift of the absorption spectrum of the oligomer in its aggregated state relative to its molecularly dissolved state indicates that self-assembly of these oligomers forms H-aggregates. Third, the aggregated oligomers emit strong phosphorescence and the triplet state is not strongly perturbed by close packing of the chromophores in the aggregates. Fourth, efficient triplet-triplet energy transfer occurs in mixed aggregates consisting of a donor and an acceptor.

After these exciting results, we continue to explore triplet exciton dynamics in phosphorescent aggregates consisting of platinum acetylide chromophores. In the current study, we designed platinum acetylide systems consisting of an electron donor and acceptor to investigate photoinduced electron transfer properties in their aggregated states. As shown in Figure 5-1, Pt2M and Pt2MT were used as electron donors and their photophysics have been previously studied. Both oligomers gel hydrocarbon solvents such as hexane, cyclohexane and dodecane. A compound consisting of the core unit of the NDI and tridodecyloxyphenyl end-groups were used as an electron acceptor (NDI-1).
Figure 5-1. Pt2M/NDI-1 and Pt2MT/NDI-1 donor-acceptor systems

In solution, charge dissociation into free and solvated radical ions is more favorable in polar solvents where the energy barrier for ion separation is not as high as in nonpolar solvents where the ions are bound more tightly together by Columbic attraction. In addition, a polar solvent can reduce Coulombic attraction by “shielding” the electrostatic attraction which exists between the positive and negative ions. However, in gel or aggregated state, solvent polarity may play a different role in photoinduced intermolecular electron transfer process due to the close packing of the aggregated donor and acceptor molecules. According to our previous study, Pt2M and Pt2MT only self-assemble in nonpolar solvents but are soluble in polar solvents. In order to explore effect of polar solvents on photoinduced electron transfer in molecular aggregates, we designed and synthesized a new platinum acetylide oligomer (Pt2MAM) that is
structurally similar to **Pt2M** but incorporates amide functional groups as shown in Figure 5-2. Its counterpart electron acceptor was also synthesized (**NDI-2**). Several studies\(^{111,130-134}\) have shown that molecular systems that incorporate amide functional groups form organogels in both nonpolar and polar solvents due to strong intermolecular hydrogen bonding interactions. The platinum acetylide oligomer **Pt2MAM** was designed to include a combination of all of three major driving forces (hydrogen bonding, van der Waals and \(\pi-\pi\) interactions) that induces molecular self-assembling, which makes it a very promising organogelator. We anticipated that it would gel in polar solvents such as acetonitrile and DMSO.

![Pt2MAM](image1.png)

**Pt2MAM** (donor)

![NDI-2](image2.png)

**NDI-2** (acceptor)

Figure 5-2. **Pt2MAM/NDI-2** donor-acceptor system

In our previous report,\(^42\) we applied the pulse radiolysis technique for the study of the properties of ion-radical state in an extended series of platinum acetylide oligomers. The study was carried out in dichloroethane and THF solutions in which the oligomers are present in their molecularly dissolved state. To extend this study into molecularly aggregated state, we used the pulse radiolysis method to investigate ion-radical properties in platinum acetylide organogelators. According to our best knowledge, this is the first time that the pulse radiolysis technique is applied to conjugated organogel systems.
In this chapter, we first describe the synthesis of new platinum acetylide oligomers and then we investigate photoinduced electron transfer dynamics in first sets of donor-acceptor systems. Second, photophysics and molecular morphology of Pt2MAM have been characterized. Finally, we report the pulse radiolysis study in Pt2M anion radical properties in its pure and mixed gels.

Synthesis

Pt2M and Pt2MT were synthesized according to procedures described before.\textsuperscript{129} Pt2MAM was prepared according to Figure 5-3. Methyl 3,4,5-trihydroxybenzoate was reacted with 1-bromododecane in N, N-dimethylformamide (DMF) in the presence of potassium carbonate and a small amount of tetra-n-butylammounium bromide (TBAB) to give methyl 3,4,5-tridodecyloxybenzoate 1. After hydrolysis under basic conditions, the resulting acid 2 was activated by using thionyl chloride to give the acid chloride 3 in 97% yield. Condensation between ethylene diamine and the acid chloride 3 in dichloromethane produced the monosubstituted amine 4. The yield of this step is only 25% due to the disubstituted side product. The amine 4 was further coupled with 4-iodo-benzoyl chloride in dichloromethane and triethylamine to yield the iodide 5. The Sonogashira coupling between the iodide 5 and trimethylsilylacetylene (TMS-A) produced the TMS-protected acetylene 6. After deprotection with TBAF in THF solution, the resulting acetylene 7 was reacted with \( cis \)-dichloro-bis-(trimethylphosphine)platinum(II) in diethylamine to give the platinum complex 8 in 70% yield. The final step is a Hagihara coupling between the platinum complex 8 and 1,4-diethynylbenzene in diethylamine and copper iodide as catalyst to yield the product Pt2MAM in 82% yield. NDI-2 was prepared in a one step condensation reaction between the amine 4 and 1,4,5,8-tetracarboxylic naphthalene dianhydride in DMF at \( 140^\circ \text{C} \) in 95% yield (Figure 5-3).
Figure 5-3. Synthesis of Pt2MAM and NDI-2

NDI-1 was synthesized according to Figure 5-4. 1,2,3-Trihydroxybenzene was reacted with 1-bromododecane in DMF with potassium carbonate and TBAB as catalysts to yield 1,2,3-tridodecyloxybenzene 9 in 92% yield. Nitration of 9 with 90% nitric acid absorbed in silica
produced compound 10 in 74% yield followed by reduction with hydrazine hydrate in ethanol and 10% Pd/C catalyst to give 3,4,5-tridodecyloxyaniline 11 in high yield. The final step is the condensation reaction between 11 and 1,4,5,8-tetracarboxylic naphthalene dianhydride in quinoline with the addition of Zn(OAc)₂ to yield the product NDI-1 in moderate yield.

Figure 5-4. Synthesis of NDI-1

Results and Discussion

Photoinduced Electron Transfer in Pt2M/NDI-1 and Pt2MT/NDI-1 Mixed Gels

To explore photoinduced electron transfer properties in aggregated donor-acceptor systems, photoluminescence spectra were measured in Pt2M and Pt2MT dodecane gels with doping the acceptor NDI-1. The doping levels of NDI-1 were kept below 5 mol% to avoid disrupting the gels. According to our previous study,¹²⁹ the photoluminescence of a Pt2M gel features two distinct bands: the band centered at λ = 495 nm originates from its aggregated state, and the band concentrated at λ = 515 nm is attributed to its molecularly dissolved state. With 5 mol% doping of the acceptor NDI-1, the band at λ = 495 nm is greatly quenched (~70%), whereas the band at λ = 515 nm shows almost no noticeable decrease (Figure 5-5A). This is a clear evidence that quenching/electron transfer is efficient in aggregates due to the close proximity of
donor/acceptor chromophores in the ordered supramolecular architectures, which is consistent with our previous study of energy transfer in the mixed gel. The fact that quenching/electron transfer only occurs in the aggregated state suggests that exciton diffusion among \textbf{Pt2M} units may be involved. For \textbf{Pt2MT/NDI-1} mixed gel, phosphorescence is quenched greater than 99% with 5 mol\% doping, once again indicating that efficient electron transfer occurs in this system (Figure 5-5B).

