PHOTOPHYSICAL STUDIES OF PI-CONJUGATED OLIGOMERS AND POLYMERS THAT INCORPORATE INORGANIC MLCT CHROMOPHORES

By

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To the brave warrior in all of us…
ACKNOWLEDGMENTS

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The use of π-conjugated polymers in various material devices has encouraged increased research interest in their photophysical properties in recent years. The integration of transition metal chromophores with metal-to-ligand charge transfer (MLCT) excited states into the polymers permits easy variation of the polymer excited-state properties, since the MLCT chromophore redox potentials are tunable via ligand variation. With this design consideration in mind, the photophysics of two different types of metal-organic polymers are presented.

First, a series of PPE-type aryleneethynylene oligomers containing a 2,2’-bipyridyl unit for transition metal coordination are considered. The oligomers have a well-defined repeat structure, unlike polymers previously studied in our group with the same subunits that exhibited unusual photophysical behavior. These oligomers are studied by
themselves and coordinated to –Re\(^{III}\)(CO)\(_3\)Cl and –Re\(^{III}\)(CO)\(_3\)(NCCH\(_3\))\(^{+}\)OTf\(^-\) chromophores. Second, a series of poly(3-alkylthiophene) polymers containing varying amounts of 2,2’-bipyridyl subunits are synthesized and coordinated to –Ru\(^{II}\)(2,2’-bipyridine)\(_2^{2+}\) and –Os\(^{II}\)(2,2’-bipyridine)\(_2^{2+}\) chromophores. The photophysical and photothermal results of these two types of molecules are presented and interpreted, paving the way for the design of better polymers for materials applications. Particular attention is paid to the following:

*The effect of oligomer and polymer coordination to the metal chromophore.*

Upon coordination of the metal chromophore to the oligomer or polymer, the primary absorption bands red-shift. Furthermore, organic-based fluorescence is quenched, giving rise to an MLCT-based emission.

*The effect of increasing the oligomer effective conjugation length.* When the conjugation length is increased by lengthening the oligomer, results show that anticipated photophysical results are not obtained for the PPE-type oligomers, suggesting conjugation breaks in the oligomer backbone via geometric twisting.

*The observed excited-state equilibrium of ligand- and metal-based states (\(^3\pi,\pi^* \leftrightarrow \(^3\)MLCT).* It is clear through ligand manipulation of the transition metal chromophore that both ligand and metal-based excited states are populated upon photoexcitation, and the observed emission and transient absorption photophysics are controlled by this equilibrium.

*The effect of oligomer and polymer structure on the observed photophysics.* Altering the repeat unit length or switching from a “linear” to “bent” \(\pi\)-backbone structure dramatically alters the observed photophysics.
The unique optical and electronic properties of π-conjugated polymers have been an area of intense research in recent decades. These polymers typically have high fluorescence quantum yields, exhibit electrical conductivity, and possess non-linear optical (NLO) properties that lead to their potential use in organic-based light emitting diodes (LEDs), photoconductive or photorefractive devices, chemical sensors, and molecular electronic devices. Two major classes of π-conjugated polymers are considered here, polymers with a phenylenevinylene or aryleneethynylene-based subunit and polymers with a thiophene-based subunit.

Phenylenevinylene- and Aryleneethynylene-Based Polymers

“Rigid rod” polymers with polyphenylenevinylene (PPV) or polyphenyleneethynylene (PPE) subunits have been popular for their unique material properties for the past 15 years. Rothberg performed extensive photophysical studies on PPV-based polymers that could serve as a “molecular wire.” The photoexcited electron (i.e., exciton) can easily travel through the “electron cloud” created along the polymer backbone by extended π-conjugation. Typical photophysical properties for PPV as a thin film include a broad ground state absorption centered at 400 nm and an intense 540 nm fluorescence. Excited-state energies, specifically the triplet excited state, are very
difficult to measure for PPV and most other π-conjugated polymers due to the absence of phosphorescence. However, the energy can be determined via indirect means such as triplet-triplet energy transfer quenching studies. A report by Monkman and coworkers\textsuperscript{22} determined the triplet energy with this method for poly(2-methoxy-5-(2'-ethyl-hexoxy)-p-phenylenevinylene) (MEH-PPV),\textsuperscript{*} calculating a value of 1.27 eV (29.3 kcal mol\textsuperscript{-1}). A previous estimate\textsuperscript{23} of triplet excited-state energies for PPV molecules placed them between 1.2 and 1.4 eV (27.7 – 32.3 kcal mol\textsuperscript{-1}), which agrees well with this measurement. 

A derivative of PPV, poly(2,5-bis(2'-ethylhexyloxy)-1,4-phenylene-vinylene (BEH-PPV), has also been very popular in photophysical studies. Additionally, a PPV polymer has been synthesized that contains a 2,2'-bipyridyl subunit for reasons discussed later. Both polymers are shown in Figure 1-1.

![Figure 1-1: BEH-PPV and 2,2'-bipyridine-containing BEH-PPV (R = CHCH(C\textsubscript{2}H\textsubscript{5})C\textsubscript{6}H\textsubscript{13} Ref. 24).](image)

\* See chapter 3 for a more detailed explanation of this technique when it is applied to oligomers and polymers presented in this text.
This BEH-PPV polymer exhibited a 504 nm absorption, a sharp 560 nm emission, and a broad singlet excited-state absorption that extends into the near-IR. The 2,2’-bipyridine-containing polymer exhibited absorption and emission maxima at 438 and 510 nm, respectively. The observed spectral blue-shifts are due to conjugation breaks in the π-delocalization of the polymer backbone produced by the twisted bipyridine subunits. This delocalization restriction is an important concept to understand in π-conjugated polymers and will be considered in subsequent chapters. A transient absorption spectrum of the bipyridine-containing polymer is shown in Figure 1-2. Note the broad excited-state absorption that extends into the near-IR and the bleach that corresponds to a ground-state \( \pi,\pi^* \) absorption.

![Figure 1-2: 2,2’-Bipyridine-containing PPV singlet excited-state difference absorption spectrum in toluene (Solid line, 417 nm excitation, Ref. 24).](image)

Another polymeric structure consisting of alternating ethynyl and aryl subunits (polyphenyleneethynylene, PPE) was considered by Davey et al.,\(^2\) Le Moigne et al.,\(^5,25\) and Swager et al.\(^26\) having the structure shown in Figure 1-3.
Figure 1-3: Aryleneethynylene-based polymer structure (R = n-octadecyl, Ref. 2).

The additional rigidity in the aryleneethynylene-based polymers compared to the phenylenevinylene samples allowed for higher emission quantum yields by decreasing the nonradiative decay rate constant ($k_{nr}$), which could make them more useful in conjugated polymer applications. Absorption spectra for the polymer shown in Figure 1-3 exhibited a sharp 452 nm absorption that is assigned as a $\pi,\pi^*$ transition of the conjugated backbone. A corresponding sharp emission band with a 482 nm maximum is observed, as shown in Figure 1-4.

Figure 1-4: PPE absorption (solid line) and emission (dashed line) spectra in chloroform (Ref. 26).
Keeping the “molecular wire” idea in mind, Swager and coworkers\(^{26}\) synthesized aryleneethynylene-based polymers containing varying amounts of anthracene repeat units as shown in Figure 1-5.

![Figure 1-5: Anthracene-containing aryleneethynylene polymer (Ref. 26).](image)

Photophysical studies of these polymers showed that excitation into absorption bands associated with the polymer backbone produced emission typically observed for anthracene and a dramatic reduction in the polymer-based fluorescence. For example, a polymer with a structure corresponding to \(x = 0.17\) in Figure 1-3 has the absorption and emission spectra shown in Figure 1-6.

This mixed polymer exhibited the same absorption and emission observed for the PPE polymer (Figure 1-3), but the presence of new absorption and emission bands at 527 and 549 nm, respectively, result from the anthracene moiety. This observation suggests that the exciton was efficiently “trapped” by the anthracene subunits. This trapping could lead to emission or energy transfer to other substituents, which would be utilized in LED or NLO applications. Therefore, polymers could be synthesized containing unique subunits (like anthracene in this example) to manipulate (i.e., tune) the excited-state properties of the polymer. Furthermore, model systems where anthracene moieties were
only present at the ends of a PPE 20-mer still exhibited pronounced anthracene emission, indicating very efficient energy transfer along the polymer backbone (e.g., “exciton hopping”).

Figure 1-6: Absorption (solid line) and emission (dashed line) spectra in chloroform of the polymer in Figure 1-5 with $x = 0.17$ (Ref. 26).

Zhou and Swager\textsuperscript{16} continued the defect-trapping idea with aryleneethynylene polymers containing a cyclophane-based “receptor” as seen in Figure 1-7.

Figure 1-7: Cyclophane-containing aryleneethynylene polymer ($R = \text{CON(C}_8\text{H}_{17})_2$, Ref. 16).
The cyclophane polymer exhibited a 427 nm absorbance and intense ($\phi_{\text{em}} = 0.70$) 459 nm emission. The presence of organic molecules that can associate within the cyclophane (e.g., methyl viologen) effectively quenched the polymer emission. As little as 60 µM methyl viologen quenched the polymer fluorescence by an order of magnitude, and 0.1 mM completely quenched the emission. This quenching is due to the formation of effective “exciton traps” analogous to the anthracene moieties discussed earlier, resulting in efficient quenching of entire polymer strands with a relatively small amount of the associating molecule.

**Polythiophene-Based Polymers**

Another series of $\pi$-conjugated polymers that have received much attention for their optical properties are polythiophenes. Yamamoto and coworkers first reported the conductivity of polythiophene in 1980, and its ease of oxidation made this polymer very popular for molecular wire and doping applications. Photophysical data for polythiophene in solution is difficult to measure, as thiophene oligomers containing six or more thiophene rings have extremely poor solubilities. For this reason, small molecular weight oligothiophenes and substituted polythiophenes have been studied that circumvent this solubility issue.

An exhaustive study by Becker and coworkers illustrated the effect increased backbone $\pi$-conjugation has on the observed photophysics. The photophysics of oligothiophenes ranging in size from one to seven thiophene rings were presented, and many trends are apparent. The absorption and fluorescence spectra both exhibited red-shifts with increasing oligomer size (from 232 to 441 nm for absorption; from 362 to 522 nm for emission in dioxane). Emission quantum yields and lifetimes also increased in the
larger oligomers, suggesting an increase in the $\pi$-delocalization of the oligomer backbone. Both absorption and emission maxima were found to be inversely related to the oligomer size, allowing for the estimation of polythiophene values (490 nm absorption; 580 nm emission). The transient absorption spectra of the oligothiophenes also red-shifted with increasing oligomer size, with the largest oligomer resembling the PPV spectrum in Figure 1-2. Absorption and transient absorption spectra of the oligothiophene series are shown in Figure 1-8.

The absence of phosphorescence in the oligothiophenes eliminated the possibility of direct determination of their triplet excited-state energies. However, a photoacoustic calorimetry technique† was used to indirectly determine the triplet energy, which decreased from 2.23 eV to 1.60 eV (51.5 – 36.9 kcal mol$^{-1}$) as the oligomer size was increased from two to seven thiophene rings.$^{30}$ The energy was found to be inversely related to the oligomer size, allowing the polythiophene value to be extrapolated (1.43 eV, 33.0 kcal mol$^{-1}$). This energy is very similar to the PPV values listed above.

Swager’s use of cyclophane subunits in aryleneethynylene-based polymers (Figure 1-7) was also used with a polythiophene backbone as shown in Figure 1-9. The cyclophane-containing polythiophene exhibited a 520 nm absorption and 624 nm emission that is considerably weaker than the PPE polymer ($\phi_{em} = 0.066$). This emission intensity decrease is due to the greater flexibility of the polythiophene backbone, which provides an alternative non-radiative mechanism for excited-state deactivation through molecular motion. The polymer fluorescence was also quenched by organic molecules

† See chapter 2 for a more detailed explanation of this technique and chapters 3 and 5 for its application to determine triplet excited-state energies and yields.
(e.g., methyl viologen) as before, indicating efficient exciton trapping by the cyclophane subunits. The quenching rate is smaller for this polymer than the PPE polymer, however, due to the weaker polythiophene emission intensity.

Figure 1-8: Absorption (in dioxane) and triplet-triplet absorption difference spectra (in benzene, 347 nm excitation) of an oligo(thiophene) series. The \( \alpha \) number indicates the number of thiophene rings in the oligomer. (Ref. 28-29)
While polythiophenes have many interesting properties, their solubilities are very poor. Furthermore, they can be oxidized by atmospheric oxygen, limiting their processibility and stability in materials applications. Elsenbaumer and coworkers synthesized an alkylated derivative of polythiophene in 1986 that was soluble and considerably more stable. Four different coupling structures are possible in these alkylated polymers, which are illustrated in Figure 1-10.

Figure 1-9: Cyclophane-containing polythiophene polymer (R = C\textsubscript{10}H\textsubscript{21}, Ref. 16).

Figure 1-10: Poly(3-alkylthiophene) repeat structures (Ref. 33).
It was found that the increased structural homogeneity improved the conductivity and optical properties of the polymer by increasing the effective conjugation lengths within the polymer strands.\textsuperscript{33,34} Random connection patterns prevented the polymer from achieving the coplanarity necessary for extended $\pi$-conjugation via steric interactions. In recent years, synthetic techniques have been refined to produce highly regiospecific polythiophenes for materials-based applications.\textsuperscript{33,35} Absorption spectra of HT-HT poly(3-alkylthiophenes) in chloroform solution exhibit a broad absorption band centered at 436 nm. Varying the alkyl chain lengths from hexyl to dodecyl did not change the solution absorption spectra but induced a red-shift of the solid-state absorption spectrum by 15 nm from the shortest to longest alkyl chain.\textsuperscript{33} Note that the absorption maximum of a TT-HH poly(3-decylthiophene) is 312 nm in chloroform,\textsuperscript{36} significantly blue-shifted from the HT-HT polymer and confirming the need for regiospecific polythiophenes to achieve the maximum extended conjugation. The polymer extended $\pi$-conjugation exerted a similar effect on 3-alkylthiophenes as seen earlier on the oligothiophenes, as the major absorption band of a series of oligo(3-octylthiophene)s in chloroform red-shifts from 302 to 405 nm with increased oligomer size from two to six thiophene rings. This trend indicates a consistent lowering of the LUMO energy.\textsuperscript{37}

Unlike the PPV and PPE-type polymers, phosphorescence has been observed at low temperature (18 K) for poly(3-hexylthiophene) by Xu and Holdcroft.\textsuperscript{38,39} A sharp 826 nm phosphorescence was observed, leading to a calculated triplet excited-state energy of 1.50 eV (34.6 kcal mol$^{-1}$). This value is higher than the MEH-PPV and polythiophene triplet energies (1.26 eV), which is surprising since the alkylated thiophene is a more planar polymer, which should increase the delocalization and lower the energy.
This observation could be due to the regiospecificity of the phosphorescence sample, but Xu and Holdcroft reported that various regiochemistries were investigated with similar spectral results. Also, the MEH-PPV triplet energy was determined by qualitative quenching studies,‡ which could result in a large error.

MLCT-Incorporated π-Conjugated Polymers

The initial photophysical work on π-conjugated polymers, coupled with the desire to more easily control their excited-state characteristics, led to the idea of introducing inorganic MLCT (metal-to-ligand charge transfer) chromophores into the polymer backbone. These chromophores have excited states that can easily be tuned by ligand substitution, potentially allowing a greater capacity to tune the polymer excited state(s).40-42 Following the initial idea, the synthesis and photophysical properties of these metal-organic π-conjugated polymers have rapidly grown in interest.43-48

Phenylenevinylene- and Aryleneethynylene-Based Polymers

Yamamoto and coworkers first suggested the introduction of MLCT chromophores into π-conjugated polymers during his studies on poly-2,2’-bipyridine.49-52 The bipyridine repeat unit allows easy ligation of ruthenium, nickel, copper, and iron chromophores, as shown with the –RuII(bpy)22+ chromophore (bpy = 2,2’-bipyridine) in Figure 1-11.

‡ In the study, when a triplet acceptor (tetracene, ET = 1.27 eV) did not quench the triplet-based transient absorption of MEH-PPV, the polymer triplet energy was “estimated” to be that value.22
Figure 1-11: Poly-2,2’-bipyridine ruthenium-containing polymer (Ref. 50).

The resulting metal-containing polymers exhibited electrochemical data largely representative of the MLCT chromophores, including Ru$^{II}$ → Ru$^{III}$ oxidation and 2,2’-bipyridine reduction. Since these polymers were synthesized for their photocatalytic and photoelectrochemical properties, little photophysical work other than an absorption spectrum in methanol was published. This absorption spectrum contained bands originating from both the polymer $\pi,\pi^*$ and ruthenium MLCT transitions at 373 and 450 nm, respectively. A copper(II)-containing polymer was also synthesized where a single copper atom had the capability to ligate two adjacent polymer strands. Absorption spectra of the copper-containing polymer exhibited a 20 nm red-shift in both the polymer-based $\pi,\pi^*$ absorptions and the metal-based MLCT transition when compared to model monomeric systems, indicating lowered LUMO energy levels due to increased delocalization.

An alternative method for introducing transition metal chromophores into $\pi$-conjugated polymers involves direct metal center substitution into the polymer chain.
Wittmann and coworkers\textsuperscript{53,54} synthesized aryleneethynylene-based polymers containing Pd[P(C\textsubscript{4}H\textsubscript{9})\textsubscript{3}]\textsubscript{2} or Pt[P(C\textsubscript{4}H\textsubscript{9})\textsubscript{3}]\textsubscript{2} subunits as shown in Figure 1-12.

![Figure 1-12: Aryleneethylylene-based polymers containing platinum subunits (M = Pd or Pt, Ref. 53).](image)

This synthetic approach produces very consistent polymer products and interesting photophysical results. An intense 380 nm singlet and weaker 510 nm triplet ground state absorption were observed in solution studies of this polymer, which is red-shifted from the model monomer spectrum (345 nm). This red-shift reflects a clear increase in delocalization across adjacent $\pi$ orbitals in the polymer backbone. A broad 520 nm luminescence was also observed from the polymer sample. However, due to their position within the polymer backbone these metal chromophores lack the “tunability” options available in other MLCT-based chromophores that are attached to the polymer backbone like the ruthenium chromophore in Figure 1-11.