![Photoluminenscence spectra of pure and mixed dodecane gels.](image)

**Figure 5-5.** Photoluminescence spectra of pure and mixed dodecane gels. The instrument was kept in the same conditions during the measurement. Both pure and mixed gels were excited at the same wavelength. A) $\lambda_{\text{ex}} = 300$ nm; B) $\lambda_{\text{ex}} = 340$ nm. Mix = \textbf{Pt2M} / \textbf{Pt2MT} + 5mol\% \textbf{NDI-1}
In order to gain insight into electron transfer dynamics, transient absorption spectra were carried on Pt2M/Pt2MT pure and mixed dodecane gels. However, we only observed that lifetimes of T₁-Tₙ absorption decrease in doped gels and the characteristic absorption of the NDI anion and corresponding cations were not detected in nanosecond transient absorption spectra. This is probably due to the very rapid charge recombination in non-polar solvent (dodecane). To study electron transfer properties in aggregated molecules in polar solvents, we designed and synthesized a new platinum acetylide based organogelator – Pt2MAM.

**Morphology and Photophysics of Pt2MAM Gelator**

**Gel formation**

The structure of Pt2MAM features the core unit of π-conjugated phenyl ring and long alkyl chain end-groups connected by amide functional groups. The feature combines all three driving forces that initiate molecular self-assembling in one molecule. The gelator Pt2MAM was subjected to gelation tests with a variety of solvents. A screw capped sample vial containing the gelator and the solvent was heated until the solid was dissolved. Then the sample vial was cooled to room temperature. The formation of the gels was evaluated by the “stable-to-inversion of a test tube” method. The testing results are listed in Table 5-1. Pt2MAM gels in both nonpolar and polar solvents. The critical gelation concentration (CGC) is ~1 wt% in cyclohexane and DMSO.

**Table 5-1. Gelation tests of Pt2MAM**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Concentration (mg/mL)*</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>12</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Benzene</td>
<td>12</td>
<td>Soluble</td>
</tr>
<tr>
<td>DMSO</td>
<td>10</td>
<td>Gel</td>
</tr>
<tr>
<td>DMF</td>
<td>12</td>
<td>Soluble</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>8</td>
<td>Gel</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>12</td>
<td>Soluble</td>
</tr>
<tr>
<td>THF</td>
<td>12</td>
<td>Soluble</td>
</tr>
</tbody>
</table>

*The maximum concentrations used for gelation tests.

Figure 5-6 shows sol-gel transitions upon heating and cooling. Pt2MAM also indicates bright
phosphorescence under UV light illumination. The cyclohexane gel is transparent, whereas the DMSO gel is slightly opaque.

Figure 5-6. Sol-gel transitions of Pt2MAM

**Morphological characterization**

The morphological feature of Pt2MAM cyclohexane gel was revealed by transmission electron microscopy (TEM) and atomic force microscopy (AFM) (Figure 5-7). TEM images of a dilute solution of Pt2MAM (1×10^{-5} M) evaporated from cyclohexane on a copper grid show the formation of a complex network of fibers consisting of the aggregated Pt2MAM molecules. The average widths of the individual fibers range from 30 to 150 nm, suggesting that the individual fibers are likely composed of many subfibers that consist of arrays of stacked Pt2MAM molecules. AFM studies of dried Pt2MAM cyclohexane solution on a mica surface support the morphological features observed in TEM images.
Figure 5-7. Morphological features of Pt2MAM xerogels: A) TEM image of a cyclohexane solution (1×10^{-5}M) evaporated on a copper grid; B) AFM image of a cyclohexane solution (1×10^{-5}M) evaporated on a mica surface

**UV-Vis absorption**

Concentration and temperature-dependent UV-Vis absorption spectra were measured in Pt2MAM dimethyl sulfoxide (DMSO) solution/gel. For concentrations above 0.1 mM, the absorbance was maintained below a value of 1.0 by using short path length (1 mm or 0.1 mm) cells as necessary. Figure 5-8A shows normalized absorption spectra of Pt2MAM in DMSO at three concentrations (1.6 × 10^{-4}, 8 × 10^{-4} and 4 × 10^{-3}M). Prior to each measurement, the solution was subjected to a heating-cooling cycle, but Pt2MAM only gels at the 4 × 10^{-3} and 8 × 10^{-4} M concentrations. The absorption spectra of Pt2MAM in its gel state are dominated by a strong absorption band with $\lambda_{\text{max}} = 345$ nm along with a shoulder at $\lambda = 362$ nm. With further decreasing concentration, the absorption spectrum ($c = 1.6 \times 10^{-4}$ M) shows a strong light scattering band above 370 nm due to insolubility of Pt2MAM in DMSO. Nevertheless, it is evident that the absorption band centered at $\lambda = 345$ nm decreases with decreasing concentration. By comparison with the absorption spectrum in dilute THF solution (Figure 5-8C), we are able to
Figure 5-8. Absorption spectra of Pt2MAM in solution/gel. A) DMSO gel/solution at room temperature; the spectra are normalized at $\lambda = 362$ nm. B) DMSO gel/solution at $c = 4 \times 10^{-3}$ M. Arrow indicates change in spectra with increasing temperature from 45 to 87 °C. The heating rate was approximately 1°C/min, and spectra were acquired within 1 min after the temperature stabilized. C) THF dilute solution
assigned the absorption shoulder (λ = 362 nm) to the long-axis polarized π, π* transition of the molecularly dissolved (monomeric) chromophore. In contrast, the primary absorption band in Pt2MAM aggregate state blue-shifts ca. 17 nm and contains some residual absorption in the region where monomer absorbs (λ = 362 nm), indicating that the Pt2MAM DMSO gel forms H-aggregates.

Figure 5-8B illustrates the temperature-dependent absorption spectra of the Pt2MAM gel/solution with c = 4 × 10^{-3} M in DMSO. With increasing temperature the absorption band concentrated at λ = 345 nm decreases, which indicates the transition from gel to solution state. Note that the spectrum at 87°C still shows strong absorption from the aggregated state, suggesting that the temperature range of the gel to solution transition has not been reached.

**Steady-state photoluminescence**

Photoluminescence spectra of Pt2MAM were measured in argon degassed solutions (or gels). For the gels, the samples were heated to the solution state to prevent gel formation while degassing. After degassing, the samples were sealed and cooled to room temperature. All of the spectra obtained with varying concentration, excitation wavelength and solvent exhibit a strong emission band at λ = 512 nm followed by a vibronic band at λ ≈ 550 nm. These bands are assigned to phosphorescence from 3π,π* state of Pt2MAM consistent with our previous studies of platinum acetylide oligomers. Figure 5-9 illustrates the emission spectra of Pt2MAM gels in DMSO with the excitation at λ_{ex} = 345 and 362 nm, and the emission spectrum recorded in dilute THF solution is also shown for comparison purposes. Note that no noticeable shifts were observed in the transition from molecular dissolved state to the gel state, indicating that the phosphorescence band is not strongly perturbed by close packing of the chromophores in the aggregates. The fact that the aggregated state of Pt2MAM exhibits almost no shift in the
phosphorescence energy is consistent with the notion that in the triplet excited state the molecules interact weakly with other chromophores in the aggregates. According to our previous study, the photoluminescence spectrum of the Pt2M gel blue shifts ca. 15 nm relative to its molecular dissolved state. The shift of Pt2M aggregates in its excited state is because a change of its conformations is hindered by tightly packed aggregates. However, the packing in Pt2MAM structure is probably less tight due to the hydrogen bonding between molecules, so molecules can undergo rapid conformation change in its excited state. Figure 5-10 shows a schematic representation of possible packing modes in Pt2M and Pt2MAM aggregates.

Figure 5-9. Photoluminescence spectra of Pt2MAM. Black line: DMSO gel (4 \times 10^{-3}M) with \( \lambda_{ex} = 362 \) nm; green line: dilute THF solution with \( \lambda_{ex} = 362 \) nm; red line: DMSO gel (4 \times 10^{-3}M) with \( \lambda_{ex} = 345 \) nm

Figure 5-10. Possible packing modes in Pt2M and Pt2MAM aggregates
The photoluminescence spectra of \textbf{Pt2MAM} with doping \textbf{NDI-2} at 3 and 5 mol\% were also recorded in DMSO gels. As shown in Figure 5-11, at 3 mol\% doping of \textbf{NDI-2}, phosphorescence is dramatically quenched (~80\%) and with increasing doping level, the phosphorescence intensity decreases further (90\% quenching with 5 mol\%), which clearly indicates that electron transfer occurs in this system. In addition, the electron transfer reaction is strongly exergonic ($\Delta G < -0.5$ eV). In contrast, the same concentration \textbf{Pt2MAM} in THF solution with doping \textbf{NDI-2} (5 mol\%) indicates that only ca. 40\% of phosphorescence is quenched. This suggests that electron transfer is more efficient in the \textbf{Pt2MAM} aggregated state where chromophores are packed in close proximity.

Taken together, the results of the mixed DMSO gels (and THF solutions) clearly indicate that the \textbf{Pt2MAM} phosphorescence quenching by the doping of \textbf{NDI-2} arises via a mechanism involving electron transfer from the triplet state of \textbf{Pt2MAM} to the \textbf{NDI-2} acceptor. In addition, the process is more efficient when \textbf{Pt2MAM} molecules are aggregated, suggesting that triplet exciton diffusion among \textbf{Pt2MAM} units may be involved.

Figure 5-11. Photoluminescence spectra of \textbf{Pt2MAM}/\textbf{NDI-2} mixed gels in deoxygenated DMSO. $[\text{Pt2MAM}] = 4 \times 10^{-3}$ M and different mol \% of \textbf{NDI-2}, $\lambda_{ex} = 345$ nm
Transient absorption

In order to gain insight into electron transfer dynamics, transient absorption spectra were measured in Pt2MAM pure and mixed gels in DMSO (Figure 5-12). A cell with 1 mm path length and positioned at 45° angle relative to the laser beam was used. Since the degassing for the gels in this cell is difficult, the spectra were recorded in non-degassed DMSO gels. While the delta absorbance is low and the spectra are therefore noisy, the results are evident. The spectra show triplet-triplet absorption band centered at $\lambda = 700$ nm and the decay is much faster in the
doped gel (Figure 5-13). Unfortunately, we did not observe the characteristic absorption bands of the radical anion and the radical cation presumably due to very rapid charge recombination even in the polar solvent.

Figure 5-13. Decay profiles of Pt2MAM in DMSO pure and mixed gels (containing 5 mol% NDI-2) at \( \lambda = 700 \text{ nm} \)

**Pulse Radiolysis in Pt2M Pure and Pt2M/NDI-1 Mixed Gels**

Pulse radiolysis experiments were carried out at the Laser Electron Accelerator Facility (LEAF) at Brookhaven National Laboratory. The facility has been previously described in detail\(^{135,136}\), so we only provide a brief description here. A schematic representation of the LEAF is shown in Figure 5-14. The LEAF uses a laser-pulsed photocathode, radio-frequency electron gun to generate \( \leq 5 \text{ ps} \) pulse of 9 MeV electrons for pulse radiolysis experiments. The electron pulse is produced by laser light impinging on a photocathode inside a resonant cavity, radio frequency (RF) gun. The emitted electrons are accelerated to \( \sim 9 \text{ MeV} \) within the length of the gun. Then the laser pulse is synchronized with the RF power to produce the electron pulse as short as 5 ps.
In our previous study,\textsuperscript{42} we have applied the pulse radiolysis technique for investigating charge transport and delocalization in an extended series of platinum acetylide oligomers (PAOs) in solutions. The generation of PAO-based ion radicals involves a series of reactions in which high energy electron pulses produce very reactive solvent cation radicals or holes (h\textsuperscript{+}) or electrons (e\textsuperscript{−}), which are then transfer to the PAO molecules. The reactions strongly depend on the solvent. For example, in 1,2-dichloroethane (DCE), the electrons are immediately captured by the solvent to form solvent radical cations and Cl\textsuperscript{−} ions. In tetrahydrofuran (THF), the high energy electron pulses produce THF radical cations and solvated electrons. Then the solvent radical cations decompose to radicals and solvated protons. As a result, the production of thermalized solvated radical cations (h\textsuperscript{+}) in DCE and thermalized solvated electrons (e\textsuperscript{−}) in THF are the net effect of the electron pulses. The formation of PAO radical anion and cation species is a bimolecular process as the attachment of holes in DCE and electrons in THF occurs only after a diffusion reaction of the primary holes or electrons with the substrate molecules. Because the substrates (PAOs) are present in excess in these experiments, these reactions are pseudo-first order and the observed rates of h\textsuperscript{+} or e\textsuperscript{−} transfer to substrate depends on the substrate concentration and the bimolecular rate constant.
In the current study, we applied the pulse radiolysis method to the platinum acetylide organogelator Pt2M. This method allows us to gain insight into the spectroscopy of the radical ion states, as well as electron transfer dynamics in Pt2M aggregates. The morphological study of the Pt2M gel indicates that Pt2M in its gel state form a fiber aggregate structure. In addition, the blue shift in its absorption spectrum suggests that self-assemble of Pt2M produces H-aggregates. With doping of the electron acceptor NDI-1, phosphorescence arising from Pt2M aggregate (the band at \( \lambda = 495 \) nm in the photoluminescence spectrum) is efficiently quenched via electron transfer to the NDI-1 acceptor. By applying the pulse radiolysis method to the Pt2M gel, we anticipated that solvated anion radicals would be first produced via high energy electron pulses followed by electron transfer to the Pt2M aggregates. Upon doping a small amount of the electron acceptor NDI-1, electrons would be finally captured by the NDI-1 acceptor. A schematic representation of electron transfer processes is shown in Figure 5-15.