Work pioneered by Yu and coworkers produced a significant advance in MLCT-containing $\pi$-conjugated polymers by introducing the well-known and characterized Ru(bpy)\textsubscript{3}\textsuperscript{2+} and Os(bpy)\textsubscript{3}\textsuperscript{2+} chromophores into a PPV-type polymer shown above (Figure 1-1) through an ingenious Heck coupling reaction\textsuperscript{43,44,55}. The polymer structure is shown in Figure 1-13.
These polymers exhibit interesting photoconductivity, photorefractivity, and NLO properties. The all-organic polymer (x = 0, y = 1 in Figure 1-13) exhibited an intense $\pi,\pi^*$ transition absorption at 470 nm, while the all-metal polymer (x = 1, y = 0) had a 550 nm “MLCT” absorption. A mixed polymer (x = 0.1, y = 0.9) absorption spectrum exhibited a superposition of the two bands. Extensive work was performed on the material properties of these polymers listed above, but the studies did not extensively probe the basic photophysical properties of the polymer excited state(s).

Further work was performed on these polymers by Wasielewski and coworkers,$^{24,56}$ including work where the polymer backbone was used as an ion sensor.$^{18}$ The complexed metal ion induced a conformational change in the 2,2'-bipyridine polymer subunit, which is twisted and serves as a break in the polymer $\pi$-conjugation as discussed earlier. The bipyridine was coplanar after complexation, resulting in a conjugation increase within the polymer as seen in Figure 1-14. This conjugation increase led to differing photophysical properties that signal the presence of the analyte ion (e.g., red-

$^*$ The molar absorptivity for this transition (ca. 90 x 10$^3$ M$^{-1}$ cm$^{-1}$) is rather high for an MLCT transition. However, the high concentration of ruthenium and the extended delocalization of the polymer backbone might contribute to its high value.
shifted absorption and emission bands) due to a lowering of the LUMO. For example, when nickel(II), zinc(II), or palladium(II) ions were titrated into a solution containing the 2,2’-bipyridine-containing PPV, the polymer $\pi,\pi^*$ 450 nm absorbance red-shifted between 50 – 100 nm depending on the metal ion. The ionochromic effect exhibited in these polymers proved to be an excellent ion-sensing device.\(^5\!\!^6\)

![Figure 1-14: Conformation change upon metal complexation (R = decyl, Ref. 18).](image)

In the wake of the PPV research, other $\pi$-conjugated polymers containing inorganic MLCT chromophores have also been investigated. Rasmussen et al.\(^5\!\!^7\) made ruthenium-containing polymers with a poly-diazabutadiene / 2,2’-bipyridine backbone as seen in Figure 1-15. An absorption spectrum of the polymer showed an intriguing blue-shift from a dimer model oligomer (from 480 to 465 nm in DMF). However, the polymer band was significantly broader, suggesting a myriad of accessible electronic transitions. The observed emission spectrum remained the same (sharp 666 nm band) for the two systems, but the polymer quantum yield was one-fourth the dimer value. This trend
suggested that increased nonradiative decay or decreased intersystem crossing to the emissive $^3$MLCT might result from the extended $\pi$-conjugation.

More recently, Wong and Chan$^{58}$ synthesized PPV-type polymers that have ruthenium chromophores attached via an alkoxy chain, as shown in Figure 1-16. This polymer configuration provides even greater ligand substitutional flexibility but removes the MLCT chromophore from direct interaction with the polymer $\pi$-conjugation, thus limiting its effects on the polymer excited state(s). The purpose of these polymers was to form metal-organic LEDs, with the chromophore not serving as a “tuning control” for the polymer excited state(s) but as a dopant to produce the electrogenerated luminescence. A $(x = 0.1, y = 0.9)$ polymer exhibited a 444 nm absorption and 606 nm emission in DMF solution, which is very similar to monomeric Ru(bpy)$_3^{2+}$ photophysics. These data indicate little electronic interaction between the polymer and MLCT chromophore. LEDs fabricated from these polymers exhibited good current-voltage properties and serve as an excellent starting point for “tunable” LEDs by varying the ruthenium
ligands. Clearly, the topic of MLCT-incorporated π-conjugated polymers is of great recent interest, and many other polymer structures are available for exploration.

![PPV-type polymer with tethered ruthenium chromophores](image)

Figure 1-16: PPV-type polymer with tethered ruthenium chromophores (Ru = Ru(bpy)$_3^{2+}$, Ref. 58).

**Polythiophene-Based Polymers**

Introducing MLCT chromophores into thiophene-based polymers has also been studied, but to a lesser degree than the PPV and PPE-based polymers. Zhu and Swager$^{59,60}$ synthesized a Ru(bpy)$_2^{2+}$-containing polythiophene via ligation to a 2,2’-bipyridine polymer subunit, as seen in Figure 1-17.

![Polythiophene with Ru](image)

Figure 1-17: Ru(bpy)$_3^{2+}$-substituted polythiophene (Ref. 59).

The monomer repeat unit of the unmetallated polymer exhibited a sharp 400 nm absorption in methylene chloride, which is blue-shifted from the estimated native
polythiophene value (490 nm) for the same reasons discussed above for the 2,2'-bipyridine-containing PPE polymers. Further work by Zhu and Swager\textsuperscript{17,61} focused upon thiophene polymers containing metallorotaxane centers with zinc or copper ions, as shown in Figure 1-18.

![Figure 1-18: Metallorotaxane-thiophene polymers (M = Zn\textsuperscript{2+} and Cu\textsuperscript{2+}, Ref. 17).](image)

These rotaxanes exhibited marked improvement in stability over the bipyridine-containing polythiophenes (Figure 1-17) and improved conductivity over native polythiophene. Detailed photophysics, however, were not presented in this study.

Reddinger and Reynolds synthesized another novel thiophene-based polymer containing MLCT chromophores.\textsuperscript{62,63} In these polymers, a nickel or copper chromophore was complexed to a SALOTH ligand that was incorporated into the thiophene backbone as shown in Figure 1-19. This polymer showed excellent conductivity properties, but again its photophysics were not the major focus of the reported research.
Previous Group Work

Based on the previous work described above, it was obvious to our group that while many different inorganic MLCT chromophore-containing $\pi$-conjugated polymers were being synthesized and applied in various materials applications, little detailed photophysical work had been performed to explore their excited state energies and dynamics. To that end, a project was initiated to synthesize polymers combining some of the ideas explored by previous groups. The work by Yamamoto and coworkers\textsuperscript{49-52} and Yu and coworkers\textsuperscript{43,44,55} incorporating MLCT chromophores through a 2,2'-bipyridine subunit in the polymer backbone was desirable since it afforded maximum tunability when selecting MLCT chromophores such as ruthenium, rhenium, and osmium complexes. Also, the increased rigidity of the aryleneethynylene-type polymers was more favorable than PPV-type structures. This rigidity would provide larger transition dipoles and hopefully more pronounced photophysical behavior. Therefore, a polymer structure combining both of these elements was devised and implemented.

A series of $\pi$-conjugated aryleneethynylene polymers with varying incorporated amounts of the well-characterized $-(\text{bpy})\text{Re}^I(\text{CO})_3\text{Cl}$ chromophore\textsuperscript{41} were synthesized via
Sonogashira coupling\textsuperscript{64} and their photophysical properties investigated in our lab.\textsuperscript{45,46,65}

The polymer structures, along with typical polymer weights obtained from GPC experiments, are shown in Figure 1-20.

![Polymers structure](image)

$\textbf{P1} : M_w = 37 \text{ kg mole}^{-1}, M_n = 14 \text{ kg mole}^{-1}, \text{PDI} = 2.7$

$\textbf{P2} : x = 0.10, y = 0.90; M_w = 21 \text{ kg mole}^{-1}, M_n = 8.8 \text{ kg mole}^{-1}, \text{PDI} = 2.3$

$\textbf{P3} : x = 0.25, y = 0.75; M_w = 16 \text{ kg mole}^{-1}, M_n = 7.9 \text{ kg mole}^{-1}, \text{PDI} = 2.1$

$\textbf{P4} : x = 0.33, y = 0.67; M_w = 26 \text{ kg mole}^{-1}, M_n = 11.3 \text{ kg mole}^{-1}, \text{PDI} = 2.3$

$\textbf{P5} : x = 0.50, y = 0.50; M_w = 16 \text{ kg mole}^{-1}, M_n = 7.8 \text{ kg mole}^{-1}, \text{PDI} = 2.0$

$R = n$-$C_{18}H_{37}$

Figure 1-20: Aryleneethynylene polymers containing (bpy)$\text{Re}^I(\text{CO})_3\text{Cl}$ (Ref. 46).

Metal-organic polymers $\textbf{P2} – \textbf{P5}$ exhibited many unique photophysical properties, including a red-shifted absorption band and unique long-wavelength luminescence when compared to the “all organic” polymer $\textbf{P1}$. These observations were believed to arise from a $d\pi(\text{Re}) \rightarrow \pi^*(\text{bpy-polymer})$ MLCT transition as seen in the PPV-based polymers presented above (Figure 1-13), which is typically observed for transition metal MLCT chromophores.\textsuperscript{41} Studies on model monomeric compounds that duplicated the repeat structure of the polymers initially supported this theory. However, certain photophysical
results were puzzling. For instance, the introduction of the rhenium MLCT chromophore into the polymer backbone decreased the polymer fluorescence quantum yield and lifetime, which would be expected due to the chromophore acting as an “exciton trap” as described above. However, polymer-based fluorescence was not completely quenched in even the P5 polymer, which was unexpected. Polymers P2, P3, and P5 were synthesized by a random copolymerization process, resulting in an inability to accurately characterize the polymer segment sequencing. Specifically, it was unclear whether the transition metal segments were homogeneously distributed throughout the polymer or segregated into “all organic” and “all metal” sections within the synthesized polymer. The inefficient fluorescence quenching suggested that a heterogeneous polymer was being produced by this procedure, allowing the organic polymer segments to behave as if the metal chromophore was not present. Further synthetic developments allowed for the synthesis of polymer P4, which has a known (organic, organic, metal) repeat structure. Nonetheless, it was evident that further work based on model systems containing this repeat structure was necessary to better interpret the polymer photophysical observations.

**Scope of This Work**

To further understand the photophysics observed for P1 – P5, a series of well-defined oligomers containing various lengths of the original polymer repeat structure were synthesized using a novel iterative synthetic scheme based around palladium-mediated coupling reactions. The detailed photophysical results of both free oligomers and oligomers bound to the ReI(CO)3Cl chromophore are presented herein. Next, the repeat units and geometries of the oligomers were varied to see how these changes affect
the observed photophysics. Particular attention is paid to the oligomer conjugation length influence and/or the possible formation of aggregates on the observed photophysical properties. Many spectroscopic techniques, including absorption, emission, transient absorption, electroabsorption spectroscopy, and transient EPR were utilized to probe the molecular excited state(s). Also, in a collaborative project with Dr. Stephan Guillerez and Lise Trouillet at CEA-Grenoble, the photophysical properties of poly(3-alkylthiophenes) with the capacity to complex MLCT chromophores through an integrated 2,2’-bipyridine subunit were studied in order to investigate the influence of the transition metal on their excited-state properties. The polymers are similar in structure to the Swager polymer shown in Figure 1-17 but with the added alkylation stability. Before these photophysics are discussed, however, a class of techniques that utilize the evolution of heat after photoexcitation to determine excited-state energetics is presented. This technique, photothermal chemistry, has received little attention in the study of inorganic complexes but is successfully utilized in the photophysical study of our PPE-type oligomers and polymers.
PHOTOTHERMAL CHEMISTRY

Photothermal chemistry involves the study of electronic transitions through the radiation of heat instead of light. The majority of photothermal chemistry studies in the literature rely on one of two techniques: Thermal lensing spectroscopy and photoacoustic spectroscopy. Thermal lensing spectroscopy involves a change in the sample refractive index due to released heat, resulting in the diffraction of a probe laser beam.\(^{66,67}\) Photoacoustic spectroscopy uses a piezoelectric transducer to analyze pressure waves in a sample caused by the emission of heat.\(^{68,69}\) The main advantage of studying excited states with photothermal studies is the lack of dependency upon the emission of light, which greatly increases the number of molecules that are amiable for study.

Both techniques have distinct advantages and disadvantages. Photoacoustic spectroscopy has a shorter (nanosecond to microsecond) observation time window than thermal lensing spectroscopy and requires external calibration, resulting in additional sample runs and increased experimental time.\(^{70}\) Time-resolved thermal lensing (TRTL) spectroscopy, however, has a long (tens of microseconds) observation time window and requires no external calibration.\(^{71}\) Furthermore, photoacoustic spectroscopy does not need to correct for probe beam absorption and can more readily study complex, multiple-process excited-state behavior. Both techniques will be addressed in turn, followed by their application to the study of inorganic and organic photophysics.
Time-Resolved Thermal Lensing

The premise of TRTL is very simple. A sample is irradiated with a pump laser, producing an excited electronic state. A second probe laser is then directed through the photoexcited sample. These two beams are commonly in a longitudinal (colinear) geometry, but they can also be applied in a transverse (perpendicular) configuration. Any heat evolved by the sample excited state decay(s) will cause a change in the sample refractive index and subsequent probe beam refraction (i.e., the formation of a “thermal lens”). A decrease in the probe beam center intensity can therefore be related to heat released by the sample. The pump beam is removed from the optical path by a filter or dispersing prism, and the probe beam center is usually isolated by a pinhole or knife edge for intensity measurement. Figure 2-1 shows a basic TRTL apparatus.

Figure 2-1: Basic TRTL longitudinal apparatus (Ref. 70).
The thermal lens theory

The thermal lens effect (also known as "thermal blooming") was first reported by Gordon and coworkers over 30 years ago.\textsuperscript{72} It was initially considered a hindrance to other laser spectroscopic methods, but Gordon determined that the degree of laser beam refraction was related to the sample solution refractive index. Since the refractive index of a liquid changes with temperature, the induced refraction can be related to heat given off by the photoexcited sample. The thermal lens does not form immediately upon the release of heat and slowly decays based on the thermal conductivity of the sample, so time-resolved experiments can also be performed.\textsuperscript{66}

The thermal lens focal length in a "steady state" equilibrium, $f(\infty)$, is given in (2-1). This value can be used in (2-2) to calculate the thermal lens focal length at time $t$, $f(t)$, during a TRTL experiment.

\begin{equation}
 f(\infty) = \frac{\pi k \omega^2}{2.303 P A \left( \frac{\partial \eta}{\partial T} \right)} \tag{2-1}
 \end{equation}

\begin{equation}
 f(t) = f(\infty) \left( 1 + \frac{\omega^2 \rho C_p}{8kT} \right) \tag{2-2}
 \end{equation}

In (2-1) and (2-2), $k$ is the sample thermal conductivity (W cm$^{-1}$ K$^{-1}$), $\omega$ is the Gaussian probe laser beam spot size (cm$^2$), $P$ is the probe beam power (W), $A$ is the sample absorbance, $\left( \frac{\partial \eta}{\partial T} \right)$ is the refraction index variation with temperature, $\rho$ is the sample density (g cm$^{-3}$) and $C_p$ is the specific heat of the sample (J g$^{-1}$ K$^{-1}$). These equations do not take into account any sample luminescence, and all excitation energy is assumed to be
released as heat. Appropriate corrections can be used if any appreciable luminescence occurs concurrent with the emission of heat.\textsuperscript{66}

If a TEM\textsubscript{00} Gaussian laser beam is used for the probe, equations can describe the beam diffraction based upon the thermal lens effect. The variables used in ensuing equations are visually defined in Figure 2-2. The relative probe beam area change at the pinhole, $\Delta \omega^2$, is defined in (2-3),\textsuperscript{73} while the beam center intensity change at the pinhole, $\Delta I_{bc}$, is defined by (2-4).\textsuperscript{66}

\[ \frac{\Delta \omega^2}{\omega^2} = \left[ -\frac{2.303 P \left( \frac{\partial n}{\partial T} \right) A}{\lambda k} \right] \left( \frac{2(Z_1)Z_c}{Z_c^2 + (Z_1)^2} \right) \quad (2-3) \]
\[
\frac{\Delta I_{bc}}{I_{bc}} = \frac{-2.303P\left(\frac{\partial \eta}{\partial T}\right)A}{\lambda k} = 2.303EA
\]  

(2-4)

In (2-3) and (2-4), \(\lambda\) is the probe laser wavelength and \(Z_c\) is the confocal distance. \(E\) is a simplified instrumental value of the various constants in (2-3), since they should not change during the experiment. Therefore, a variation of sample absorbance should produce a linear relation and allow the sample refraction change with temperature to be determined. Both (2-3) and (2-4) are considered the fundamental TRTL theory equations, but they are rarely used in everyday experimental practice.

Another treatment of TRTL theory\(^7^4\) discusses the relationship of the sample refractive index change and the commonly-used TRTL signal, \(S(t)\), which is defined in (2-5). The proposed equation for this relationship, assuming longitudinal geometry of the pump and probe beams, is given in (2-6).

\[
S(t) = \frac{V_0 - V(t)}{V_0} 
\]  

(2-5)

\[
S_L(t) = \frac{8\alpha E_0 l_z}{\pi \rho C_p} \left( \frac{\partial \eta}{\partial T} \right) \left( 2 - \frac{4(x - v_x t)^2}{a^2 + 8Dt} \right) \exp \left( \frac{-2(x - v_x t)^2}{a^2 + 8Dt} \right) 
\]  

(2-6)

In (2-5), \(V_0\) is the intensity of the probe beam center before pump beam excitation and \(V(t)\) is its intensity at time \(t\) after pump excitation. Therefore, \(S(t)\) can vary between 0 (no beam divergence) and 1 ("complete" theoretical beam divergence). In (2-6), the sample is assumed to be analyzed perpendicular to the sample flow which has a velocity of \(v_x\), \(\alpha\) is the absorption coefficient, \(E_0\) is the pump beam energy, \(l_z\) is the pump/probe beam interaction length within the sample, \(a\) is the probe beam Gaussian radius, and \(D\) is the
sample thermal diffusivity \((m^2 \text{s}^{-1})\). An equation similar to (2-6) can also be derived for the transverse (perpendicular) orientation of the pump and probe beams. Both (2-4)\(^{66}\) and (2-6)\(^{74}\) show the relationship between the sample refractive index change (e.g., evolution of heat) and the degree of probe beam diffraction. Although these equations are complex, it is not necessary to use such quantitative measurements of thermal lensing to calorimetrically determine excited state energies and excited state process quantum yields.