Figure 5-15. Possible electron transfer processes in the Pt2M/NDI-1 mixed gel
A screw-capped cell with 5 mm path length was used for pulse radiolysis experiments. The samples were prepared in a glove box with isoctane as solvent. Isoctane is a good solvent for pulse radiolysis as it easily captures electrons, and the electrons are weakly solvated and consequently they diffuse very rapidly. In addition, both Pt2M and NDI-1 gel in isoctane with critical gelation concentration (CGC) of 1 mM. Prior to each measurement, the sealed sample was subjected to a heating-cooling cycle to form stable gel. For comparison purposes, pulse radiolysis was first carried out in Pt2M THF solution with 1 mM concentration (Figure 5-16A). The spectrum features a dominant band centered at $\lambda = 540$ nm and a high energy vibronic band concentrated at $\lambda = 490$ nm. This band is assigned to the absorption of the anion radical $\text{Pt2M}^-$, and the result is consistent with our previous study.\(^{42}\) The anion radical of Pt2M decays within several microseconds. Then the Pt2M isoctane gels were subjected to pulse radiolysis at three concentrations ($5 \times 10^{-3}$, $1.5 \times 10^{-2}$ and $3 \times 10^{-2}$ M). With the concentration at $5 \times 10^{-3}$ M, the absorption bands are extremely weak and non-identifiable. When the concentration is increased to $1.5 \times 10^{-2}$ M, we began to see a weak absorption band below 500 nm and this band becomes stronger when the concentration reaches to $3 \times 10^{-2}$ M (Figure 5-16B). Note that the absorption band shows a growing trend at the blue edge of the detector limit (440 nm). Due to the fact that the gel sample was somewhat opaque, little light passed through it at shorter wavelengths, making detection below 440 nm impossible. Nevertheless, the spectrum of Pt2M in the isoctane gel suggests that electrons are captured by Pt2M aggregates and the absorption of Pt2M$^-$ is below 440 nm and blue-shifts compared with its absorption in THF solution. Note that an intense band centered at $\lambda = 460$ nm appears at 3 ns after electron pulses. While further measurements are needed in order to confirm if this band arises from absorption of Pt2M$^-$, this
band decays quickly (within several nanoseconds). The decay profiles of \textbf{Pt2M} in isooctane gel and THF solution are shown in Figure 5-16C.

Figure 5-16. Pulse radiolysis transient absorption spectra and decay profiles for radical anions of \textbf{Pt2M}. A) in 1 mM THF solution; B) in 30 mM isooctane gel; C) decay profiles at \( \lambda = 490 \) nm for THF solution (1 mM) and at \( \lambda = 460 \) nm for isooctane gel (30 mM)
In order to gain insight concerning electron transfer dynamics in the aggregated state, the Pt2M isoctane gel (15 mM) was doped a small amount of NDI-1 (5 mol%) and the resulting mixed gel was subjected to pulse radiolysis experiments. At room temperature, the spectrum exhibits a narrow absorption band centered at \( \lambda = 470 \) nm (Figure 5-17A). In order to assign this band, pulse radiolysis of the pure NDI-1 isoctane gel (5 mM) was carried out at high temperature (88 °C). Note that NDI gels in isoctane at 5 mM concentration but the gel is so opaque that the probe light is completely blocked. Thus we were not able to carry out pulse radiolysis study on the pure NDI-1 isoctane gel at room temperature. As shown in Figure 5-17B, the spectrum features a dominant absorption band centered at \( \lambda = 470 \) nm, which apparently arises from the anion radical NDI-1\(^-\) consistent with literature reports of anion radicals spectroscopy of NDI derivatives.\(^{46,52}\) Thus, the band in Pt2M/NDI-1 mixed gel is assigned to the absorption arising from NDI-1\(^-\). The decay profiles of NDI-1\(^-\) at 470 nm in pure and mixed gels (or solution) are similar, which further supports the assignment of the absorption band in the mixed gel (Figure 5-17C).

There are two possible mechanisms for the formation of NDI-1\(^-\) in the Pt2M/NDI-1 mixed gel: (1) NDI-1 directly captures electrons; (2) electrons are first attached to Pt2M and then transferred to NDI-1. In order to determine which mechanism applies in this system, pulse radiolysis measurements were carried out for both the pure Pt2M and Pt2M/NDI-1 mixed gels at 88 °C, which is above the sol-gel transition temperature. If electrons were directly captured by NDI-1, the spectrum is expected to show the characteristic absorption of NDI-1\(^-\) (\( \lambda = 470 \) nm) as we observed in the pure NDI-1 at high temperature. In addition, at this temperature, both pure and mixed gels are less aggregated due to gel-sol transition. As shown in Figure 5-18A and B, both spectra indicate similar absorption bands at 88 °C. By comparing with the spectrum of
Figure 5-17. Pulse radiolysis transient absorption spectra and decay profiles of A) Pt2M (15 mM) + 5 mol% NDI-1 isoctane gel at RT; B) Pure NDI-1 (5 mM) in isoctane at 88 °C; C) Decay profiles at λ = 470 nm
Pt2M in THF solution, these bands mainly arise from the molecularly dissolved state of Pt2M· with possibly some contributions of its aggregated state absorption. The NDI· absorption band ($\lambda = 470$ nm) does not appear in the Pt2M/NDI-1 mixture at 88 °C, suggesting that it is not likely that electrons are directly attached on NDI-1. The Pt2M· decay at high temperature is faster than the decay in THF solution (Figure 5-18C).