**A simplified calculation method**

The calculation scheme presented here for TRTL studies was first used by Braslavsky and coworkers in a study of singlet oxygen quantum yields of various organic sensitizers.\(^{75}\) If the analyte under study involves a single, long-lived triplet state following intersystem crossing from an emissive singlet state (many organic photochemical systems of interest fall into this category), then (2-7) can be applied to determine the intersystem crossing quantum yield \((\Phi_{\text{ISC}})\).

\[
\frac{U_{\text{Slow}}}{U_{\text{Total}}} = \frac{\Phi_{\text{ISC}} E_T}{E_{\text{ex}} - \Phi_{\text{fl}} E_S}
\]

(2-7)

In (2-7), \(E_T\) is the triplet excited state energy, \(E_{\text{ex}}\) is the pump laser energy, \(\Phi_{\text{fl}}\) is the fluorescence quantum yield, and \(E_S\) is the singlet excited state energy. If either \(\Phi_{\text{ISC}}\) or \(E_T\) is known from other photophysical measurements, TRTL can be used to determine the unknown parameter. \(U_{\text{Slow}}\) and \(U_{\text{Total}}\) values are obtained directly from the TRTL spectrum. A sample TRTL response of phthalazine, which qualifies for the use of (2-7), measured in benzene by Terazima and Azumi\(^{71}\) illustrates \(U_{\text{Slow}}\) and \(U_{\text{Total}}\) and is shown in
Figure 2-3. TRTL intensity ($S(t)$ from (2-5)) is plotted versus time after pump beam excitation.

![Graph showing TRTL intensity vs. Time]

Figure 2-3: TRTL spectrum of phthalazine in benzene (Ref. 71).

In Figure 2-3, $U_{\text{Total}}$ represents the entire heat given off by the sample after pump laser excitation (occurring at $t = 0 \, \mu s$), while $U_{\text{Slow}}$ represents the heat gradually given off by the nonradiative decay of the triplet excited state to the singlet ground state. The fast heat ($U_{\text{Total}} - U_{\text{Slow}}$) immediately given off at time zero represents fast processes (e.g., fluorescence and intersystem crossing) with lifetimes faster than the acoustic transit time ($\tau_a$) of the sample$^{75}$ ($\tau_a = \frac{R}{v_a}$; $R$ = radius of probe beam, $v_a$ = velocity of sound in the sample medium), which was around 50 ns for Terazima and Azumi.$^{71}$ A third
component, a gradual decay of the TRTL signal on the order of milliseconds resulting from thermal conductivity within the sample, is not shown in Figure 2-3.*

The true beauty of this method is that no calorimetric standards are required to measure $\Phi_{ISC}$ (or $E_T$), so long as the other variables in (2-7) are determined by other spectroscopic techniques. A plot of $\log[U_{\text{Total}} - S(t)]$ versus time can yield a linear plot from which the triplet lifetime can be calculated. The only specific requirement for this calculation method is that the triplet excited state lifetime must be longer than about $4\tau_a$ (200 ns in the Terazima and Azumi example)$^{71}$ but shorter than the thermal conductivity decay time of the sample (usually a few milliseconds). If the excited state lifetime is outside these boundaries, $U_{\text{Slow}}$ cannot be distinguished from $U_{\text{Fast}}$ in the TRTL spectrum.

It is important to note that (2-7) presumes that fluorescence is the only alternative decay process to the release of heat.$^{68}$ If phosphorescence (e.g., emission from the triplet excited state) is observed instead of fluorescence, (2-7) must be adapted to allow for this new excited-state deactivation pathway, as shown in (2-8).

$$\frac{U_{\text{Slow}}}{U_{\text{Total}}} = \frac{E_T (1 - \Phi_{em})}{E_{ex} - E_T + E_T (1 - \Phi_{em})}$$  \hspace{1cm} (2-8)

In (2-8), $\Phi_{em}$ is the triplet phosphorescence quantum yield. The intersystem quantum yield is assumed to be unity, which is valid for most inorganic chromophores due to spin-orbit coupling induced by the presence of heavy atoms.$^{76}$ Equations like (2-8) can easily be derived for other photochemical systems with multiple excited state processes. However, for complex systems photoacoustic spectroscopy is likely to be more informative.

* See Figure 2-4 for a TRTL spectrum with this component.
Limitations and instrumental considerations

One problem experienced in TRTL spectroscopy results from the presence of singlet oxygen. If singlet oxygen is produced by the excited state quenching process, its decay is readily observed in the thermal lens response (and possibly falsely interpreted as an excited-state decay of the analyte). While this may be a hindrance in many experiments, TRTL can provide an easy singlet oxygen detection method if it is an expected product in a photochemical process. However, if this decay is not desired rigorous degassing of all samples should be performed prior to experimentation to eliminate the possibility of its production.

The main culprit by far in TRTL that leads to errant signals is the absorption of the probe beam by the sample. The excited state of most inorganic chromophores produced by photoexcitation readily absorbs at visible wavelengths typically used for the probe laser, which results in an erroneously high TL signal. Chartier and coworkers have also observed abnormal TRTL signals with erythrosine that are attributed to an excited-state triplet-triplet absorption at the probe beam wavelength. This errant signal was characterized by a rapidly decaying component in the TL signal that was readily eliminated with the addition of oxygen to quench the excited state absorption. These abnormal TL signals are obvious in the spectra in Figure 2-4. The excited state absorption error can be reduced with an appropriate apparatus design, as described below.

The majority of all TRTL experimentation is performed with an apparatus similar to that in Figure 2-1. An extensive study by Berthoud and coworkers analyzed the optimal beam geometries for the pump and probe laser beams. They determined that for maximum TRTL sensitivity and resolution the pump beam should be focused in the
sample cell, while the probe beam should be focused about 10 cm in front of the cell. Since the thermal lens spreads the probe beam, if its focus is before the sample the beam will already be diverging through the sample cell. Therefore, the beam divergence will further increase after passing through the sample thermal lens, increasing the sensitivity of the technique. If the probe beam is focused after the cell, the thermal lensing signal will be inverted relative to the typical TRTL spectrum (i.e., the probe beam center intensity increases as heat is given off). If the probe beam focus is after the sample the beam will be diverging after the thermal lens before it reaches the beam waist, resulting in a smaller probe beam after the beam focus. With these optimal conditions, it was determined that the detection limit for TRTL could be as much as two to three orders of magnitude lower than those determined for absorption spectrophotometry (≈ 1 x 10⁻⁸ M for a strongly absorbing species).

Figure 2-4: Time-resolved pulsed thermal lens signal obtained for 10⁻⁵ M erythrosine in water (Ref. 78). (a) air saturated; (b) oxygen-saturated; (c) nitrogen-saturated.
Several other instrumental concerns must be considered. The pinhole radius must be at most 1/10 the radius of the probe beam to ensure accurate measurement of only the beam center intensity. This pinhole is placed about 2.5 – 3 m from the sample to allow maximum probe beam divergence and, consequently, instrumental sensitivity. Also, experimentation\textsuperscript{81} concluded that the probe beam radius should be approximately four times the size of the pump beam radius for optimal response. The laser beam diameter manipulation cannot simply be done with apertures, as Fresnel diffraction rings would be created which would severely distort the intensity measurement. Instead, a laser telescope should be used to properly size the pump and probe beams.\textsuperscript{81} The sample is commonly in a flow cell to ensure a constant supply of ground state analyte molecules and reduce sample degradation from extended periods of photoexcitation.\textsuperscript{67} The majority of the referenced studies use the longitudinal pump and probe beam geometry with both beams overlapping each other in a collinear and concentric manner within the sample cell.

Cambron and Harris devised a more complicated TRTL apparatus to help alleviate the concern of any possible probe beam absorption.\textsuperscript{73} Their apparatus is illustrated in Figure 2-5. The key feature of their design is the use of a second PMT detector (after L5 in Figure 2-5) that measures the intensity of the entire probe beam after it passes through the sample. This “time-resolved” reference signal corrects for any laser fluctuations and, more importantly, sample excited-state absorbance of the probe beam after pump excitation. This design feature will be implemented in our study.
Photoacoustic/Laser-Induced Optoacoustic Spectroscopy

Instead of monitoring heat evolution through a refractive index change, photoacoustic spectroscopy "listens" for the shock waves that travel through the sample medium as heat is released. The pressure waves are detected with a piezoelectric transducer that is placed in contact with the sample cuvette, as seen in Figure 2-6. Heavily damped transducers are used to keep the relaxation time short and allow for better temporal resolution while minimizing the influence of shock wave reflections within the sample cell on the observed signal. The transducer response versus time illustrating the shock waves produced by heat emission is shown in Figure 2-7. The initial signal spike in the figure indicated by the arrow is the only usable data in this plot, as all subsequent responses are reflections of the shock waves off the sides and bottom of the sample cuvette.

Initially, it was believed that photoacoustic techniques would not be as practical as TRTL for our research purposes, as it has a limited time window and required the
purchase of piezoelectric transducers and a preamplifier. However, photoacoustic spectroscopy has the marked advantage over TRTL measurements in that no implementations are needed to correct for any sample excited-state absorption of the sample under investigation. Photoacoustic spectroscopy measures pressure waves instead of light, so transient light absorption is not a concern.

Figure 2-6: Basic photoacoustic experimental setup (Ref. 69).
Early photoacoustic techniques

Early photoacoustic experiments sought to determine the conversion efficiency of photoexcitation energy to heat ($\alpha$) as determined in (2-9).

\[ h\nu_c = \sum \left( \Phi_i E_i \right) + \alpha E_{ex} \quad (2-9) \]

In (2-9), all relaxation processes of a particular excited-state system are included in the summation, where $\Phi_i$ is the excited state process quantum yield and $E_i$ is the retained energy of that process. A conversion efficiency of 1 indicates all the excitation energy is released as heat only during the experiment timescale.\(^\dagger\) A specific quantum yield or process energy can be determined from (2-9) (if all other parameters are known by other methods) by calculating $\alpha$ in (2-10).

\[ U = K\alpha I_i \left( 1 - 10^{-\lambda} \right) \quad (2-10) \]

\(^\dagger\) Common examples of these $\alpha = 1$ systems are benzophenone, ferrocene and crystal violet.\(^{83}\)
In (2-10), \( U \) is the initial photoacoustic signal spike intensity (e.g., the "heat" given off by the sample), \( I_L \) is the laser power, and \( K \) is an experimental constant that is determined from a calorimetric standard with a known \( \alpha \) value.

If \( \frac{U}{I_L} \) for an unknown system is plotted versus \( 1 - 10^{-A} \), a line is obtained with a slope equal to \( K\alpha \). If an additional plot is constructed with data obtained from a calorimetric standard and compared to the plot of the unknown system, \( \alpha \) for the unknown can be calculated as illustrated in Figure 2-8. The conversion efficiency can then be applied in (2-9) to determine the unknown quantum yield or excited state energy for the analyte molecule.

While this calculation technique is straightforward, it fails to provide any time-resolved information for multiple excited-state processes, and the use of calibration standards can greatly complicate the procedure and increase the chances for error. Therefore, our attentions were turned to a modified photoacoustic technique, Laser-Induced Optoacoustic Spectroscopy (LIOAS).

**Laser-induced optoacoustic spectroscopy**

LIOAS observes in a *time-resolved* manner the pressure waves produced by either heat released from a photoexcited sample or structural volume changes following excitation. The evolution of heat is central to our interest in the technique, and corrections for volume changes will be discussed later. The evolution of the transducer response to pressure waves with time \( (V(t)) \) is defined in (2-11).
Figure 2-8: Photoacoustic calibration plots. Circles are benzophenone (reference) data points, while crosses are pyridazine (unknown) data points (Ref. 83).

\[
V(t) = \frac{h_0 A}{4\pi r_0} \frac{\left(\frac{\nu}{t}\right)}{\nu^2 + \left(\frac{1}{\tau}\right)} \exp\left(\frac{-t}{\tau}\right) - \exp\left(\frac{-t}{\tau_0}\right) \cos(\nu t) - \frac{1}{\nu t} \sin(\nu t)
\]

(2-11)

In (2-11), \(\frac{h_0 A}{4\pi r_0}\) is an instrumental constant, \(\nu\) is the transducer characteristic oscillation frequency, \(\tau_0\) is the transducer relaxation time, \(\tau\) is the excited-state process lifetime, and

\[
\frac{1}{\tau'} = \frac{1}{\tau} - \frac{1}{\tau_0}
\]

Equation (2-11) was used to model simulated transducer responses with various excited-state lifetimes, and the responses are shown in Figure 2-9.
Figure 2-9: Simulated transducer responses based on (2-11) with varying $\tau$ values as indicated, where $\nu = 1 \times 10^6$ Hz and $\tau_0 = 1$ ms (Ref. 84).

It can clearly be seen that any transducer response falls into one of three categories. Exceedingly short timescale processes ($\tau < 1$ ns, the fast lifetime response region) all produced the same waveform. Medium lifetime processes ($\tau = $ several ns to a few $\mu$s) resulted in a response phase shift and amplitude decrease, and long lifetime processes ($\tau = $ several $\mu$s and greater) became indistinguishable with the baseline. Also, the delineation between lifetime categories is governed by both the characteristic frequency of the transducer and the previously defined acoustic transit time of the sample ($\tau_a$), which represents the theoretical lower limit of detectable excited-state lifetimes.

In order to extract information from the transducer response signal, deconvolution using an iterative nonlinear least squares algorithm is necessary. This technique requires three separate data sets for one measurement: 1) A baseline signal; 2) A fast lifetime reference signal (i.e., a sample which releases all excitation energy as heat in a
single fast lifetime process); and 3) A sample signal. To minimize the use of correction factors in the data analysis, the sample and reference signals are in the same solvent and with matched excitation absorbances. These signals are normalized by subtracting the baseline signal and dividing by both an absorbance factor \((1 – 10^{-A})\) and the average excitation laser pulse energy. Only the first few oscillations are selected for analysis since subsequent oscillations are acoustic reflections from the sample cell walls. In the deconvolution process, fast lifetime excited-state processes will be grouped together into one component with a meaningless lifetime fit but the correct amplitude (i.e., the total heat fraction released by the sample from all fast lifetime processes). Medium lifetime processes produce meaningful amplitudes and lifetimes. Long lifetime processes should not be detected by the transducer. While LIOAS is used mostly in aqueous media biological applications, the technique can be applied to organic and inorganic systems in nonaqueous solutions to distinguish between multiple excited-state processes.

**Accounting for solution volume changes**

As noted earlier, the main possibility for LIOAS measurement error involves transducer response correction for any sample structural volume changes \((\Delta V_R)\). These volume changes can be due to either photoexcited molecule structural changes or solvent molecules ordering around the excited analyte. If we assume that each of the components obtained from the deconvolution process discussed previously contains contributions from both thermal and volumetric changes, (2-12) can be derived.\(^8_6\)

\[
E_{cx} \varphi_i = \Phi_i E_i + \Phi_i \Delta V_{R,i} \left( \frac{c_p \rho}{\alpha} \right)
\]  
\[(2-12)\]
In (2-12), $\varphi_i$ is the deconvolution amplitude for excited state process $i$, $c_p$ is the solvent heat capacity, $\rho$ is the solvent density, and $\alpha$ is the solvent thermal expansion coefficient.\textsuperscript{§} The first term in (2-12) is the contribution due to emitted heat, while the second term is due to structural volume changes. These terms can be separated on the basis of altering the solvent thermal expansivity parameters. The majority of LIOAS studies focusing on reaction volume changes\textsuperscript{85,86} were done in aqueous solution, which allows for easy manipulation of these parameters due to the significant temperature dependence of $\alpha$ in water. The same parameter manipulation can be achieved in nonaqueous environments by making several LIOAS measurements in a series of similar solvents. This strategy was used in studies with a series of $n$-alkane solvents.\textsuperscript{87,88} Of course, the assumption must be made that the analyte photochemistry is similar in each of the solvents in the series, so care must be taken when selecting the series. If a plot is made of $E_{em}\varphi_i$ versus $\frac{c_p\rho}{\alpha}$, a linear relation is expected with a slope of $\Phi_i \Delta V_{R,i}$ (the volumetric component of the signal) and an intercept of $\Phi_i E_i$ (the thermal component of the signal).

It is important to note that Hung and Grabowski\textsuperscript{88} suggested the assumption that all observed LIOAS signals are thermal in nature leads to only “small calculation errors” when the system under investigation undergoes no net photochemistry and exhibits only minimal structural change upon photoexcitation. While this assumption might appear to cover the majority of our systems of interest, the possibility that $\Delta V_R$ might contribute to the observed LIOAS signal must be recognized and anticipated.

\textsuperscript{§} $\alpha$ is also referred to as $\beta$, the cubic expansion coefficient.
Instrument Design and Calibration Studies

Time-Resolved Thermal Lensing

An apparatus was set up to study TRTL with various organic and inorganic systems of interest in our group. Before experimentation was undertaken, initial calibration studies were first performed on the TRTL apparatus involving the triplet excited-state energy measurement of various organic molecules and studying two previously investigated donor-acceptor systems that are described below.

Apparatus setup

A diagram of the final apparatus is shown in Figure 2-10. The third harmonic of a Nd:YAG laser (355 nm, Spectra-Physics GCR-14) is used as the pump beam, which is attenuated with neutral density filters to an energy of approximately 100 – 200 µJ pulse\(^{-1}\). This pump beam is directed through a plano-convex focusing lens that is mounted on a two-axis positioning stage to simplify beam alignment. The focus of the pump beam is generally in the center of the sample cell, although its position is tweaked using the positioning stage to give the cleanest TRTL signal. A 1 mJ frequency-stabilized CW He-Ne laser (633 nm, Aerotech 100-SF) is used as the probe beam, which is expanded through two lenses to double the beam radius. The ratio of probe to pump beam radius in our apparatus is 10:1. The expanded probe beam is directed through a plano-convex focusing lens so that the focus of the beam is 10 cm in front of the cell based on the Berthoud study.\(^79\) The probe and pump beams are combined in a colinear and concentric fashion with the use of a 50% reflecting 633 nm beam splitter. The beams travel through a 1 cm pathlength quartz sample cell and are then separated by the use of a dispersing
prism. The probe beam continues through a shutter to a pellicle beam splitter, which reflects 8% of the beam through a plano-convex focus lens, an OG-590 cutoff filter, diffuser (to minimize any possible position dependency of the PMT detector), and a 633 nm interference filter before being detected with a R446 PMT. This PMT serves as the experiment reference signal, which should correct for any transient absorption seen in the excited sample. The remaining bulk of the probe beam travels 2.5 m until it reaches a 1.19 mm diameter pinhole. The center of the probe beam travels through an OG-590 cutoff filter and a 633 nm interference filter before being detected with a 1P28 PMT. This PMT serves as the experiment sample signal.