Figure 5-18. Pulse radiolysis transient absorption spectra and decay profiles of A) Pt2M (5 mM) in isoctane at 88°C; B) Pt2M + 5 mol% NDI-1 in isoctane at 88°C; C) Decay profiles of Pt2M anion radicals at $\lambda = 490$ nm
Taken together, several points can be drawn from pulse radiolysis measurements in \( \text{Pt2M} \) pure and \( \text{Pt2M}/\text{NDI-1} \) mixed gels. First, \( \text{Pt2M} \) gels capture electrons and the absorption band of \( \text{Pt2M}^- \) is located in the blue region (below 440 nm). Compared with \( \text{Pt2M}^- \) absorption in THF solution, the band in \( \text{Pt2M} \) gel state blue-shifts. Second, \( \text{Pt2M}/\text{NDI-1} \) mixed gels capture electrons and the spectrum is dominated by the absorption of \( \text{NDI}^- \). This result suggests that formation of \( \text{NDI-1}^- \) in the \( \text{Pt2M}/\text{NDI-1} \) mixed gel occurs via an indirect mechanism. The electrons are initially attached to \( \text{Pt2M} \) aggregates (Equation 5-1). Then electron transfer from \( \text{Pt2M}^- \) to the \( \text{NDI-1} \) electron acceptor to produces \( \text{NDI-1}^- \) (Equation 5-2). The reaction 5-2 is strongly exergonic (\( \Delta G < -0.6 \) eV), suggesting that the electron transfer process is very rapid.

\[
\text{Pt2M} + e^- (\text{solvated}) \rightarrow \text{Pt2M}^-
\]

\[
\text{Pt2M}^- + \text{NDI-1} \rightarrow \text{Pt2M} + \text{NDI-1}^-
\] (5-2)

**Conclusion**

The photoluminescence of a donor-acceptor system consisting of \( \text{Pt2M} \) (or \( \text{Pt2MT} \)) (donor) and \( \text{NDI-1} \) (acceptor) in its gel state is efficiently quenched due to electron transfer from the donor to the acceptor. In order to investigate electron transfer properties in polar solvent, a new electron donor (\( \text{Pt2MAM} \)) and its corresponding acceptor (\( \text{NDI-2} \)) were synthesized. The organogelator \( \text{Pt2MAM} \) with the structure that features all three driving forces for molecular self-assembly gels both nonpolar and polar solvents. The morphology of \( \text{Pt2MAM} \) gels has fiber-like networks as shown in the TEM and AFM images. Blue shift of \( \text{Pt2MAM} \) absorption bands in its gel state relative to its molecular dissolved state indicates that self-assembly of \( \text{Pt2MAM} \) molecules produces H-aggregates. No significant change is shown in the photoluminescence spectra of \( \text{Pt2MAM} \) gels, suggesting that the triplet exciton is not strongly perturbed by close packing of the aggregated chromophores. Photoluminescence spectra of
Pt2MAM/NDI-2 mixed gels shows efficient phosphorescence quenching, indicating that electron transfer occurs in this system. Further evidence regarding electron transfer in this system is given by transient absorption measurements which illustrate by much faster triplet decay in the mixed gel. The absorption of the radical anion or cation was not observed in the transient spectra, suggesting that charge recombination is very rapid even in polar solvents. The pulse radiolysis technique was applied to study radical ion states of \( \pi \)-conjugated organogels (Pt2M and Pt2M/NDI-1 gels). The results indicate that the Pt2M isoctane gel captures electrons and its radical anion absorption blue-shifts relative to the absorption in THF solution. The Pt2M/NDI-1 mixed gel also captures electrons and the corresponding spectrum shows the NDI-1\(^-\) absorption band. The analysis of the detailed electron transfer dynamics indicates that electron transfer in the aggregated state adopts an indirect mechanism which electrons are initially attached to the Pt2M aggregates followed by electron transfer to the acceptor NDI-1 to form NDI-1\(^-\).

**Experimental**

**Photophysical Measurements**

Steady-state absorption spectra were recorded on a Varian Cary 100 dual-beam spectrophotometer. Samples were placed in adequate short path length cell (1 or 0.1 mm) and absorbance was kept below 1. Corrected steady-state photoluminescence measurements were conducted on a SPEX F-112 fluorescence spectrometer. Samples were degassed by argon purging for 30 min and heated to an isotropic state regularly during this time for adequate degassing of gel-forming solutions. Samples were placed in a triangular-shaped cell and spectra recorded under pseudo front-face geometry to limit self-absorption. The sample cell was positioned so that the incident beam was at 45° from the face of the cell and emission detected at 45°.
Transient absorption measurements were conducted on a home-built apparatus, which has been described elsewhere. Samples were contained in a cell with 1 mm path length and were subjected to a heating-cooling cycle before measurements. The cell was positioned at an angle of 45° relative to the laser beam.

**Pulse Radiolysis**

This work was carried out at the Brookhaven National Laboratory Laser-Electron Accelerator Facility (LEAF). The LEAF facility and the methods used have been described elsewhere. The electron pulse (≤ 120 ps duration) was focused into a quartz cell with an optical path length of 5 mm containing the solution/gel of interest. The monitoring light source was a 75 W Osram xenon arc lamp pulsed to a few hundred times its normal intensity. Wavelengths were selected using either 40 or 10 mm band-pass interference filters. Transient absorption signals were detected with either FND-100G silicon (≤ 1000 nm) or GAP-500L InGas (≥ 1100 nm) diodes and digitized with a Tektronix TDS-680B oscilloscope.

**Synthesis**

**General.** The same procedures were used as described in Chapter 2. *cis*-Dichloro-bis-(trimethylphosphine)-platinum(II) was prepared according to the literature methods. 4-Iodobenzoyl chloride was prepared according to the literature procedure.

**Methyl 3,4,5-tris(n-dodecan-1-yloxy)benzoate (1).** To a solution of methyl 3,4,5-trihydroxybenzoate (4 g, 21.7 mmol) in DMF (50 mL) was added potassium carbonate (14.4 g, 104.2 mmol) while stirring at room temperature. The reaction mixture was stirred at 60 °C for 1 h. Then 1-bromododecane (17.3 g, 69.4 mmol) was added dropwise within 10 min followed by the addition of tetra-n-butylammonium bromide (TBAB) (0.31 g, 1 mmol). The resulting mixture was stirred at 70 °C for 20 h. After cooling to room temperature, the mixture was poured into 250 mL of ice/water with vigorous stirring. The suspension was filtered and the resulting light yellow
solid was subjected to column chromatography on silica (4:1 hexane/ethyl acetate) to give a pale solid as the product (13 g, 87%) after removing the solvents. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.24 (s, 2H), 4.0 (tt, overlap, 6H), 3.88 (s, 3H), 1.83-1.73 (m, 6H), 1.53-1.26 (m, 54H), 0.9 (t, 9H).

3,4,5-Tris(n-dodecan-1-yloxy)benzoic acid (2).\(^{140}\) Potassium hydroxide (0.5 g, 8.9 mmol) was added to a suspension of methyl 3,4,5-tris(n-dodecan-1-yloxy)benzoate (1) (3 g, 4.35 mmol) in 95% ethanol (40 mL) at room temperature. Then the mixture (clear solution) was stirred at 78 °C for 4 h. After cooling to room temperature, the solution was poured into 250 mL DI water and acidified with 5% hydrochloric acid to pH 1. The white precipitate was filtered as the product (2.79 g, 95%). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.3 (s, 2H), 4.0 (tt, overlap, 6H), 1.84-1.77 (m, 6H), 1.49-1.27 (m, 54H), 0.88 (t, 9H).

3,4,5-Tris(n-dodecan-1-yloxy)benzoyl chloride (3).\(^{140}\) To a solution of 3,4,5-tris(n-dodecan-1-yloxy)benzoic acid (2) (1.01 g, 1.5 mmol) in methylene chloride was added a catalytic amount of DMF (~0.5 mL). The reaction flask was cooled in an ice bath and thionyl chloride (0.16 mL, 2.2 mmol) was added dropwise. A white suspension was formed immediately. Then the ice bath was removed and the mixture was stirred at room temperature for 4 h. The solvent was evaporated under vacuum and the crude product was used for the next step without further purification.

**Compound 4.**\(^{134}\) A solution of ethylene diamine (5 mL) and triethylamine (2 mL) in methylene chloride (10 mL) was placed in an ice-bath and degassed for 10 min. Then, the solution of 3,4,5-tris(n-dodecan-1-yloxy)benzoyl chloride (3) (1.2 g, 1.73 mmol) in methylene chloride (10 mL) was added dropwise to the ethylene diamine solution. The resulting yellow suspension was brought to room temperature overnight. Methylene chloride (50 mL) was added to the suspension and the mixture was washed with 1 M HCl (100 mL, twice). The aqueous layer
was extracted with methylene chloride. The combined organic solution was dried over anhydrous sodium sulfate. After the solvents were evaporated under vacuum, the resulting light yellow solid was recrystallized from ethanol. Further purification by column chromatography on silica (10:1→5:1 chloroform/methanol) gave an off-white solid as the product (0.3 g, 25%) after removing solvents. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.01 (s, 2H), 6.61 (t, 1H), 4.00 (m, 6H), 3.49 (q, 2H), 2.95 (t, 2H), 1.70-1.82 (m, 6H), 1.45-1.49 (m, 6H), 1.26-1.33 (m, 48H), 0.84-0.88 (m, 9H).

**Compound 5.** This compound was synthesized according to the same procedure used for compound 4, except compound 4 (0.2 g, 0.28 mmol) and 4-iodobenzoyl chloride (82 mg, 0.31 mmol) were used. The desired product 5 was obtained as an off-white solid (0.2 g, 76%). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.75 (d, 2H), 7.55 (d, 2H), 7.44 (broad singlet, 1H), 7.11 (broad singlet, 1H), 6.98 (s, 2H), 4.00 (m, 6H), 3.67 (broad singlet, 4H), 1.70-1.82 (m, 6H), 1.45-1.49 (m, 6H), 1.26-1.33 (m, 48H), 0.84-0.90 (m, 9H).

**Compound 6.** To a solution of compound 5 (0.28 g, 0.296 mmol) in diethylamine/THF (7 mL/5 mL) was added Pd(II) (20.8 mg, 0.0296 mmol) and CuI (2.8 mg, 0.0148 mmol). The mixture was degassed for 15 min and then trimethylsilyl acetylene (44 mg, 0.45 mmol) was added via syringe. The reaction mixture was stirred at room temperature for 5 h at which time TLC analysis showed that no starting material remained. The solution was diluted with 50 mL methylene chloride, washed with water. The combined organic solution was dried over sodium sulfate. After removing solvents under vacuum, the red solid was recrystallized from ethanol to give an off-white solid as the product (0.21 g, 77%). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.76 (d, 2H), 7.50 (d, 2H), 7.26 (broad singlet, 1H), 7.12 (broad singlet, 1H), 6.98 (s, 2H), 4.00 (m, 6H), 3.67
Compound 7. To a solution of compound 6 (0.21 g, 0.23 mmol) in THF (8 mL) was added TBAF (0.92 mL) via syringe. The resulting solution was stirred at room temperature for 0.5 h at which time TLC analysis indicated that no starting material remained. Then methylene chloride (50 mL) was added to dilute the solution. After washing with water, the combined organic solutions were dried over sodium sulfate. A red solid was obtained after removing the solvents under vacuum. The solid was dissolved in a few milliliters of hot ethanol. An off-white precipitate was collected as the product (0.18 g, 93%). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.83 (d, 2H), 7.67 (broad singlet, 1H), 7.50 (d, 2H), 7.42 (broad singlet, 1H), 6.98 (s, 2H), 4.00 (m, 6H), 3.67 (broad singlet, 4H), 3.17 (broad singlet, 1H), 1.70-1.82 (m, 6H), 1.45-1.49 (m, 6H), 1.26-1.33 (m, 48H), 0.84-0.90 (m, 9H).

Compound 8. To a solution of compound 7 (0.18 g, 0.21 mmol) in diethylamine (3 mL) and THF (3 mL) was added cis-dichloro-bis-(trimethylphosphine)platinum(II) (0.106 g, 0.25 mmol). The resulting solution was stirred at room temperature for 20 h at which time methylene chloride (100 mL) was added to dilute the solution. After washed with water, the combined organic solution was dried over sodium sulfate. A yellow solid was obtained after removing the solvents. The solid was precipitated from ethanol to give a light yellow solid as the product (0.18 g, 70%). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.65 (d, 2H), 7.32 (d, 2H), 7.18 (broad singlet, 1H), 7.08 (broad singlet, 1H), 6.98 (s, 2H), 4.00 (m, 6H), 3.67 (broad singlet, 4H), 3.17 (broad singlet, 1H), 1.70-1.82 (m, 6H), 1.45-1.49 (m, 6H), 1.26-1.33 (m, 48H), 0.84-0.90 (m, 9H). $^{31}$P NMR (CDCl$_3$, 121 MHz) $\delta$ -13.54 ($J_{\text{Pt-P}} = 2321.7$ Hz).
**Pt2MAM.** To a solution of compound 8 (0.16 g, 0.129 mmol) in diethylamine/THF (5 mL/5 mL) was added 1,4-diethynylbenzene (7.9 mg, 0.063 mmol) and CuI (1.2 mg, 0.0063 mmol). The reaction mixture was stirred at room temperature for 3 h. At which time, TLC analysis showed that no 1,4-diethynylbenzene remained. The solution was diluted with 100 mL of methylene chloride, washed with water. The combined organic solution was dried over sodium sulfate. After removing solvents under vacuum, the red solid was precipitated from ethanol to give a yellow solid as the product (0.13 g, 82%). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.66 (d, 4H), 7.34 (d, 4H), 7.25 (s, 2H), 7.17 (s, 2H), 7.00 (s, 4H), 4.00 (m, 12H), 3.67 (broad singlet, 8H), 1.64-1.84 (m, 48H), 1.40-1.48 (m, 12H), 1.26-1.33 (m, 96H), 0.84-0.90 (m, 18H). $^{31}$P NMR (CDCl$_3$, 121 MHz) $\delta$ -19.39 ($J_{Pt-P} =$ 2292.6 Hz).