The two PMT signals are simultaneously recorded on a Tektronix TDS 540 digital oscilloscope using a 10 Hz sampling rate, with typically 1000 laser shots averaged during each data collection cycle. The PMT signals are internally terminated (50 Ω) with a 20 MHz internal bandwidth filter to reduce signal noise. The two decay traces are fed into an analysis program written by the author in Microsoft Visual Basic 6.0, where the two individual signals are initially normalized on a scale of 0 to 1. The normalized reference signal is then subtracted from the normalized sample signal as specified in (2-5) to give the observed TRTL signal, which is renormalized for final presentation to the user.
Calibration studies

Initial TRTL work involved the triplet energy measurement of several common organic triplet sensitizers in both polar and non-polar nitrogen-degassed solutions using
Benzophenone, phenanthrene, anthracene, and 9-methylanthracene were selected as the triplet sensitizers. Unfortunately, triplet energies obtained with our instrument failed to agree well with literature values for all the sensitizers except benzophenone. Errors as high as 50% were obtained in some cases. The ineffective TRTL measurement of these energies could stem from the rapid (several ns) excited-state decay of these sensitizers, which is well below the sample acoustic transit time (200 ns). Furthermore, a recurring problem with our apparatus involved obtaining a pure reference signal from the reference PMT, where it was very common to see some evidence of thermal lensing. The typical cure for bad reference signals was a careful adjustment of the probe and pump beam geometries in the sample cell so that a good signal was recorded by the sample PMT while as clean a reference signal as possible was recorded by the reference PMT. It was not uncommon to obtain only one "good" experimental run during an hour of constant measuring, as the beam positioning slowly drifted over time. While this trial-and-error method was time consuming and tedious, it was the only effective way to achieve reasonable data.

A second calibration study involved the use of donor-acceptor systems that had considerably longer-lived excited states. Both tris(2,2'-bipyridine)RuII / methyl viologen (MV2+)40,89 and (2,2'-bipyridine)ReI(CO)3(4-benzylpyridine)+ / diaza[2.2.2]octane (DABCO)90,91 were studied with a significantly higher degree of success than the organic triplet sensitizers. The excited state processes of the ruthenium / viologen system is illustrated in Figure 2-11.
Figure 2-11: Ruthenium / viologen donor-acceptor system.

The calculation for this system can be greatly simplified by making the paraquat concentration high enough to effectively quench all ruthenium emission (i.e., in Figure 2-11, $\Phi_{\text{em}} = 0$ and $\Phi_{\text{q}} = 1$). It is also assumed that the intersystem crossing yield ($\Phi_{\text{isc}}$) is unity. The calculation is now straightforward, as shown in (2-13).

$$\frac{U_{\text{Slow}}}{U_{\text{Total}}} = \frac{\Phi_{\text{sep}} E_{\text{FI}}}{E_{\nu}}$$  \hspace{1cm} (2-13)

If previously determined values for $\Phi_{\text{sep}}$ (0.31) and $E_{\text{FI}}$ (free ion energy; 1.69 eV = 2.7 x $10^{-19}$ J molecule$^{-1}$) are used, the expected ratio is 0.15. Our ruthenium / paraquat measurements obtained a ratio of 0.20, which had a lower error than the organic triplet sensitizer measurements. Furthermore, our rhenium / DABCO measurements, which would exhibit the same behavior described in Figure
2-11,90,91 almost exactly matched the predicted results (0.41 predicted; 0.42 experimentally determined). Eventually, TRTL was abandoned for LIOAS when the excessively tedious process to correct for sample transient absorption proved to not be worth the uncertain results obtained with our apparatus. However, our TRTL apparatus was successfully used for the triplet energy determination of polymer P1, which is described in chapter 3.

**Laser-Induced Optoacoustic Spectroscopy**

**Apparatus setup**

The layout for our LIOAS apparatus is illustrated in Figure 2-12. The instrumental demands for LIOAS are straightforward compared to TRTL. A pellicle beamsplitter diverts 8% of the 355 nm Nd:YAG radiation (Spectra Physics GCR-14) through a stack of neutral density filters (typically 10% and 25% ND filters are used). A very low excitation energy (8 – 40 µJ pulse⁻¹) is required in LIOAS studies to prevent multiphoton events. The remaining portion of the pump beam is sampled with an energy meter (Scientech S310 with a P09 Probe) to allow for energy normalization. After passing through a 2 mm slit to minimize beam wandering effects, the pump beam is focused with a plano-convex lens (f = 10.0 cm), producing a beam diameter of 0.25 mm within the sample cell. The transducer is held to the side of the sample cuvette perpendicular to the pump beam propagation by means of an in-house designed cell holder. A film of vacuum grease is applied between the transducer and cell wall to better facilitate the relay of acoustic waves. The cell holder is mounted on a linear translation stage to allow variation of the excitation region distance from the transducer surface within the sample. Varying this distance allows for temporal movement of the transducer
response from any initial laser RF noise. Since the cell / transducer geometry cannot change between reference and sample experiments, the cell is firmly clamped in place and a solvent delivery system is constructed to distribute rinsing solvent, nitrogen purging gas, and sample solutions without moving the cell. The sample cell was typically rinsed with flowing solvent for 5 minutes and dried with flowing nitrogen gas between experiments.

Figure 2-12: LIOAS apparatus layout.

Two transducers are used with differing characteristic frequencies, 1 MHz (Panametrics V103) and 5 MHz (Panametrics V109). The higher frequency transducer should be more sensitive to shorter-lifetime excited-state processes. The signals are intensified with a Panametrics 5670 40 dB preamplifier and recorded with a Tektronix TDS 540 digitizing oscilloscope. Initial data processing, instrument control and data normalization are conducted with software written in Microsoft Visual Basic 6.0 by the author. Sound Analysis 3000 software is used to deconvolute the processed acoustic
waves and provide amplitudes and lifetimes.\textsuperscript{92} Pictures of the LIOAS apparatus are shown in Figure 2-13.

**Calibration study – (b)Re\textsuperscript{l}(CO)\textsubscript{3}(bzpy)\textsuperscript{+} triplet energies**

A detailed LIOAS calibration study was conducted to determine the triplet metal-to-ligand charge transfer (\textsuperscript{3}MLCT) energy of a series of rhenium complexes, \textit{fac}- (b)Re\textsuperscript{l}(CO)\textsubscript{3}(bzpy)\textsuperscript{+}, where b is a substituted diimine ligand and bzpy is 4-benzylpyridine (Figure 2-14). This inorganic chromophore has been widely studied, and its photophysical properties are well known.\textsuperscript{93} Furthermore, the \textsuperscript{3}MLCT energy is easily varied over several kcal mol\textsuperscript{-1} by changing the substituted diimine.\textsuperscript{41,42} Since the (b)Re\textsuperscript{l}(CO)\textsubscript{3}(bzpy)\textsuperscript{+} \textsuperscript{3}MLCT state is emissive, its spectrum can serve as a second independent means of measuring its energy through Franck-Condon emission lineshape fitting.\textsuperscript{76,91} The series of complexes also has different \textsuperscript{3}MLCT lifetimes due to their varying excited state energies, so the delineation between fast, intermediate, and slow lifetime processes detected by our LIOAS apparatus can be studied and confirmed.

\textit{The \textsuperscript{3}MLCT Energy}. The \textsuperscript{3}MLCT energy for the (b)Re(CO)\textsubscript{3}(bzpy)\textsuperscript{+} complexes, along with other emissive transition metal complexes, is traditionally determined with a single-mode Franck-Condon line-shape analysis of the observed \textsuperscript{3}MLCT emission band observed at ambient temperature.\textsuperscript{76,91} Therefore, experimental emission spectra for the complexes obtained from nitrogen-degassed acetonitrile solutions were fitted to (2-14).

\[
I(\nu) = \sum_{\nu_m=0}^{5} \left\{ \left( \frac{\nu_{00} - \nu_m \hbar \omega_m}{\nu_{00}} \right)^3 \frac{S_m}{\nu_m!} \exp \left[ -4 \ln 2 \left( \frac{\nu - \nu_{00} + \nu_m \hbar \omega_m}{\Delta \nu_{0,1/2}} \right)^2 \right] \right\} \quad (2-14)
\]
Figure 2-13: LIOAS apparatus images.
Figure 2-14: (b)Re(CO)$_3$(bzpy)$^+$ complexes.

In (2-14), $I(\bar{\nu})$ is the relative emission intensity at energy $\bar{\nu}$, $\bar{\nu}_{00}$ is the zero-zero transition energy (i.e., the $^3$MLCT energy), $\nu_m$ is the average medium frequency vibrational mode quantum number, $\hbar \omega_m$ is the medium frequency acceptor modes average coupled to the MLCT transition (1450 cm$^{-1}$), $S_m$ is the Huang-Rhys factor (i.e., the electron-vibration coupling constant), and $\Delta \nu_{0,1/2}$ is the individual vibronic band half-width. The $\nu_{00}$ values obtained from (2-14) for the (b)Re(CO)$_3$(bzpy)$^+$ series are listed in Table 2-1, and fitted emission spectra are shown in Figure 2-16 along with the fit parameters. These fit parameters are consistent with a previous study conducted in our group on similar complexes.$^{91}$
Table 2-1: Emission data for (b)Re\(_{(\mathrm{CO})_3}\)bzpy\(^+\).

<table>
<thead>
<tr>
<th>(b)(^a)</th>
<th>(\Phi_{em})</th>
<th>(\tau_{em}/\text{ns})</th>
<th>(\nu_{\text{max}}/\text{cm}^{-1} )(^b)</th>
<th>(\nu_{\text{00}}/\text{cm}^{-1} )(^c)</th>
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<td>tmb</td>
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<td>19400</td>
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<td></td>
<td></td>
<td></td>
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<td>dmb</td>
<td>0.06</td>
<td>274</td>
<td>17450</td>
<td>18375</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>bpy</td>
<td>0.045</td>
<td>208</td>
<td>17210</td>
<td>17975</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(51.4)</td>
<td></td>
</tr>
<tr>
<td>damb</td>
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<td>116</td>
<td>16700</td>
<td>17280</td>
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<td></td>
<td></td>
<td></td>
<td>(49.4)</td>
<td></td>
</tr>
<tr>
<td>deb</td>
<td>0.0145</td>
<td>93</td>
<td>15360</td>
<td>16050</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>(45.9)</td>
<td></td>
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\(^a\)Argon-degassed CH\(_3\)CN solutions, 298 K. Estimated errors: \(\Phi_{em}, \pm 15\%\); \(\tau_{em}, \pm 5\%\); \(\nu_{\text{max}}, \pm 100 \text{ cm}^{-1}\); \(\nu_{\text{00}}, \pm 500 \text{ cm}^{-1}\). \(^b\)Emission maximum. \(^c\)0-0 emission energy estimated by Franck-Condon analysis (2-14).

Since the \(^3\)MLCT excited state lifetime for the (b)Re\(_{(\mathrm{CO})_3}\)bzpy\(^+\) complexes falls within the medium lifetime category of LIOAS responses, the energy of the lowest MLCT excited state can be independently calculated from both of the two expected components recovered from the LIOAS data deconvolution analysis. In principle, the first “fast” heat deposition process (\(\tau_1\) and \(\phi_1\)) corresponds to heat released when the singlet MLCT state (\(^1\)MLCT, the excited state produced by photon absorption) relaxes to \(^3\)MLCT with unit efficiency. The second heat deposition process (\(\tau_2\) and \(\phi_2\)) corresponds to heat released concomitant with nonradiative decay of \(^3\)MLCT. Based on these definitions, the amplitudes can be related to the \(^3\)MLCT energy by (2-15) and (2-16).

\[
\phi_1 = \frac{E_{hv} - E_T}{E_{hv}} \quad (2-15)
\]

\[
\phi_2 = \frac{E_T (1 - \Phi_{em})}{E_{hv}} \quad (2-16)
\]
In (2-15) and (2-16), \( E_{hv} \) is the excitation energy (355 nm = 80.5 kcal mol\(^{-1}\)), \( \Phi_{em} \) is the emission quantum yield from \(^3\)MLCT and \( E_T \) is the \(^3\)MLCT energy. LIOAS decays were obtained from degassed acetonitrile solutions with both the 1 MHz and 5 MHz ultrasonic transducers of each complex in the \( (b)\text{Re(CO)}_3(bzpy)^+ \) series. Figure 2-15 illustrates typical analysis results for the \( (b)\text{ReI(CO)}_3(bzpy)^+ \) series. Table 2-2 contains the average normalized amplitudes \( \phi_i \) recovered from deconvolution analysis of four independent LIOAS measurements on each complex, the lifetime of the medium lifetime heat-deposition component \( (\tau_2) \), and \( E_T \) values calculated from the experimental \( \phi_i \) values with (2-15) and (2-16). Figure 2-16 shows the emission spectra and compares \(^3\)MLCT energies for the five \( (b)\text{Re(CO)}_3(bzpy)^+ \) complexes obtained from the LIOAS data using both transducers (four \( E_T \) values for each complex) and the emission Franck-Condon analysis.

**The Validity of LIOAS Measurements** Several assumptions must be made in order to assess the potential use of LIOAS data for the determination of excited state energies. First, the emission spectra and Franck-Condon bandshape analysis is assumed to provide the best available estimate for the \(^3\)MLCT energy, which is less than ideal due to the convoluted mathematical fit. However, since this methodology is widely accepted in the literature it is deemed sufficient for a yardstick in evaluating the LIOAS technique for this purpose. Second, our LIOAS data analysis neglects contributions to the acoustic wave arising from the potential volume change that occurs concomitant with \(^3\)MLCT decay as discussed earlier.
Figure 2-15: LIOAS data (signal vs. time) for (b)Re(CO)$_3$(bzpy)$^+$ in acetonitrile. Solid (highest intensity) lines are the ferrocene reference waveform, dotted lines are the sample waveform, and dashed lines are the deconvolution fit. Note that $\tau_1 = 10$ and 1 ns for the 1 and 5 MHz transducers, respectively.
Three major conclusions can be drawn concerning the measurement of excited state energies and lifetimes using the LIOAS apparatus and deconvolution analysis.

1. **LIOAS Measurements are accurate only when the excited state lifetime is greater than 200 ns.** It can clearly be seen in Figure 2-16 that for the complexes with tmb, dmb, and bpy ligands, the $^3$MLCT energies derived from LIOAS and emission spectral fitting are in reasonable agreement. In stark contrast, the LIOAS energy values for complexes with damb and deb ligands vary widely and are in poor agreement with the emission spectral fitting energies. The $^3$MLCT lifetimes of the three complexes with
concurrent energy measurements range from 210 to 1500 ns, while the two disparate complex lifetimes range from 90 to 120 ns (see $\tau_{em}$ in Table 2-1 and the $\tau_2$ deconvolution component in Table 2-2). This result clearly indicates that the validity of the LIOAS data is strongly influenced by the probed excited state lifetime, and the lower lifetime limit for reliability with our apparatus is $\tau \geq 200$ ns. This limit is directly related to the acoustic transit time ($\tau_a$) of the LIOAS apparatus as defined above. If a beam radius of 0.25 mm and a velocity of sound in acetonitrile of 1300 m s$^{-1}$ is assumed for our instrument, an acoustic transit time of 192 ns is obtained. This acoustic transit time is not small enough to accurately resolve the fast relaxation of the $^1$MLCT state and the nonradiative decay of the $^3$MLCT state for complexes with $^3$MLCT lifetimes less than 200 ns (i.e., the dumb and deb complexes).

2. **Excited state energies derived from deconvolution of the second medium lifetime deconvolution component are less precise and accurate compared to those derived from the first fast lifetime deconvolution component.** The error bars shown in Figure 2-16 clearly indicate that the precision and accuracy of the energies determined from $\phi_2$ and (2-15) are generally poorer compared with those derived from $\phi_1$ and (2-16). Simulated LIOAS responses derived by reconvolution of two decay components similar to those observed for (b)Re$^I$(CO)$_3$(bzpy)$^+$ indicate that $\phi_1$ is primarily influenced by the fit quality in the initial spike of the LIOAS signal, while $\phi_2$ is determined mainly by the fit quality in the subsequent LIOAS signal oscillations after the initial peak. This secondary oscillation region of the LIOAS signal is complex and relatively noisy in our recorded LIOAS data, which inherently decreases the precision of the fitted $\phi_2$ values.
Table 2-2: LIOAS data for (b)Re^1(CO)_3(bzpy)^+.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>1 MHz Transducer</th>
<th>5 MHz Transducer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \phi_1 )</td>
<td>( \phi_2 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tmb</td>
<td>0.2698 ± 0.02</td>
<td>0.4402 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>(58.8 ± 1.8)</td>
<td>(53.2 ± 1.3)</td>
</tr>
<tr>
<td>dmb</td>
<td>0.3281 ± 0.02</td>
<td>0.6267 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>(53.2 ± 1.3)</td>
<td>(53.7 ± 2.3)</td>
</tr>
<tr>
<td>bpy</td>
<td>0.3059 ± 0.04</td>
<td>0.6410 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>(55.9 ± 2.9)</td>
<td>(54.0 ± 1.2)</td>
</tr>
<tr>
<td>damb</td>
<td>0.3534 ± 0.08</td>
<td>0.5908 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>(52.1 ± 6.6)</td>
<td>(48.8 ± 5.0)</td>
</tr>
<tr>
<td>deb</td>
<td>0.3070 ± 0.02</td>
<td>0.6493 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>(55.8 ± 2.0)</td>
<td>(53.0 ± 6.0)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ligand</th>
<th>1 MHz Transducer</th>
<th>5 MHz Transducer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \phi_1 )</td>
<td>( \phi_2 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tmb</td>
<td>0.3122 ± 0.03</td>
<td>0.5123 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>(55.4 ± 2.1)</td>
<td>(55.0 ± 4.0)</td>
</tr>
<tr>
<td>dmb</td>
<td>0.3486 ± 0.04</td>
<td>0.6302 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>(52.5 ± 2.9)</td>
<td>(54.0 ± 2.5)</td>
</tr>
<tr>
<td>bpy</td>
<td>0.3587 ± 0.04</td>
<td>0.6780 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>(51.6 ± 3.3)</td>
<td>(57.2 ± 4.1)</td>
</tr>
<tr>
<td>damb</td>
<td>0.4238 ± 0.03</td>
<td>0.5475 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>(46.4 ± 2.6)</td>
<td>(45.3 ± 3.2)</td>
</tr>
<tr>
<td>deb</td>
<td>0.5156 ± 0.12</td>
<td>0.5499 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>(39.0 ± 9.6)</td>
<td>(44.9 ± 8.0)</td>
</tr>
</tbody>
</table>

*aArgon-degassed CH\(_3\)CN solution, 298 K. Reported values are averages of four runs of fresh sample and ferrocene reference solutions, and errors are ± \( \sigma \). \( \tau_1 \) fixed at 10 ns for the 1 MHz transducer and 1 ns for the 5 MHz transducer. 