**NDI-2.**$^{134}$ To a solution of compound 4 (0.59 g, 0.82 mmol) in DMF (20 mL) was added 1,4,5,8-tetracarboxylic naphthalene dianhydride (74 mg, 0.27 mmol) at room temperature. The reaction mixture was stirred at 140 °C for 7 h. After cooled to room temperature, the reaction mixture was placed in a freezer overnight. The resulting precipitate was filtered out and dissolved in hot ethanol. A yellow solid was obtained as the product after filtration (0.43 g, 95%). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.73 (s, 4H), 6.98 (s, 4H), 6.72 (t, 2H), 4.54 (m, 4H), 4.00 (m, 12H), 3.87 (m, 4H), 1.75-1.82 (m, 12H), 1.47(m, 12H), 1.26-1.33 (m, 96H), 0.84-0.90 (m, 18H); Elemental anal. calc’d C: 74.96, H: 10.16, N: 3.36; Found C: 74.91, H: 11.05, N: 3.34.

**1,2,3-Tris(n-dodecan-1-yloxy)benzene (9).**$^{141}$ To a solution of 1,2,3-trihydroxybenzene (4 g, 31.76 mmol) in DMF was added potassium carbonate (21.04 g, 152.45 mmol) at room temperature while stirring. The resulting colorless solution was heated to 60 °C. 1-bromododecane (25.33 g, 101.63 mmol) was added dropwise within 10 min followed by the addition of TBAB (0.31 g). The reaction mixture was stirred at 65 °C for 4 h and then poured into
250 mL ice/water with vigorous stirring. The creamy, granular solid was filtered out and passed through a short plug of silica with ethyl acetate/hexane (19:1) as the eluent. An off-white solid was obtained as the product after removing solvents under vacuum (18.44 g, 92%). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 6.9 (t, 1H), 6.55 (d, 2H), 3.9 (t, 6H), 1.78 (m, 6H), 1.47 (m, 6H), 1.26 (m, 48H), 0.88 (t, 9H).

**3,4,5-Tris(n-dodecan-1-yloxy)-1-nitrobenzene (10).** To a stirred suspension of nitric acid (0.15 g, 2.38 mmol, 25% on SiO$_2$) in methylene chloride (4 mL) was rapidly added 1,2,3-tridodecyloxybenzene (9) (0.3 g, 0.475 mmol) in methylene chloride (2 mL). The resulting red solution was stirred at room temperature for 20 min, after which time the SiO$_2$ was filtered and washed several times with methylene chloride. After removing solvent under vacuum, the resultant orange oil was dissolved in hexane (3 mL). Upon addition of methanol (20 mL) with vigorous shaking, the product was separated as a white solid. The solid was filtered, washed with cold methanol and dried in air (0.238 g, 74%). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.47 (s, 2H), 4.00 (m, 6H), 1.78 (m, 6H), 1.47 (m, 6H), 1.26 (m, 48 H), 0.88 (t, 9H).

**3,4,5-Tris(n-dodecan-1-yloxy)-1-aminobenzene (11).** To a suspension of 3,4,5-tridodecyloxy-1-nitrobenzene (10) (1 g, 1.48 mmol) and Pd/C (10%) (32 mg, 0.3 mmol) in ethanol (15 mL) was added hydrazine monohydrate (0.71 g, 22.2 mmol). The reaction mixture was refluxed for 20 h under an argon atmosphere. The cooled mixture was diluted with methylene chloride (50 mL). Carbon was filtered and washed several times with methylene chloride. The solution was concentrated in a rotary evaporator. An off-white solid was obtained as the product (0.918 g, 96%). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 5.91 (s, 2H), 3.91 (t, 4H), 3.84 (t, 2H), 3.46 (bs, 2H), 1.76 (m, 6H), 1.47 (m, 6H), 1.26 (m, 48 H), 0.88 (t, 9H).
NDI-1. 142 3,4,5-Tridodecyloxy-1-aminobenzene (11) (0.541 g, 0.84 mmol), 1,4,5,8-tetracarboxylic naphthalene dianhydride (94 mg, 0.35 mmol) and zinc acetate (76 mg, 0.35 mmol) was added to quinoline (10 mL). The mixture was stirred at 180°C for 3 h. The cooled solution was poured into 1 M HCl (100 mL) and the precipitate was filtered and washed with water and methanol to give a yellow solid. After column chromatography on silica (3:7 hexane/methylene chloride), the resulting solid was dissolved in methylene chloride and precipitated by adding methanol. After filtration, a light red solid was obtained as the product (0.33 g, 62%). 1H NMR (CDCl$_3$, 300 MHz): δ 8.84 (s, 4H), 6.5 (s, 4H), 4.1 (t, 4H), 3.97 (t, 8H), 1.8 (m, 12H), 1.47 (m, 12H), 1.26 (m, 96H), 0.88 (t, 18H).
CHAPTER 6
CONCLUSION

In the previous chapters, the photophysical properties of several different types of \( \pi \)-conjugated platinum containing oligomers have been studied. The studies examined the basic photophysics of the oligomers, as well as intra- and inter-molecular interactions, such as photoinduced electron transfer and energy transfer and the effects of molecular self-assembly on the photophysical properties. These studies provide a fundamental guidance for the application of these materials or their analogues in electronic or optoelectronic devices.

The studies began with a comprehensive investigation of photophysics and photoinduced electron transfer in a series of platinum acetylide oligomers that feature a donor-spacer-acceptor architecture. The phosphorescence quenching and the characteristic absorption bands of radical anions and radical cations observed in the transient absorption spectra provide evidence that intramolecular electron transfer occurs from the triplet state of the oligomers to the electron acceptors. One of the key findings of this study is that photoinduced electron transfer in PtnT2A series of oligomers is excitation wavelength-dependent. When the spacer chromophore is excited, an indirect electron transfer mechanism occurs. Initial charge separation arises from the triplet state of the spacer to the acceptor followed by hole shift from the spacer to the donor. This gives rise to the formation of a charge separated state that has a lifetime in excess of 100 ns. However, when the donor chromophore is directly excited, a direct electron transfer mechanism which occurs from the triplet state of the donor to the acceptor is applied. Interestingly, while electron transfer occurs in the short chain oligomer, in the long chain oligomers, only the triplet state of the donor is present in the transient absorption spectra, indicating that electron transfer does not occur due to the absence of sufficient electronic coupling between the donor and the acceptor.
In a second study, two anthracene-based platinum acetylide oligomers were prepared to investigate intramolecular energy transfer dynamics. Our previous studies and current DFT calculations indicate that the triplet state of the anthracene segment lies about 1.1 eV lower than that of the platinum acetylide segment in the Pt4An oligomer. The large energy gap provides an ideal environment for the occurrence of singlet-triplet energy transfer. Indeed, the S-T energy transfer process is proved by the efficient quenching of the fluorescence emission in Pt4An, and the strong triplet absorption of the anthracene segment in its transient absorption spectra. Following S-T energy transfer, T-T energy transfer from the platinum acetylide segment to the anthracene segment takes place, which is confirmed by the rapid quenching of the phosphorescence emission in time-resolved emission spectra. The anthracene-based platinum acetylide systems provide a unique platform for studying rarely occurred singlet-triplet energy transfer dynamics.