*bTriplet energy calculated from the first deconvolution amplitude (2-15). 

*cTriplet energy calculated from the second deconvolution amplitude (2-16).
Figure 2-16: Corrected emission spectra of (b)ReI(CO)3(bzpy)+ in acetonitrile solution at 298 K. Points are experimental data, and solid lines are spectra calculated using Franck-Condon analysis (2-14) with the fitting parameters listed on each spectrum. 3MLCT energies are presented on each plot with ± σ errors. (a) b = (tmb); (b) b = (dmb); (c) b = (bpy); (d) b = (damb); (e) b = (deb).
3. Lifetimes can be accurately measured with LIOAS for medium lifetime decay processes. It is clearly seen in Tables 2-1 and 2-2 that the $^3$MLCT lifetime independently obtained by LIOAS and emission measurements is in reasonable agreement for the complexes with dmb and bpy ligands. These complexes represent the medium lifetime processes that are correctly measured by the transducer. For a slow lifetime process (i.e., the tmb complex) the transducer detected a signal that is partially damped by the transducer, resulting in an erroneously low lifetime. This damping increases for the 5 MHz transducer due to its higher characteristic oscillation, which leads to the larger observed errors. The narrow range of lifetimes correctly measured by LIOAS suggests that traditional (e.g., optically-based) methods are more suitable for determining these values.

This calibration study demonstrates the validity of LIOAS measurements to measure excited state energies and lifetimes so long as the excited-state lifetime is higher than the acoustic transit time of the apparatus (ca. 200 ns). LIOAS will be further used to determine the triplet energies and/or yields of several π-conjugated oligomers and inorganic complexes discussed in chapters 3 and 5.

---

**Experimental**

(b)Re$^1$(CO)$_3$(bzpy)$^+$ Synthesis

Synthesis of (b)Re$^1$(CO)$_3$Cl. This synthesis proceeded via analogous procedures for each complex, so a representative procedure is given. For (4,4',5,5'-tetramethyl-2,2'-bipyridine)Re$^1$(CO)$_3$Cl, 300 mg of Re(CO)$_3$Cl (0.833 mmol, prepared by literature method),$^{94}$ 194 mg 4,4',5,5'-tetramethyl-2,2'-bipyridine (tmb, 0.916 mmol, 1.1
equivalents), and 15 mL toluene were placed in a roundbottom flask. The solution was stirred and refluxed under nitrogen for 1.5 hours, during which time the off-white solution turned a golden yellow. A yellow precipitate formed, and the mixture was stirred at room temperature under nitrogen overnight to complete the reaction. The precipitate was filtered with a medium porosity glass frit, washed with three toluene washes, and dried under vacuum for several hours to remove excess toluene. 400 mg of (tmb)ReI(CO)3Cl was collected (93% yield). The remaining complexes were synthesized with similar yields.

**Synthesis of (b)ReI(CO)3(bzpy)^+.** The synthesis of each complex is similar for the entire series, so extensive details are only given for the (tmb)ReI(CO)3(bzpy)^+ complex. All other complexes were synthesized with analogous procedures but varying reaction times.

\[(4,4',5,5'-\text{tetramethyl-2,2'-bipyridine})\text{ReI(CO)}_3\text{(bzpy)}\] \[\text{[OTf]}\]

In a roundbottom flask 200 mg of (tmb)ReI(CO)3Cl (0.386 mmol) and 124 mg silver triflate (0.425 mmol, 1.25 equivalents) were dissolved in 15 mL methylene chloride. The solution was stirred in the dark at room temperature overnight to complete the counteranion exchange. A dark yellow solution resulted with a fine white silver chloride precipitate. The precipitate was removed by filtration through celite on a medium porosity glass frit. The filtrate was placed in a clean roundbottom flask, and 185 mg of 4-benzylpyridine (1.16 mmol, 3 equivalents) was added while the solution stirred. The solution was stirred at room temperature for 24 hours, during which time its luminescence dramatically increased when excited with UV light. A dull yellow precipitate was obtained after rotary evaporation of the solvent, which was washed twice with ether and
dried under vacuum. A light yellow powdery precipitate, [(tmb)Re(I(CO)3(bzpy))[OTf], resulted (52 mg, 17% yield). 1H NMR (CDCl3) δ 2.40 (s, 6H, methyl), 2.56 (s, 6H, methyl), 3.91 (s, 2H, benzylic), 7.10 (d, pyridyl), 7.20 – 7.40 (m, phenyl), 7.93 (s, tmb), 7.98 (d, pyridyl), 8.57 (s, tmb).

[(4,4'-dimethyl-2,2'-bipyridine)ReI(CO)3(bzpy)][OTf]. A yellow powdery precipitate, [(dmb)ReI(CO)3(bzpy)][OTf], resulted (89% yield). 1H NMR (CDCl3) δ 1.60 (s, 6H, methyl), 3.90 (s, 2H, benzylic), 7.10 (d, 2H, pyridyl), 7.20 – 7.40 (m, phenyl), 7.52 (d, 2H, dmb), 7.92 (d, 2H, pyridyl), 8.70 (s, 2H, dmb), 8.82 (d, 2H, dmb).

[(2,2'-bipyridine)ReI(CO)3(bzpy)][OTf]. A bright yellow crystalline precipitate, [(bpy)ReI(CO)3(bzpy)][OTf], resulted (62% yield). 1H NMR (CDCl3) δ 3.90 (s, 2H, benzylic), 7.09 (d, pyridyl), 7.20 – 7.40 (m, phenyl), 7.78 (dd, 2H, bpy), 8.00 (d, 2H, pyridyl), 8.35 (d, 2H, bpy), 8.95 (dd, 2H, bpy), 9.03 (d, 2H bpy).

[(4,4'-bis(diethylamino)-2,2'-bipyridine)ReI(CO)3(bzpy)][OTf]. A dark yellow crystalline precipitate, [(damb)ReI(CO)3(bzpy)][OTf], resulted (50% yield). 1H NMR (CDCl3) δ 1.21 (t, methyl), 3.47 (qq, methylene), 3.92 (s, 2H, benzylic), 7.08 (d, pyridyl), 7.10 – 7.40 (m, phenyl), 7.59 (d, damb), 8.12 (d, pyridyl), 8.42 (s, damb), 9.01 (d, damb).

[(4,4',5,5'-diethoxy-2,2'-bipyridine)ReI(CO)3(bzpy)][OTf]. A dark red crystalline precipitate, [(deb)ReI(CO)3(bzpy)][OTf], resulted (low yield, but it was the most difficult by far to synthesize). 1H NMR (CDCl3) 1.48 (t, 6H, methyl), 3.88 (s, 2H, benzylic), 4.55 (q, 4H, methylene), 7.09 (d, pyridyl), 7.20 – 7.40 (m, phenyl), 8.09 (d, 2H, pyridyl), 8.27 (d, 2H, deb), 8.98 (s, 2H, deb), 9.24 (d, 2H, deb).
(b)Re(CO)$_3$(bzpy)$^+$ Photophysics

**Steady-state emission spectroscopy and emission quantum yields.** Corrected steady-state emission spectra were recorded on degassed acetonitrile solutions of each complex with a SPEX F-112 fluorimeter. Samples were contained in 1 cm x 1 cm quartz cuvettes and excited at 350 nm. Emission quantum yields ($\Phi_{em}$) were calculated relative to two actinometers using (2-17). \(^95\)

$$\Phi_{em}^x = \Phi_{em}^r \left( \frac{1}{1-10^{-A_x}} \right) \left( \frac{\eta_x^2}{\eta_r^2} \right) \left( \frac{D_x}{D_r} \right)$$ \hspace{1cm} (2-17)

In (2-17), x represents properties of the unknown solution and r represents properties of the actinometer, A is the sample solution absorbance at the excitation wavelength, $\eta$ is the sample solvent refractive index, and D is the area under the emission band. Ru$^{II}$(bpy)$_3$ in degassed water ($\Phi_{em} = 0.055$)\(^96\) and 9,10-dicyanoanthracene in ethanol ($\Phi_{em} = 0.89$)\(^97\) were used as actinometers. All solution concentrations were adjusted to result in optically dilute solutions ($A_{350 \text{ nm}} = 0.14$).

**Emission Lifetimes.** Time-correlated single-photon counting (FLI, Photochemical Research Associates) was used to measure emission lifetimes. The excitation and emission wavelengths were selected with bandpass filters (excitation, Schott UG-11 (350 nm maximum); emission, 550 nm interference filter). Degassed acetonitrile samples were contained in 1 cm x 1 cm quartz cuvettes. Lifetimes were calculated from single-exponential fits with the DECAN fluorescence lifetime deconvolution software.\(^98\)

**LIOAS Measurements.** LIOAS measurements were conducted on acetonitrile samples with the apparatus described above. Before each experimental run, a linearity
test was performed with the ferrocene reference to determine the maximum usable laser energy while maintaining linearity. Based on these tests, laser energies of 2 and 20 µJ pulse\(^{-1}\) were used for the 1 and 5 MHz transducers, respectively. Four experimental cycles were performed for each compound and averaged, with each cycle consisting of fresh ferrocene reference solution and (b)Re\(^I\)(CO)\(_3\)(bzpy) solution measurements. Each measurement was the average of acoustic waveforms collected from 1000 laser pulses at a 10 Hz repetition rate. All samples were nitrogen degassed in the fixed LIOAS cell for 20 minutes before data acquisition.

Deconvolution analysis was performed with the two-component sequential step model. Lifetimes for the fast decay component were fixed at 10 and 1 ns for the 1 MHz and 5 MHz transducers, respectively, while the other fit parameters were allowed to float. For the 1 MHz transducer data, only a background correction was necessary to achieve the desired fit, but the narrower bandwidth of the 5 MHz transducer data required both background and reference shift correction factors in the final deconvolution process.
5-5' BIPHENYL OLIGOMER PHOTOPHYSICS

Introduction

As discussed earlier, a series of oligomers (5-L series) was synthesized containing biphenyl subunits in the conjugated backbone. The oligomers contain a 5,5’-(2,2’-bipyridyl) core with primary repeat units on either side consisting of 5,5’-diethynyl(2,2’-biphenyl) and dialkoxybenzenes. These oligomers were synthesized via Sonogashira coupling, an iterative sequence involving palladium-mediated cross coupling of a terminal acetylene and aryl iodide. Complexes were synthesized by ligating these oligomers to the –ReI(CO)₃Cl (5-Re series) and –ReI(CO)₃(NCCH₃)⁺ (5-ReAN-2 and 5-ReAN-3 complexes) chromophores. The structures of the 5-L oligomers and 5-Re complexes are shown in Figure 3-1. Extensive photophysical and photothermal studies were conducted on these molecules, and the results are presented in this chapter.

Results

Various photophysical parameters from many different measurements are presented for the uncomplexed 5-L oligomers and 5-Re rhenium complexes in Tables 3-1 and 3-2, respectively. The individual measurements are discussed below. For comparative purposes, some of the photophysical data collected for polymers P1 and P4 described in chapter 1 (Figure 1-15) are also presented.
**Figure 3-1:** 5-L oligomer and 5-Re rhenium complex structures.

**Table 3-1:** 5-L oligomer photophysics.

<table>
<thead>
<tr>
<th></th>
<th>5-L-1</th>
<th>5-L-2</th>
<th>5-L-3</th>
<th>5-L-4</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Absorption</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda_{\text{max}} / \text{nm}$</td>
<td>330 (3.85)</td>
<td>320 (6.90)</td>
<td>340 (9.05)</td>
<td>336 (15.2)</td>
</tr>
<tr>
<td>$\varepsilon_{\text{max}} / 10^4 \text{ M}^{-1} \text{ cm}^{-1}$</td>
<td>370 (5.40)</td>
<td>400 (9.80)</td>
<td>404 (13.5)</td>
<td>406 (25.1)</td>
</tr>
<tr>
<td><strong>Emission</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda_{\text{max}, 298 \text{ K}} / \text{nm}$</td>
<td>455</td>
<td>454</td>
<td>453</td>
<td>452</td>
</tr>
<tr>
<td>$\lambda_{\text{max}, 80 \text{ K}} / \text{nm}$</td>
<td>413</td>
<td>469</td>
<td>482</td>
<td>496</td>
</tr>
<tr>
<td>$\phi_{\text{em}}$</td>
<td>0.89</td>
<td>0.72</td>
<td>0.68</td>
<td>0.79</td>
</tr>
<tr>
<td><strong>TA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\tau_{298 \text{ K}} / \mu\text{s}$</td>
<td>158</td>
<td>452</td>
<td>343</td>
<td>411</td>
</tr>
</tbody>
</table>

Note: Measurements were conducted on argon bubble-degassed THF solutions. Additional experimental conditions are discussed in the text.
Table 3-2: **5-Re** rhenium complex photophysics.

<table>
<thead>
<tr>
<th></th>
<th>5-Re-1</th>
<th>5-Re-2</th>
<th>5-Re-3</th>
<th>5-Re-4</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Absorption</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda_{\text{max}}$ / nm</td>
<td>332 (2.90)</td>
<td>336 (8.30)</td>
<td>352 (11.8)</td>
<td>338 (16.8)</td>
</tr>
<tr>
<td>($\varepsilon_{\text{max}}$ / 10$^4$ M$^{-1}$ cm$^{-1}$)</td>
<td>410 (3.40)</td>
<td>440 (7.34)</td>
<td>444 (8.30)</td>
<td>388 (20.7)</td>
</tr>
<tr>
<td><strong>Emission</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda_{\text{max}, 298 K}$ / nm</td>
<td>690</td>
<td>650</td>
<td>652</td>
<td>650</td>
</tr>
<tr>
<td>$\lambda_{\text{max}, 80 K}$ / nm</td>
<td>586</td>
<td>659</td>
<td>642</td>
<td>642</td>
</tr>
<tr>
<td>TA $\tau_{298 K}$ / ns</td>
<td>20</td>
<td>145</td>
<td>198</td>
<td>161</td>
</tr>
<tr>
<td><strong>Electrochem</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E^\text{red}_{1/2}$ / V vs. SCE</td>
<td>-0.89$^a$</td>
<td>-0.87$^a$</td>
<td>-0.86$^a$</td>
<td>-0.91$^{a,c}$</td>
</tr>
<tr>
<td>($\varepsilon$ M$^{-1}$ cm$^{-1}$)</td>
<td>-0.90$^b$</td>
<td>-0.92$^b$</td>
<td>-0.85$^{b,c}$</td>
<td></td>
</tr>
</tbody>
</table>

Note: Measurements were conducted on argon bubble-degassed THF solutions. Additional experimental conditions are discussed in the text. $^a$Pt disc working electrode. $^b$GCE disc working electrode. $^c$Irreversible reduction.

<table>
<thead>
<tr>
<th></th>
<th>5-ReAN-2</th>
<th>5-ReAN-3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Absorption</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda_{\text{max}}$ / nm</td>
<td>340 (9.49)</td>
<td>348 (14.7)</td>
</tr>
<tr>
<td>($\varepsilon_{\text{max}}$ / 10$^4$ M$^{-1}$ cm$^{-1}$)</td>
<td>449 (7.38)</td>
<td>447 (9.49)</td>
</tr>
<tr>
<td><strong>Emission</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda_{\text{max}, 298 K}$ / nm</td>
<td>652</td>
<td>650</td>
</tr>
<tr>
<td>$\lambda_{\text{max}, 80 K}$ / nm</td>
<td>589, 625</td>
<td>629</td>
</tr>
<tr>
<td>TA $\tau_{298 K}$ / ns</td>
<td>9710</td>
<td>5010</td>
</tr>
</tbody>
</table>

Note: Measurements were conducted on argon bubble-degassed THF solutions (except for transient absorption measurements, which are conducted in methylene chloride). Additional experimental conditions are discussed in the text.

**Absorption Spectra**

Absorption spectra were obtained on dilute THF solutions of the various oligomers and rhenium complexes, and molar absorptivity values ($\varepsilon$, M$^{-1}$ cm$^{-1}$) were calculated based on (3-1).

$$A = \varepsilon b c \quad (3-1)$$
In (3-1), $A$ is the sample absorbance, $b$ is the cell pathlength (1 cm), and $c$ is the sample concentration (M). Absorption spectra for the 5-L and 5-Re series, along with P1 and P4, are shown in Figure 3-2. Absorptivity for P1 was calculated based upon the polymer repeat unit. Absorptivity calculations were not performed on P4. Absorption maxima for all oligomers and rhenium complexes are listed in Tables 3-1 and 3-2, respectively.

The oligomer spectra exhibit two $\pi,\pi^*$ transitions, with the lower energy (HOMO $\rightarrow$ LUMO) transition corresponding to a long-axis polarized transition and the higher energy transition corresponding to a perpendicular short-axis transition. The low-energy band red-shifts to lower energies from 5-L-1 to 5-L-2. However, further shifting does not readily occur as the oligomer size increases from 5-L-2 to 5-L-4. This observation suggests that the effective conjugation length (i.e., oligomer “bandgap”) is reached relatively early in the series. Note the similarity in the 5-L-4 and P1 spectra, which are similar to other reported PPE-type oligomer and polymer absorption spectra (Figure 1-4).5,26,101-103 The oligomer bands are blue-shifted compared to PPE (Figure 1-4) due to the incorporation of the bipyridine and biphenyl subunits, which is analogous to the bipyridine-containing BEH-PPV blue-shift discussed in chapter 1.
Figure 3-2: Absorption spectra in THF. (a) 5-L oligomers and P1; (b) 5-Re complexes and P4; (c) 5-ReAN-2 and 5-ReAN-3 complexes.
While the **5-Re** rhenium complex spectra exhibit at least two similar $\pi,\pi^*$ transitions, a significant long-axis $\pi,\pi^*$ transition (HOMO $\rightarrow$ LUMO) red-shift and smaller short-axis transition red-shift in comparison to the free oligomer spectra is observed. The energy of the low-energy band remained fairly constant in the complexes, while the high-energy band continues to red-shift with increasing oligomer length. This feature suggests that for **5-Re-2 – 5-Re-4** the low-energy band is associated with a “constant” chromophore, while the higher energy band arises from a separate “varying” chromophore that is dependent on the oligomer length. The implications of this observation are discussed later. Note that the molar absorptivities are considerably higher than expected for any MLCT-based absorptions,$^{104}$ so it is believed that these absorptions are “buried” under the more intense oligomer $\pi,\pi^*$ transitions. Also, the **5-Re-4** and **P4** spectra are very similar, suggesting that the oligomers readily reflect the polymer photophysics.

**Emission Spectra**

Emission spectra of the **5-L** oligomers in optically dilute 2-methyltetrahydrofuran (2-MTHF) solutions at temperatures ranging from room temperature to 80 K are shown in Figure 3-3. Emission maxima at room temperature and 80 K are listed in Table 3-1. The oligomer fluorescence spectra at room temperature feature a strong band that exhibits a small Stokes shift (i.e., shift to lower energies) from the lowest-energy absorption. On this basis, the emission is assigned to the long-axis polarized $^1\pi,\pi^*$ state. This fluorescence is very similar in energy and bandshape to related PPE (Figure 1-4) and PPV $\pi$-conjugated polymers and oligomers, including **P1.$^{1,21,26,46,105-107}$** The fluorescence
maximum did not vary significantly throughout the oligomer series. Therefore, the \(^1\pi,\pi^*\) excited-state energy essentially remained constant upon variation of the oligomer length, which mirrors the lack of variation in the lowest-energy absorption band maximum. Comparison of the oligomer fluorescence spectra reveals that the spectral bandwidth decreases with increasing oligomer length. In addition, a clear trend emerges for oligomers 5-L-2 – 5-L-4 as the intensity of the (0,1) shoulder decreases relative to the (0,0) maximum with increasing oligomer size. These observations signal that the electron-vibration coupling in the \(^1\pi,\pi^*\) state decreases with increasing oligomer length due to greater \(^1\pi,\pi^*\) state delocalization. This decrease suggests that the excited state is less “distorted” upon photoexcitation, possibly due to the increased steric bulk of the alkyl chains as the oligomer size increases. A similar fluorescence trend was observed by Becker and coworkers for a series of oligothiophenes, and they suggested a similar conclusion.\(^{29}\) No phosphorescence was detected at low temperatures for any of the 5-L oligomers or P1. This observation for the polymers is not terribly surprising, as the presence of defect sites or “exciton traps” would provide a nonradiative decay route, consequently excluding the observation of phosphorescence.

The oligomer fluorescence red-shifted with decreasing temperature, and at the lowest examined temperatures for all of the oligomers (except 5-L-1) the emission was dominated by a broad band at a lower energy than the assigned room temperature (0,0) band. A corresponding thermochromism was seen in the lowest-energy \(^1\pi,\pi^*\) absorption band for 5-L-3 and 5-L-4 (data not shown). Excitation spectra for the oligomers measured at different wavelengths on the emission band were generally indistinguishable, suggesting that the states involved in the observed photophysics were in strong electronic
communication. Low temperature spectra of 5-L-1 show a dramatic blue-shift below 110 K leading to a final structured spectra after exhibiting the red-shift seen in all other oligomers at higher temperatures.

Figure 3-3: Emission spectra of the 5-L oligomers in 2-MTHF (350 nm excitation) at temperatures varying from 298 to 80 K. Emission intensity decreases as temperature decreases, and spectra are in 20 K increments. (a) 5-L-1 (note unusual low-temperature trends); (b) 5-L-2; (c) 5-L-3; (d) 5-L-4.
Emission quantum yields were measured for the oligomers using (2-17), and calculated values are listed in Table 3-1. The high emission quantum yield is typical of rigid-rod π-conjugated polymers and other rigid organic fluorophores. The quantum yields decrease as the oligomer size increases (except 5-L-4), suggesting more efficient intersystem crossing as the extended structure of the oligomer increases.

Polarized emission measurements were performed on oligomers 5-L-3 and 5-L-4 to further study the interesting thermochromism. Wavelength-resolved polarization anisotropies \( r(\lambda) \) were calculated with (3-2).

\[
\begin{align*}
\text{(3-2a)} \quad r(\lambda) &= \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}} \\
\text{(3-2b)} \quad G &= \frac{I_{HV}}{I_{HH}}
\end{align*}
\]

In (3-2), \( I_{XY} \) is the emission intensity with the excitation and emission polarizers adjusted according to \( x \) and \( y \), respectively (e.g., \( I_{HV} \) is the emission intensity with horizontally polarized excitation light and vertically polarized emission detection). Anisotropy measures the polarized light component ratio to its total intensity and is a direct indication of the angle between absorption and emission dipoles, \( \alpha \). Anisotropy values vary from 0.4 (\( \alpha = 0^\circ \)) to –0.2 (\( \alpha = 90^\circ \)), with an anisotropy value of zero statistically representing unpolarized light (e.g., a uniform statistical distribution of emitting dipole angles relative to the absorption dipole).

Emission spectra at room temperature and 170 K in 2-MTHF and calculated anisotropies at these temperatures are shown in Figure 3-4, and the anisotropy temperature dependence at 525 nm for both oligomers is shown in Figure 3-5. The 170 K
experiment temperature is slightly above the 2-MTHF freezing point, thus eliminating solvent glass effects on the observed anisotropy. At 298 K, $r(\lambda)$ is relatively constant across the fluorescence band ($r = 0.24$) for both oligomers. With decreasing temperature $r(\lambda)$ slightly increases on the blue side of the fluorescence band, but a sharp decrease on the far red side of the band is observed for 5-L-3 at $T < 190$ K and for 5-L-4 at $T < 230$ K. The implications of these observations are discussed below.

![Figure 3-4](image)

Figure 3-4: Emission (dashed line) and emission polarization (solid line) $r(\lambda)$ spectra (350 nm excitation) in 2-MTHF. (a) 5-L-3, 298 K; (b) 5-L-3, 170 K; (c) 5-L-4, 298 K; (d) 5-L-4, 170 K.
Figure 3-5: Emission anisotropy temperature dependence observed at 525 nm. Solid circles are $\text{5-L-3}$ data, and open circles are $\text{5-L-4}$ data.

Emission spectra for the $\text{5-Re}$ complexes in optically dilute 2-MTHF solutions at temperatures ranging from 298 to 80 K are shown in Figure 3-6. Emission maxima at 298 and 80 K are listed in Table 3-2. Although not shown, a weak emission was observed in all the rhenium complex samples that matched the free oligomer $^1\pi,\pi^*$ fluorescence seen in Figure 3-3. This emission is two orders of magnitude smaller than those observed for the uncomplexed oligomers. It is impossible to know whether this fluorescence originates from the rhenium complexes or is a trace oligomer impurity in the rhenium complex samples. Nonetheless, it is clear that the oligomer fluorescence is strongly quenched by the MLCT chromophore.
The rhenium complexes exhibited a weak, low-energy emission that increased with decreasing temperature (about twenty-fold from 298 to 80 K). Spectra for 5-Re-1 evolved from a broad structureless 680 nm band at 298 K to a blue-shifted, highly structured 586 nm band at 80 K. This thermally-induced emission energy shift exhibits trends typically observed for (b)ReI(CO)3Cl 3MLCT emission. For the remaining
rhenium complexes, a 650 nm band was observed at 298 K with a poorly defined vibronic structure, and a superposition of a structureless 600 nm band and a structured (0,0) 650 nm band with a vibronic (0,1) shoulder was obtained at 80 K. In general, there was very little band shifting of the structured emission to higher or lower energies as the temperature decreased for these complexes, and the observed band superposition “blurs” as the oligomer size increases. Attempts to measure the luminescence quantum yields of the 5-Re complexes were unsuccessful, as in each case the emission was too weak to be effectively measured ($\phi_{em} < 10^{-4}$). Excitation spectra probing this emission (not shown) agree well with the absorption spectra, suggesting efficient electronic communication between the $\pi,\pi^*$ oligomer and d$\pi$ (Re) $\rightarrow \pi^*$ MLCT excited states.

In order to further probe the superimposed emission spectra at low temperatures, excitation polarization studies were conducted at 80 K on 2-MTHF solutions of 5-Re-3 using various emission wavelengths. Excitation spectra and r($\lambda$) values are shown in Figure 3-7 along with an 80 K emission spectrum that indicates the examined wavelengths. For the blue structureless shoulder of the emission spectrum, the anisotropy value is high for the lowest-energy absorption band (0.3), which strongly suggests that the absorbing and emitting states are the same (i.e., little electronic rearrangement occurs between the absorbing and emitting states). As expected, the anisotropy value drops as the excitation wavelength decreases, since the absorbing state is now a higher-energy excited state than the emitting state. The excited complex must undergo internal conversion in this situation to reach the emitting state, which would certainly change the transition dipole and, consequently, the observed anisotropy. The anisotropies recorded at the maximum of the structured emission shows a lower anisotropy value (0.1)
that does not vary across the excitation spectrum. This observation that the anisotropy is nearly zero (i.e., the emission is almost completely unpolarized) and independent of excitation wavelength is common when phosphorescence from a triplet excited state is observed, since this state is typically very delocalized in the photoexcited chromophore.109-111

Figure 3-7: Excitation (dashed line) and excitation polarization (solid line) r(\(\lambda\)) spectra at 80 K of 5-Re-3 2-MTHF solution at various emission wavelengths.
Based on the polarization data, the structured emission observed at low temperatures is $3\pi,\pi^*$ phosphorescence originating from the complexed oligomer, while the overlapping structureless emission that retains anisotropy is the MLCT emission after undergoing an expected blue-shift from its room temperature position. Note, however, that the phosphorescence anisotropy does not equal zero, indicating that some mixing of phosphorescence and metal-based $3\text{MLCT}$ emission still occurs at low temperature. Furthermore, the $3\text{MLCT}$ emission band wavelength is close to the 5-Re-1 80 K emission maximum, further confirming its assignment. The presence of phosphorescence at lower temperatures is likely due to nonradiative decay pathway restriction after the sample is frozen in a glass. Similar overlapping MLCT and ligand emissions were reported by Schmehl and coworkers in a rhenium complex with a styryl-substituted bipyridine ligand. Low-temperature emission spectra of this complex exhibited overlapping metal-centered and ligand-centered luminescence with differing lifetimes. The smaller oligomer present in 5-Re-1 evidently lacks the electron delocalization necessary to achieve the “mixed-state” emission observed for the larger oligomers, since only $3\text{MLCT}$ emission is observed.

One of the purposes for synthesizing the 5-ReAN complexes was to increase the emission quantum yield and shift the MLCT emission away from the observed ligand phosphorescence at low temperatures. Ligand substitution on (bpy)Re(CO)$_3$Cl to form (bpy)Re(CO)$_3$(NCCH$_3$)$^+$ resulted in a $3\text{MLCT}$ emission maximum blue-shift of nearly 100 nm (from 642 to 540 nm), $3\text{MLCT}$ lifetime increase (from 150 to 1100 ns) and emission quantum yield increase by two orders of magnitude (from 0.003 to 0.22). However, emission maxima of the 5-ReAN complexes are very similar to the
corresponding 5-Re molecules. The 80 K 3MLCT emission portion of the overlapping spectrum is more prominent and slightly blue-shifted (around 575 nm) with respect to the 5-Re complexes, which might reflect the different chromophore excited state manifold and potentially higher quantum yield relative to the $^3\pi,\pi^*$ phosphorescence resulting from ligand substitution. Furthermore, room temperature quantum yield measurements on 5-ReAN-2 and 5-ReAN-3 remained very low (< 0.005), which is surprising. The implications of these observations are presented below.

**Emission Lifetimes**

Emission decay lifetimes were recorded for the 5-L oligomers in 2-MTHF at various temperatures and emission wavelengths. Both monoexponential and biexponential decays were observed, and lifetime results are listed in Table 3-3. Biexponential fits were performed using (3-3), yielding decay times ($\tau_i$) and normalized amplitudes ($\alpha_i$).

$$I(t) = \alpha_1 \exp\left(-\frac{t}{\tau_1}\right) + \alpha_2 \exp\left(-\frac{t}{\tau_2}\right)$$ (3-3)

The room temperature lifetime of the oligomer $\pi,\pi^*$ fluorescence generally decreases with increasing oligomer size. On the blue side of the fluorescence band (450 nm), the fluorescence decay kinetics are single exponential at all temperatures (except 5-L-2). By contrast, on the low energy side of the fluorescence band (550 nm) the decays become biexponential as the temperature decreases, featuring a long-lived component that increases in amplitude with decreasing temperature. For 5-L-1, room temperature biexponential decays are observed with little exhibited temperature dependence. Although the amplitude of the long-lived component is small (< 0.04), the decay time is
significant, suggesting that at low temperatures this component substantially contributes to the total emission yield. Note that the abrupt change in \( r(\lambda) \) for both 5-L-3 (180 K) and 5-L-4 (220 K) occurs at the same temperature where the emission decay kinetics become biexponential.

Table 3-3: Variable temperature emission decay times of the 5-L oligomers.

<table>
<thead>
<tr>
<th>Oligomer*</th>
<th>T / K</th>
<th>( \alpha_1 )</th>
<th>450 nm Emission</th>
<th>550 nm Emission</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( \tau_1 ) / ps</td>
<td>( \alpha_2 )</td>
<td>( \tau_2 ) / ps</td>
</tr>
<tr>
<td>5-L-1</td>
<td>298</td>
<td>1</td>
<td>2215</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>1</td>
<td>1335</td>
<td>-</td>
</tr>
<tr>
<td>5-L-2</td>
<td>298</td>
<td>1</td>
<td>1124</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.964</td>
<td>870</td>
<td>0.036</td>
</tr>
<tr>
<td>5-L-3</td>
<td>298</td>
<td>1</td>
<td>952.2</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>1</td>
<td>969.4</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>1</td>
<td>1031.5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1</td>
<td>979.3</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>1</td>
<td>945.9</td>
<td>-</td>
</tr>
<tr>
<td>5-L-4</td>
<td>298</td>
<td>1</td>
<td>770.8</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>1</td>
<td>719.3</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>1</td>
<td>737.2</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>1</td>
<td>493.6</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>210</td>
<td>1</td>
<td>434.3</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>190</td>
<td>1</td>
<td>458.3</td>
<td>-</td>
</tr>
</tbody>
</table>

*2-MTHF solutions; 350 or 405 nm excitation. Biexponential fits were performed with (3-3). Errors for the fit parameters are ± 5%.

Emission decay lifetimes were recorded for the 5-Re complexes in 2-MTHF at various temperatures, and lifetime results are listed in Table 3-4. At all temperatures, the emission decays were biexponential and generally characterized by a large amplitude, short-lived component (\( \tau \approx 1 \text{ ns}, \alpha > 0.95 \)) and a low amplitude component with a
considerably longer lifetime ($\tau \approx 20 - 200$ ns, $\alpha < 0.05$). The short-lived component shows little temperature dependence, but the long-lived component increases from a few hundred nanoseconds to several microseconds as temperature decreases. Note that the short-lived component amplitude for 5-Re-2 – 5-Re-4 increases with increasing oligomer size. Considering the fit error, the long-lived room temperature lifetimes (except 5-Re-1) are equivalent.

Table 3-4: Variable temperature emission decay times of the 5-Re complexes.

<table>
<thead>
<tr>
<th>Complex$^a$</th>
<th>Temp. / K</th>
<th>$\alpha_1$</th>
<th>$\tau_1$ / ns</th>
<th>$\alpha_2$</th>
<th>$\tau_2$ / ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-Re-1</td>
<td>280</td>
<td>0.927</td>
<td>1.598</td>
<td>0.073</td>
<td>14.1</td>
</tr>
<tr>
<td></td>
<td>171</td>
<td>0.996</td>
<td>1.951</td>
<td>0.004</td>
<td>204</td>
</tr>
<tr>
<td></td>
<td>81</td>
<td>0.528</td>
<td>60.8</td>
<td>0.472</td>
<td>6237</td>
</tr>
<tr>
<td>5-Re-2</td>
<td>280</td>
<td>0.987</td>
<td>1.969</td>
<td>0.013</td>
<td>153.6</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>0.999</td>
<td>0.831</td>
<td>0.001</td>
<td>843.8</td>
</tr>
<tr>
<td></td>
<td>82</td>
<td>0.999</td>
<td>2.39</td>
<td>0.001</td>
<td>2489</td>
</tr>
<tr>
<td>5-Re-3</td>
<td>298</td>
<td>0.994</td>
<td>2.36</td>
<td>0.006</td>
<td>174</td>
</tr>
<tr>
<td></td>
<td>169</td>
<td>0.999</td>
<td>2.05</td>
<td>0.001</td>
<td>2430</td>
</tr>
<tr>
<td></td>
<td>82</td>
<td>0.999</td>
<td>5.12</td>
<td>0.001</td>
<td>5107</td>
</tr>
<tr>
<td>5-Re-4</td>
<td>298</td>
<td>0.991</td>
<td>3.834</td>
<td>0.009</td>
<td>170.5</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.999</td>
<td>7.753</td>
<td>0.001</td>
<td>7608</td>
</tr>
<tr>
<td>5-ReAN-2</td>
<td>298</td>
<td>0.998</td>
<td>0.182</td>
<td>0.002</td>
<td>8.506</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>0.995</td>
<td>0.389</td>
<td>0.005</td>
<td>6.363</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.993</td>
<td>0.362</td>
<td>0.007</td>
<td>5.733</td>
</tr>
<tr>
<td>5-ReAN-3</td>
<td>298</td>
<td>0.997</td>
<td>0.165</td>
<td>0.003</td>
<td>9.250</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>0.992</td>
<td>0.507</td>
<td>0.008</td>
<td>6.852</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.991</td>
<td>0.321</td>
<td>0.009</td>
<td>5.705</td>
</tr>
</tbody>
</table>

$^a$2-MTHF solutions, 350 or 405 nm Excitation. Decays were recorded at 600 nm. Biexponential decay fits were calculated based on (3-3).
Exhaustive studies of emission decays at various temperatures and emission wavelengths were performed on all rhenium complexes, and representative data for 5-Re-2 are shown in Figure 3-8. Similar data sets were observed for the other rhenium complexes. On the blue side of the emission (600 nm), the short-lived component dominates the emission decay. The longer-lived component increases in amplitude as the emission wavelength increases. For all wavelengths (as also seen in Table 3-4 for 600 nm), the longer-lived component amplitude decreases with decreasing temperature, rendering the component relatively indistinguishable from the baseline at temperatures less than 220 K. This data is further discussed below.

As described above, the low temperature emission for these complexes is believed to be overlapping MLCT emission and oligomer \( ^3\pi,\pi^* \) phosphorescence. Typically, phosphorescence lifetimes are very long (tens to hundreds of microseconds). Clearly these lifetimes were not observed in this data, which might indicate configurational mixing of the two excited states. The increasing long-lifetime amplitude with increasing emission wavelength suggests a greater contribution from the longer-lived oligomer \( ^3\pi,\pi^* \) phosphorescence for these wavelengths, which agrees with the excitation polarization data.