To continue our studies on triplet exciton delocalization in \(\pi\)-conjugated organometallic systems, we carried out a detailed photophysical investigation in a series of platinum tetrayne oligomers. The photoluminescence spectra of the oligomers feature a narrow and intense phosphorescence band followed by a vibronic progression of sub-bands separated by \(ca.\) 2100 cm\(^{-1}\). Both absorption and low temperature emission spectra indicate that triplet excited states of the series of oligomers are localized and restricted within \(~2\) repeat units. In addition, the spectra are well-fitted a Frank-Condon expression. The parameters recovered from the spectral fitting are also consistent with the notion of the localization of the triplet excited state. According to our previous studies in an extended series of platinum acetylide oligomers, the triplet excited state is confined within \(~1\) repeat unit. In the current study, the triplet excited state of platinum tetrayne
oligomers is restricted within ~ 2 repeat units likely due to the slightly rigid geometry of ethynylene groups and the low S-T splitting energy.

The final study was devoted to photophysics and electron transfer properties of phosphorescent platinum acetylide organogelators. We doped a small amount of the electron acceptor into aggregated platinum acetylide oligomers. The effective phosphorescence quenching in the doped gels indicates that electron transfer occurs from the triplet state of the donor to the acceptor. Interestingly, the quenching is more efficient in the aggregated state than in the molecularly dissolved state, which suggests that triplet exciton diffusion may be involved.

To explore electron transfer properties in the aggregated platinum acetylide oligomer in polar solvents, a new organogelator (Pt2MAM) that structurally combines all three driving forces that are responsible for molecular self-assembly was synthesized. The oligomer gels both nonpolar and polar solvents. Its morphology features fiber networks as shown in the TEM and AFM images. The blue shift in its absorption spectrum suggests that self-assembly of Pt2MAM produces H-aggregates. With a small amount doping of an acceptor, photoluminescence and transient absorption spectra confirm that electron transfer occurs in this system. To further gain insight into ion-radical states of the aggregated platinum acetylide oligomers, the pulse radiolysis technique was applied for this study. The results indicate that electrons are captured by the organogelator. The corresponding radical anion absorption blue-shifts in the aggregated state relative to its molecularly dissolved state. With a small amount doping of an electron acceptor, the radical-ion spectrum features the absorption of the acceptor anion radical, suggesting that electron transfer occurs from the surrounded host molecules to the electron acceptor molecules.
Figure A-1. Chemical structure of the NDI model compound

Figure A-2. Emission spectra of platinum acetylide oligomers
Figure A-3. Emission spectrum of the NDI model compound

Figure A-4. Chemical structure and absorption spectra of Pt2T2
Figure B-1. Fitting spectra of (PtC₈)₁, (PtC₈)₂ and (PtC₈)₃ (100 K in Me-THF glass)
APPENDIX C
NMR SPECTRA

Figure C-1. The $^1$H NMR (300 MHz, CDCl$_3$) spectrum of Pt2T1A

Figure C-2. The $^{31}$P NMR (121 MHz, CDCl$_3$) spectrum of Pt2T1A
Figure C-3. The $^1$H NMR (300 MHz, CDCl$_3$) spectrum of Pt$_2$T$_2$A

Figure C-4. The $^{31}$P NMR (121 MHz, CDCl$_3$) spectrum of Pt$_2$T$_2$A
Figure C-5. The $^1$H NMR (300 MHz, CDCl$_3$) spectrum of Pt$_4$T$_1$A

Figure C-6. The $^{31}$P NMR (121 MHz, CDCl$_3$) spectrum of Pt$_4$T$_1$A
Figure C-7. The $^1$H NMR (300 MHz, CDCl$_3$) spectrum of Pt$_4$T$_2$A

Figure C-8. The $^{31}$P NMR (121 MHz, CDCl$_3$) spectrum of Pt$_4$T$_2$A
Figure C-9. The $^1$H NMR (300 MHz, CDCl$_3$) spectrum of Pt6T1A

Figure C-10. The $^{31}$P NMR (121 MHz, CDCl$_3$) spectrum of Pt6T1A
Figure C-11. The $^1$H NMR (300 MHz, CDCl$_3$) spectrum of Pt6T2A

Figure C-12. The $^{31}$P NMR (121 MHz, CDCl$_3$) spectrum of Pt6T2A
Figure C-13. The $^1$H NMR (300 MHz, CDCl$_3$) spectrum of Pt$_2$An

Figure C-14. The $^{31}$P NMR (121 MHz, CDCl$_3$) spectrum of Pt$_2$An
Figure C-15. The $^1$H NMR (300 MHz, CDCl$_3$) spectrum of Pt$_4$An

Figure C-16. The $^{31}$P NMR (121 MHz, CDCl$_3$) spectrum of Pt$_4$An
Figure C-17. The $^1$H NMR (300 MHz, CDCl$_3$) spectrum of Pt2MAM

Figure C-18. The $^{31}$P NMR (121 MHz, CDCl$_3$) spectrum of Pt2MAM
Figure C-19. The $^1$H NMR (300 MHz, CDCl$_3$) spectrum of NDI-2

Figure C-20. The $^1$H NMR (300 MHz, CDCl$_3$) spectrum of NDI-1
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Yongjun Li was born in Chifeng, Inner Mongolia province, China. He received his B.E. in chemistry from Nanjing University of Science and Technology in July 1998. After graduation, he started his career as a junior researcher in Xi’an Modern Chemistry Research Institute, Xi’an, China. He worked there for five years and at the same time, he received his master’s degree in organic chemistry. In 2004, Yongjun had a chance to come to the University of Florida to continue his education pursuing a Ph.D in chemistry. He joined Dr. Schanze’s group and focused his study on photochemistry. After his Ph.D., Yongjun will work as a postdoctoral associate in Dr. Turro’s group at Columbia University, New York City, NY.