It is worth noting that the 5-ReAN complexes have short lifetimes for each of the decay components that are temperature independent, unlike the other rhenium complexes. Again, this is counter to the expected photophysical trends for acetonitrile-substituted complexes as described above.
Figure 3-8: Normalized emission decays (intensity versus time) of 5-Re-2 at various emission wavelengths and temperatures. Emission decays increase in rate (i.e., more rapid decay) with decreasing temperature. (a) 600 nm emission; (b) 650 nm emission; (c) 700 nm emission.

Transient Absorption Spectra

Transient absorption spectra were recorded for all the oligomers and complexes, and spectra for the 5-L oligomers are shown in Figure 3-9. Excited state lifetimes obtained from factor analysis and global decay fitting\textsuperscript{114} are listed in Table 3-1.

Equivalent first order decays were observed for all features of the various transient
absorption spectra. Bleaching of the long-axis $\pi,\pi^*$ ground state absorption (Figure 3-2) was observed, along with a broad long-lived excited-state absorption extending into the near-IR for all oligomers. However, 5-L-1 shows a pronounced additional absorption at 500 nm. This absorption could be due to the lack of extended $\pi$-conjugation in 5-L-1, which could move excited states to higher energies and consequently blue-shift the transition(s). Excited state lifetimes are very long (several hundred $\mu$s), which is typical for organic triplets. Based on the lifetime, these transients are assigned to the $^3\pi,\pi^*$ excited state of the oligomers. The lack of a consistent trend in the TA lifetimes (Table 3-1) is a result of the extreme susceptibility of organic triplet excited states to oxygen quenching, prompting the use of more rigorous freeze-pump-thaw degassing for these compounds. The 5-L-3 and 5-L-4 transient absorption spectra also agree well with the previously reported $P_1$ spectrum and other $\pi$-conjugated polymers (Figures 1-2 and 1-8).

Transient absorption spectra for the 5-Re complexes in THF solutions are shown in Figure 3-10. Spectra were recorded in $\text{CH}_2\text{Cl}_2$ for the 5-ReAN complexes to prevent $\text{CH}_3\text{CN}$ ligand photosubstitution. Excited state lifetimes obtained from factor analysis and global decay fitting are listed in Table 3-2. Generally, equivalent first order decays were observed for all features of the various transient absorption spectra. However, the 450 nm bleach transient sometimes exhibited biexponential decay with a rapid decay component ($\tau < 1$ ns) followed by a longer-lived decay that agrees with the lifetimes of the other transients. The lack of consistent biexponential behavior in all samples for this decay suggests that trace 5-L fluorescence impurities were likely responsible for this rapid decay component, since a similar rapid decay was evident in 5-L transient
absorption spectra when measured with a time resolution short enough to observe the rapid signal.

Ground state $\pi,\pi^*$ absorption bleaching similar to the free oligomer spectra was observed at 450 nm, along with a strong absorption band around 500 nm and a broader absorption band extending into the near-IR. The transient decay lifetimes are significantly shorter than those for the free oligomers (10 – 200 ns). The similarity of the bleach and 500 nm absorption to a derivative shape suggests that the lowest energy $\pi,\pi^*$ excited-state transition overlaps but is red-shifted with respect to the ground state, thus producing the observed transient. The long-lived emission component and transient absorption decay lifetimes are equivalent for all the 5-Re complexes except 5-ReAN-2 and 5-ReAN-3. This correspondence suggests that the transient absorption arises from either the emitting excited state or an excited state that is in equilibrium with the luminescent state. For 5-ReAN-2 and 5-ReAN-3, a considerably longer transient absorption decay (several microseconds) was observed that is several orders of magnitude longer than the emission lifetimes. The ramifications of the 5-ReAN observations are discussed below.
Figure 3-9: Transient absorption spectra of the 5-L oligomers in freeze-pump-thaw degassed THF solutions. Arrows show the spectral trend with increasing time after laser excitation. A value of zero indicates no change between the ground and excited state absorption spectra. Transients are 40 µs increments after laser excitation. (a) 5-L-1; (b) 5-L-2; (c) 5-L-3; (d) 5-L-4.
Figure 3-10: Transient absorption spectra of the 5-Re complexes in argon bubble-degassed THF solutions (except for 5-ReAN-2 and 5-ReAN-3, which are in CH₂Cl₂). Arrows show the spectral trend with increasing time after laser excitation. (a) 5-Re-1 (Transients are 4 ns increments after laser excitation); (b) 5-Re-2 (Transients are 80 ns increments after laser excitation); (c) 5-Re-3 (Transients are 80 ns increments after laser excitation); (d) 5-Re-4 (Transients are 80 ns increments after laser excitation); (e) 5-ReAN-2 (Transients are 4000 ns increments after laser excitation); (f) 5-ReAN-3 (Transients are 4000 ns increments after laser excitation).
Photothermal Measurements

Using the TRTL apparatus described in chapter 2, the $U_{\text{Slow}} / U_{\text{Total}}$ ratio of a degassed THF solution of P1 was determined to be 0.15. LIOAS measurements were performed on THF solutions of the 5-L oligomers with the 1 MHz transducer and 5-Re complexes with the 5 MHz transducer. For the 5-L oligomers, a single fast decay component was observed, producing a single amplitude with an insignificant lifetime. Results of multiple 5-L oligomer measurements are listed in Table 3-5. For the 5-Re complexes, two components (fast and intermediate lifetimes) were observed. Measurements on 5-Re-1 were impractical due to its short excited-state lifetime, which is below the $\tau_a$ value of our instrument. Results of multiple 5-Re complex measurements are listed in Table 3-6. The triplet energies and yields of the 5-L oligomers are calculated below. The triplet ($^3\text{MLCT}$) energies of the 5-Re complexes can be calculated from each of the two deconvolution amplitudes obtained from the LIOAS data in an analogous manner to the (b)ReI(CO)$_3$(bzpy)$^+$ study described in chapter 2. Equations (2-15) and (2-16) were used to determine the $^3\text{MLCT}$ energies, and the results are listed in Table 3-7. It was assumed that $\Phi_{\text{em}} = 0$ and $\Phi_{\text{isc}} = 1$ since the emission quantum yields are $< 10^{-4}$.

Unfortunately, the measured triplet energies are radically lower than the observed MLCT emission (anywhere from 686 to greater than 900 nm). The reason for this discrepancy could stem from the assumption that the $^3\text{MLCT}$ state yield is unity. Instead, there could be a second excited state with a rapid nonradiative decay pathway that is accessed to some degree upon photoexcitation. Alternatively, the presence of free oligomer impurities could increase the radiated heat and lead to an erroneously low energy calculation. Solvent electrostriction stemming from the large oligomers might
also cause incorrect photoacoustic measurements. Attempts at measuring LIOAS transducer responses for 5-ReAN-2 and 5-ReAN-3 were unsuccessful due to possible ligand dissociation and/or the presence of free oligomer.

Table 3-5: 5-L oligomer LIOAS data.

<table>
<thead>
<tr>
<th>Oligomer&lt;sup&gt;a&lt;/sup&gt;</th>
<th>φ&lt;sub&gt;1&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-L-1</td>
<td>0.2959 ± 0.01</td>
</tr>
<tr>
<td>5-L-2</td>
<td>0.3021 ± 0.04</td>
</tr>
<tr>
<td>5-L-3</td>
<td>0.3023 ± 0.02</td>
</tr>
<tr>
<td>5-L-4</td>
<td>0.2735 ± 0.02</td>
</tr>
</tbody>
</table>

<sup>a</sup>THF Solutions, 298 K. LIOAS deconvolution parameters are averages of four measurements on fresh sample solutions with a reported error of ± σ. τ<sub>1</sub> fixed at 10 ns.

Table 3-6: 5-Re complex LIOAS data.

<table>
<thead>
<tr>
<th>Complex&lt;sup&gt;a&lt;/sup&gt;</th>
<th>φ&lt;sub&gt;1&lt;/sub&gt;</th>
<th>φ&lt;sub&gt;2&lt;/sub&gt;</th>
<th>τ&lt;sub&gt;2&lt;/sub&gt; / ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-Re-2</td>
<td>0.5150 ± 0.032</td>
<td>0.4683 ± 0.036</td>
<td>122.2 ± 11.7</td>
</tr>
<tr>
<td>5-Re-3</td>
<td>0.5738 ± 0.022</td>
<td>0.3782 ± 0.074</td>
<td>152.7 ± 15.0</td>
</tr>
<tr>
<td>5-Re-4</td>
<td>0.5951 ± 0.017</td>
<td>0.4383 ± 0.078</td>
<td>147.1 ± 14.7</td>
</tr>
</tbody>
</table>

<sup>a</sup>THF Solutions, 298 K. LIOAS deconvolution parameters are averages of four measurements on fresh sample solutions with a reported error of ± σ. τ<sub>1</sub> fixed at 1 ns.

Table 3-7: Triplet energies of the 5-Re complexes.

<table>
<thead>
<tr>
<th>Complex&lt;sup&gt;a&lt;/sup&gt;</th>
<th>E&lt;sub&gt;T&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt; / kcal mol&lt;sup&gt;−1&lt;/sup&gt;</th>
<th>E&lt;sub&gt;T&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt; / kcal mol&lt;sup&gt;−1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-Re-2</td>
<td>39.1 ± 2.6</td>
<td>37.7 ± 2.9</td>
</tr>
<tr>
<td>5-Re-3</td>
<td>34.3 ± 1.8</td>
<td>30.4 ± 6.0</td>
</tr>
<tr>
<td>5-Re-4</td>
<td>32.6 ± 1.3</td>
<td>35.3 ± 6.3</td>
</tr>
</tbody>
</table>

<sup>a</sup>THF Solutions, 298 K. <sup>b</sup>Triplet energy based on the first deconvolution amplitude and (2-15). <sup>c</sup>Triplet energy based on the second deconvolution amplitude with the assumptions that Φ<sub>em</sub> = 0, Φ<sub>bc</sub> = 1 and (2-16).
Transient Absorption Quenching / Oligomer Triplet Energy

Triplet quenching rate constants \( (k_q) \) for P1, 5-L-1, 5-L-3, and 5-L-4 were obtained from Stern-Volmer analysis of the observed transient absorption triplet decay lifetimes in freeze-pump-thaw degassed THF solutions as a function of quencher concentration based on (3-4).

\[
\frac{\tau_0}{\tau} = 1 + k_q \tau_0 [Q]
\]  

(3-4)

In (3-4), \( \tau_0 \) is the oligomer lifetime in the absence of quencher and \( \tau \) is the oligomer lifetime observed with \([Q]\) quencher concentration. A series of triplet acceptors of varying energy\(^ {41,97} \) were used as the excited state quenchers. All measured quenching rate constants are listed in Table 3-8.

Table 3-8: 5-L oligomer and P1 triplet quenching study results.

<table>
<thead>
<tr>
<th>Quencher(^a)</th>
<th>( E_A ) / kcal mol(^{-1})</th>
<th>( k_q ) / M(^{-1}) s(^{-1})</th>
<th>P1</th>
<th>5-L-1</th>
<th>5-L-3</th>
<th>5-L-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracene</td>
<td>42.5</td>
<td>1.2 x 10(^9)</td>
<td>6.9 x 10(^9)</td>
<td>7.8 x 10(^9)</td>
<td>9.0 x 10(^9)</td>
<td></td>
</tr>
<tr>
<td>(deb)Re(CO)(_3)Cl(^+)</td>
<td>46.6</td>
<td>1.3 x 10(^9)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pyrene</td>
<td>48.2</td>
<td>-</td>
<td>4.5 x 10(^8)</td>
<td>4.4 x 10(^8)</td>
<td>7.2 x 10(^8)</td>
<td></td>
</tr>
<tr>
<td>trans-Stilbene</td>
<td>49.2</td>
<td>3.2 x 10(^8)</td>
<td>1.0 x 10(^9)</td>
<td>2.4 x 10(^8)</td>
<td>2.7 x 10(^8)</td>
<td></td>
</tr>
<tr>
<td>(bpy)Re(CO)(_3)Cl(^+)</td>
<td>52.0</td>
<td>3.7 x 10(^7)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9-Fluorenone</td>
<td>53.3</td>
<td>-</td>
<td>9.6 x 10(^7)</td>
<td>4.5 x 10(^6)</td>
<td>4.1 x 10(^6)</td>
<td></td>
</tr>
<tr>
<td>Biacetyl</td>
<td>56.4</td>
<td>1.5 x 10(^5)</td>
<td>3.6 x 10(^5)</td>
<td>9.5 x 10(^4)</td>
<td>9.9 x 10(^4)</td>
<td></td>
</tr>
<tr>
<td>( p )-terphenyl</td>
<td>58.3</td>
<td>8.6 x 10(^4)</td>
<td>1.4 x 10(^5)</td>
<td>9.8 x 10(^3)</td>
<td>2.8 x 10(^3)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)(deb) = 4,4’-bis(carboxethoxy)-2,2’-bipyridine; (bpy) = 2,2’-bipyridine. A correction factor of 5.7 kcal mol\(^{-1}\) was added to the rhenium complex \( E_A \) values to correct for inaccurate Frank-Condon estimates.

Next, these quenching rate constants were used along with the photothermal data to calculate the triplet \( \pi,\pi^* \) excited state energy. Unfortunately, due to the absence of
phosphorescence in most $\pi$-conjugated polymers little is known about the absolute energies and/or yields of triplets produced by direct excitation. In fact, to our knowledge only one report from Bässler and coworkers on a rigid “ladder type” PPV polymer reported $\pi$–conjugated polymer phosphorescence. However, there are indirect methods with which the triplet energy and yield can be determined. Here, the oligomer triplet energies are calculated by fitting experimental Sandros plots ($\log k_q$ vs. $E_{\text{Accept}}$) with (3-5), a Marcus equation that is appropriate for bimolecular reactions that occur at or near diffusion control. This same method was used to calculate the triplet energy for MEH-PPV as mentioned in chapter 1.

\[
\begin{align*}
\frac{k_d}{1 + \exp \left( \frac{\Delta G}{RT} \right) + \left( \frac{k_{d}}{k_{en}} \right) \exp \{ \Delta G^\# \}} & = k_q \\
\Delta G^\# = \Delta G + \frac{\lambda}{\ln 2} \ln \left( 1 + \exp \left( -\frac{\Delta G \ln 2}{\lambda} \right) \right) & = \Delta G + \\
\end{align*}
\]

In (3-5), $k_d$ and $k_{d}$ are the rate constants for forward and reverse diffusion in solution, $k_{en}^0$ is a preexponential factor, $\lambda$ is the reorganizational energy and $\Delta G = (E_{\text{00,Accept}} - E_T)$. By using parameters derived from a previous report of rhenium complex quenching studies ($k_d = 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $k_{d} = 2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $k_{en}^0 = 5 \times 10^{10} \text{ s}^{-1}$), best fits of the Sandros plots for $P1$ and the $5-L$ oligomers are obtained by varying $\lambda$ and $E_T$ in (3-5). These values are listed in Table 3-9, and plots of the fitted quenching data are shown in Figure 3-11.

The photothermal data obtained for $P1$ and the $5-L$ oligomers can now be used in conjunction with the calculated triplet energy to determine the triplet yield, which is
derived from the P1 TRTL data and the 5-L LIOAS single component deconvolution with (3-6) and (3-7), respectively. Calculated triplet yields for P1 and the 5-L oligomers are listed in Table 3-9.

\[
\frac{U_{\text{Slow}}}{U_{\text{Total}}} = \frac{E_T \Phi_T}{E_{hv} - E_S \Phi_{fl}} \tag{3-6}
\]

\[
\phi_T = \frac{E_{hv} - E_S \Phi_{em} - E_T \Phi_T}{E_{hv}} \tag{3-7}
\]

The triplet yields increase from 5-L-1 – 5-L-3 followed by an observed decrease in 5-L-4. Furthermore, the sum of the fluorescence (Table 3-1) and triplet yields is close to unity (0.939 to 0.959), which indicates that photoexcitation of the oligomers leads almost exclusively to radiative decay or intersystem crossing (i.e., very little nonradiative decay occurs from the singlet state). The singlet-triplet splitting energy (\(E_{ST} = E_S - E_T\)) is also listed in Table 3-9 and shows a steady increase as the oligomer length increases, with the largest reported splitting found in the P1 polymer.

**Decay Rate Calculations**

Sufficient data is now available to calculate the radiative \(k_r\), intersystem crossing \(k_{isc}\), and nonradiative \(k_{nr}\) decay rate constants for the 5-L oligomers based on (3-8).

\[
k_r = \frac{\phi_{em}}{\tau_{em}} \tag{3-8a}
\]

\[
k_{isc} = \frac{\phi_T}{\tau_{em}} \tag{3-8b}
\]

\[
k_{nr} = \frac{1 - \tau_{em} (k_r + k_{isc})}{\tau_{em}} \tag{3-8c}
\]
The spectral data can also be used to calculate $k_r$ with the Strickler-Berg equation,
\[(3-9)\]

$$k_r^{SB} = 2.88 \times 10^{-9} \eta^2 \langle \nu_F^{-3} \rangle_{AV^{-1}} \int \frac{e(\nu)}{\nu} d\nu$$ \hspace{1cm} (3-9a)

$$\langle \nu_F^{-3} \rangle_{AV^{-1}} = \frac{\int I(\nu_F) d\nu_F}{\int \nu_F^{-3} I(\nu_F) d\nu_F}$$ \hspace{1cm} (3-9b)

In (3-9), $\eta$ is the solvent refractive index (THF, 1.4070), $e(\nu)$ is the molar absorptivity of
the absorption spectrum ($M^{-1} \text{ cm}^{-1}$), $\nu$ is the absorbance wavenumber ($\text{cm}^{-1}$), $I(\nu_F)$ is the
intensity of the normalized fluorescence spectrum, and $\nu_F$ is the fluorescence
wavenumber ($\text{cm}^{-1}$). For these calculations, only the lowest-energy absorption band was
integrated. The experimental and calculation results are listed in Table 3-10.

Many observations are suggested from this data. First, note that $k_r$ increases as the
oligomer size increases. This trend is not surprising considering the delocalization
increase provided by the oligomer size increase. Second, the calculated $k_r^{SB}$ values agree
well with the experimentally-determined rates within a factor of two. This agreement
confirms that the fluorescence originates from the same state that gives rise to the
lowest-energy absorption band. In addition, the fact that the radiative decay rates are
relatively large and close to those calculated with the Strickler-Berg equation indicates
that the fluorescence arises from a strongly allowed radiative transition.\[29\] Third, $k_{nr}$ and
$k_{isc}$ exhibit the same increase with oligomer size, but to a much lesser extent. The relative
steadiness in $k_{nr}$ from 5-L-2 – 5-L-4 shows that the increased oligomer conjugation does
not extensively alter the excited state manifold energy levels.
Figure 3-11: Sandros energy-transfer quenching plots ($\log (k_q)$ versus acceptor energy). Points are experimentally determined rate constants with various triplet energy acceptors (1. anthracene, 2. [4,4’-bis(carboethoxy)-2,2’-bipyridyl]Re(CO)3Cl, 3. pyrene, 4. trans-stilbene, 5. (2,2’-bipyridyl)Re(CO)3Cl, 6. 9-fluorenone, 7. biacetyl, 8. $p$-terphenyl), and fitted lines are calculated based on (3-5). (a) P1; (b) 5-L-1; (c) 5-L-3; (d) 5-L-4.
Table 3-9: Triplet photophysics of P1 and 5-L oligomers.

<table>
<thead>
<tr>
<th>Compound</th>
<th>E_S / cm⁻¹ (kcal mol⁻¹)</th>
<th>λ / cm⁻¹ (kcal mol⁻¹)</th>
<th>E_T / cm⁻¹ (kcal mol⁻¹)</th>
<th>Φ_T</th>
<th>E_ST / cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>23,100 (66.0)</td>
<td>1200 (3.43)</td>
<td>17,500 (51.2)</td>
<td>0.12</td>
<td>5,600</td>
</tr>
<tr>
<td>5-L-1</td>
<td>22,000 (62.9)</td>
<td>1050 (3.00)</td>
<td>18,300 (52.3)</td>
<td>0.049</td>
<td>3,700</td>
</tr>
<tr>
<td>5-L-2</td>
<td>22,030 (63.0)</td>
<td>–</td>
<td>17,700 (50.6)</td>
<td>0.214b</td>
<td>4,330</td>
</tr>
<tr>
<td>5-L-3</td>
<td>22,080 (63.1)</td>
<td>1200 (3.43)</td>
<td>17,700 (50.6)</td>
<td>0.262</td>
<td>4,380</td>
</tr>
<tr>
<td>5-L-4</td>
<td>22,120 (63.3)</td>
<td>1100 (3.14)</td>
<td>17,500 (50.0)</td>
<td>0.169</td>
<td>4,620</td>
</tr>
</tbody>
</table>

*Errors for the triplet yield are ± 15%. bValues for 5-L-2 are estimated from 5-L-3 values.

Table 3-10: Decay rates of the 5-L oligomers.

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>k_r / 10⁸ s⁻¹</th>
<th>k_m / 10⁷ s⁻¹</th>
<th>k ISC / 10⁸ s⁻¹</th>
<th>k_rSB / 10⁸ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-L-1</td>
<td>4.02</td>
<td>2.75</td>
<td>0.221</td>
<td>6.48</td>
</tr>
<tr>
<td>5-L-2</td>
<td>6.41</td>
<td>5.87</td>
<td>1.90</td>
<td>8.66</td>
</tr>
<tr>
<td>5-L-3</td>
<td>7.14</td>
<td>6.09</td>
<td>2.75</td>
<td>11.6</td>
</tr>
<tr>
<td>5-L-4</td>
<td>10.2</td>
<td>5.32</td>
<td>2.19</td>
<td>22.6</td>
</tr>
<tr>
<td>P1</td>
<td>11.0</td>
<td>5.70</td>
<td>2.30</td>
<td>–</td>
</tr>
</tbody>
</table>

Excited-State Energy Transfer

Emission studies were conducted on mixtures of various 5-L oligomers and 5-Re complexes with the intent of observing energy transfer between the oligomer (donor) and rhenium complex (acceptor). A representative variable temperature study of a 1:1 mixture of 5-L-3 and 5-Re-3 in 2-MTHF is shown in Figure 3-12. As the sample temperature decreased, the 5-L-3 π,π* fluorescence decreased and the 5-Re-3 MLCT luminescence increased.* Recall that the oligomer fluorescence quantum yield is at least

* The initial emission intensity increase seen in Figure 3-11b was due to the 5-L-3 π,π* fluorescence red-shift.
three orders of magnitude greater than the complex luminescence, which explains the very weak \textbf{5-Re-3} emission. The observed behavior is not surprising, as each individual component mirrors their temperature responses reported above (Figures 3-3 and 3-5). What appears different in the mixed sample is the complete loss of oligomer fluorescence between 190 and 170 K, which is close to the freezing point of 2-MTHF. Table 3-11 lists ratios of the oligomer $\pi,\pi^*$ fluorescence at room and low temperatures both by itself and mixed with rhenium complexes in varying proportions.

Figure 3-12: Emission spectra of a 1:1 mixture of \textbf{5-L-3} and \textbf{5-Re-3} (2 x 10^{-6} M) in 2-MTHF at various temperatures ranging from 298 to 80 K in 20 K increments. Arrows show the spectral trend with decreasing temperature. Note the sharp drop in $\pi,\pi^*$ fluorescence at 170 K, signifying energy transfer. (a) \textbf{5-L-3} $\pi,\pi^*$ fluorescence (350 nm excitation); (b) \textbf{5-Re-3} MLCT luminescence (450 nm excitation).
Table 3-11: Fluorescence intensity ratios for mixed samples.

<table>
<thead>
<tr>
<th>Samplea</th>
<th>$I_{298K}/I_{80K}$</th>
<th>$I_{298K}/I_{80K}$ (rel)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-L-3</td>
<td>7.14</td>
<td>1.00</td>
</tr>
<tr>
<td>1:1 5-L-3:5-Re-3</td>
<td>96.69</td>
<td>13.54</td>
</tr>
<tr>
<td>1:2 5-L-3:5-Re-3</td>
<td>128.8</td>
<td>18.04</td>
</tr>
<tr>
<td>2:1 5-L-3:5-Re-3</td>
<td>185.4</td>
<td>25.97</td>
</tr>
<tr>
<td>1:1 P1:5-Re-3</td>
<td>34.53</td>
<td>4.84</td>
</tr>
<tr>
<td>5-L-4</td>
<td>8.69</td>
<td>1.22</td>
</tr>
<tr>
<td>1:1 5-L-4:5-Re-4</td>
<td>31.90</td>
<td>4.47</td>
</tr>
</tbody>
</table>

aMeasurements were conducted on optically dilute 2-MTHF solutions ($2 \times 10^{-6}$ M). Emission intensities used for the ratios are the fluorescence band maxima at 298 and 80 K.

Oligomer fluorescence quenching markedly increased with the addition of the rhenium complexes, indicating energy transfer between the two excited states. Note that efficient energy transfer occurred even with a 2:1 ratio of oligomer to complex. The increased ratio observed for the 2:1 5-L-3:5-Re-3 sample, which is counter to the expected trend, is due to the larger initial oligomer emission while the low temperature intensity for all the 5-L-3:5-Re-3 samples is essentially equivalent to the baseline noise as seen in the Figure 3-17a inset. This indication of energy transfer in fluid solutions prompted further investigation into solid-state energy transfer.

**Langmuir-Blodgett Films**

The Langmuir-Blodgett (LB) film process has been utilized for several years to produce multi-layer films of complex molecular systems with the purpose of studying their material properties. This process has been used to create films of rigid-rod polymers similar in structure to the 5-L oligomers. Therefore, it was theorized
that the energy transfer observed in solution could also be observed in LB films where the donor (5-L oligomer) and acceptor (5-Re complex) could be mixed in the same layer or deposited in alternating layers. A collaboration with Dr. Dan Talham and postdoctoral associate Dr. Aiping Wu at the University of Florida was initiated to explore this theory.

LB films consisting of a single component were initially transferred to compare with the solution photophysics. A –Ru(bpy)_2^{2+} analogue of 5-Re-2, 5-Ru-2, was used because of its higher luminescence quantum yield, allowing for easier detection in the presence of the highly fluorescent free oligomer. A spread layer of 5-Ru-2 exhibited a good compression isotherm, indicating that a reasonable monolayer was formed on the LB trough surface. Films of varying layer thicknesses were transferred onto glass substrates and their photophysics studied. Transfer ratios of these films were close to unity for both the up and down transfer strokes. Absorption and emission spectra of the 5-Ru-2 films along with solution spectra are shown in Figure 3-13.

The 5-Ru-2 LB film absorption spectra feature two π,π* absorptions similar to those observed in the solution spectra. Only a slight red-shift is observed between the solution and LB film maxima. Except for the thickest film, the lowest-energy absorption maximum exhibits a linear dependence on film thickness (0.0038 a.u. layer^{-1}) as seen in the Figure 3-13b inset. Using this trend, the LB film surface coverage can be calculated using (3-10), a modified Lambert-Beer equation.

\[
A = \varepsilon \Gamma L
\]  

In (3-10), \(\Gamma\) is the surface coverage (mol cm^{-2} layer^{-1}) and \(L\) is the number of layers within the film. If it is assumed that the molar absorptivity of the band maximum in solution and the LB film is equivalent (5.31 x 10^7 cm^2 mol^{-1}), using the calculated absorption
increase above a surface coverage of $7.16 \times 10^{-11}$ mol cm$^{-2}$ layer$^{-1}$ is determined. The inverse of this value after unit conversion produces the mean molecular area (MMA) of a single 5-Ru-2 molecule, 231.9 Å$^2$ molecule$^{-1}$. Another method of determining MMA, the construction of a line tangent to the pressure isotherm of the 5-Ru-2 monolayer, gives a MMA essentially equivalent to the value determined by absorption spectroscopy (208 Å$^2$ molecule$^{-1}$).

The 5-Ru-2 LB film emission spectra exhibit a fairly weak $^3$MLCT luminescence that is slightly red-shifted from solution 5-Ru-2 spectra.$^{124}$ Unlike the absorption spectra, no decisive trend is observed between emission intensity and film thickness. There could be many reasons for this observation, including LB film heterogeneity and/or self-quenching. However, emission intensity varied only by ±10% when different areas of the sample were probed, and preliminary fluorescence microscopy studies indicated that the LB films were homogeneous. Note that polarized absorption and emission measurements on these films failed to indicate any preferential anisotropy, which was observed for PPE-type polymer LB films.$^{51,125}$ The absence of polarization in these films is likely due to the formation of mesoscale-sized domains that would exhibit polarization on a microscopic measurement but cancel each other out in the macroscopic measurements presented here.
Figure 3-13: Photophysics of 5-Ru-2 Langmuir-Blodgett films. (a) 5-Ru-2 THF solution absorption (solid line) and emission (dashed line) spectra; (b) Absorption spectra (inset: absorbance maximum vs. number of layers); (b) Emission spectra (450 nm excitation; inset: emission maximum vs. number of layers).
Several attempts were also made to transfer LB films of 5-L-3, but the lack of charge on the oligomer presented a large handicap. Pressure isotherms of the oligomer indicate a very small MMA (50 Å², see Figure 3-14), and aggregation was visibly observed on the trough surface. Films were not transferrable from these rigid aggregates. Several different “tricks” were utilized to overcome the aggregation problem and/or induce charge on the oligomer, including protonation of the bipyridyl nitrogens at low pH, addition of a surfactant (didodecyldimethylammonium bromide), and the formation of oligomer complexes with other metal cations (Cu²⁺, Ni²⁺ and Mn²⁺). In all cases, transferred LB films were visually heterogeneous and exhibited grossly broadened fluorescence, suggesting aggregation.

A series of five-layer LB films were transferred with varying ratios of the 5-L-3 oligomer and 5-Ru-2 complex which are pre-mixed prior to spreading. Transfer ratios of these films are again close to unity for both up and down transfer strokes. Pressure-area isotherms of the mixed 5-L-3 / 5-Ru-2 films are shown in Figure 3-14. Reported ratios are the molar ratios of the premixed solution that is spread on the LB trough.

All the mixed LB film pressure isotherms are reasonably well behaved. Note that the MMA increases with increasing amounts of 5-Ru-2, which is reasonable since the ruthenium complex has a larger molecular area than the free oligomer. Absorption, emission, and excitation spectra of the mixed LB films are shown in Figure 3-15. Absorption spectra of the mixed LB films exhibited two π,π* absorptions and a low-energy tail which is assigned to an MLCT-based absorption. Absorbance decreases with increasing 5-Ru-2 concentration, which is expected since the free oligomer has a higher absorptivity. A 15 nm red-shift in the lowest-energy π,π* absorption was also observed.
with increasing **5-Ru-2** concentration. It is interesting to note that the MLCT “shoulder”
does not dramatically change in intensity between the various films, but the relative
intensity of the π,π* compared to MLCT absorptions decreases with increasing **5-Ru-2**
concentration. Using (3-10) and solution molar absorptivity values, MMA values were
calculated based upon the low-energy π,π* absorption maximum. A comparison of
MMA values calculated spectroscopically and from the pressure isotherms is presented in
Table 3-12. The calculated MMA values are lower than the pressure isotherm data.
These differences are likely due to errors introduced by assuming the calculated solution
absorptivities are valid for LB film measurements or the existence of an extended
interaction between donor and acceptor molecules in the mixed LB films.

![Graph](image)

**Figure 3-14:** Pressure isotherms of Langmuir-Blodgett films of **5-L-3 / 5-Ru-2** mixtures.
Ratios are [**5-L-3** : **5-Ru-2**] in the premixed solution prior to spreading.
Table 3-12: Surface coverage calculations for mixed 5-L-3 / 5-Ru-2 LB films.

<table>
<thead>
<tr>
<th>[5-L-3] : [5-Ru-2]</th>
<th>MMA$^a$ / Å$^2$</th>
<th>$\Gamma$ / 1$^{10}$ mole cm$^2$ layer$^{-1}$</th>
<th>MMA$^b$ / Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 : 1</td>
<td>123</td>
<td>1.69</td>
<td>98.8</td>
</tr>
<tr>
<td>1 : 1</td>
<td>150</td>
<td>1.52</td>
<td>109</td>
</tr>
<tr>
<td>1 : 2</td>
<td>180</td>
<td>1.28</td>
<td>130</td>
</tr>
<tr>
<td>1 : 4</td>
<td>205</td>
<td>1.26</td>
<td>132</td>
</tr>
</tbody>
</table>

$^a$MMA calculated from pressure isotherms. $^b$MMA calculated from absorption spectra.

Emission spectra show 5-Ru-2 MLCT luminescence that is very similar to the emission observed in the single-component LB film (Figure 3-13). The relative intensity of the 5-L-3 $\pi,\pi^*$ fluorescence (the peak extending to lower wavelengths in Figure 3-15b) decreases with increasing 5-Ru-2 concentration, which is not surprising. However, examination of the excitation spectra shows that excitation wavelengths producing the MLCT luminescence blue-shift with increasing 5-L-3 concentration. This trend indicates that energy transfer is occurring between the two components, since excitation into the oligomer $\pi,\pi^*$ absorption clearly produces $^3$MLCT emission.

Unfortunately, there were problems with the mixed LB film experiments. Note that the emission and excitation spectra in Figure 3-15 are normalized. The absolute $^3$MLCT emission intensities for these films varied wildly, with the highest concentration 5-L-3 film exhibiting MLCT emission five times more intense than any of the other films. Again, heterogeneity within these mixed films could be responsible for these photophysical observations, and fluorescence microscopy appeared to indicate some striation within the LB films that may be due to mesoscale-range phase segregation. Furthermore, the inability to transfer single-component 5-L-3 LB films prevents the full understanding of the mixed film photophysics.
Figure 3-15: Photophysics of 5-L-3 / 5-Ru-2 mixed Langmuir-Blodgett films. (a) Absorption spectra; (b) MLCT Emission spectra (409 nm excitation); (c) MLCT Excitation spectra (694 nm emission).
Electrochemistry

Cyclic voltammetry was performed on the 5-Re complexes in THF with 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as supporting electrolyte. Unfortunately, the complexes were not soluble in more polar solvents typically used for electrochemistry, and measurements on CH$_2$Cl$_2$ solutions produced poor results. Due to the limited potential window of THF (anodic limit $\approx +1.4$ V), oxidation potentials could not be measured. However, quasi-reversible reduction waves of the ligated oligomer were observed in all cases except 5-Re-4, which had a non-reversible reduction. Reduction half-wave potentials are listed in Table 3-2. Note that the reduction potential does not dramatically shift with increasing oligomer size. The reduction potentials are less than the parent complex (bpy)Re(CO)$_3$Cl ($-1.35$ V vs. SCE)$^{41}$ which indicates that the 5,5’-substituted aryl-ethynyl moieties on the bipyridine stabilize the reduced complex (i.e., the LUMO energy is lowered by the $\pi$-conjugation). This observation further implies that in the reduced complex there is some electron density delocalization in the appended aryl-ethynyl units. Reduction half-wave potentials were also measured for 5-L-3 and 5-L-4 under similar conditions. For both oligomers, values of $-1.46$ V vs. SCE were obtained. Therefore, complexation of the oligomer to the metal center makes it easier to reduce the oligomer by nearly 0.5 V.

Discussion

Oligomer Ligand Conformation

Many spectroscopic observations reported above can be better understood when the effective conjugation length due to oligomer conformation is considered. The extent
of oligomer conjugation is dominated by “breaks” caused by twists in the bipyridine and biphenyl subunits of the oligomer backbone. These twists are induced by steric effects due to the close proximity of \( \alpha \)-hydrogens on adjacent phenyl rings. Wasielewski and coworkers discussed this same phenomenon with a 2,2’-bipyridyl-containing BEH-PPV (Figure 1-1),\(^2^4\) where the excited-state energy via absorption spectroscopy is higher for the polymer with the 2,2’-bipyridine subunit due to these conjugation breaks. Two major conclusions lead from this structural observation: 1) An oligomer size increase may not bring a corresponding conjugation length increase; and 2) Rhenium complexation leads to a marked oligomer conjugation increase. For example, when the oligomer length is increased from 5-L-1 to 5-L-2, a conjugation increase is expected because the majority of each side of the oligomer is expected to be planar. However, further lengthening to oligomers 5-L-3 and 5-L-4 introduce opportunities for the conjugation to be broken at the biphenyl subunits. Therefore, the resulting conjugation increase may not be as large as anticipated. Furthermore, the long alkyl chains on the dialkoxybenzene subunits present for solubility provide a driving force for varied conformations that may be entropic in nature.

When the oligomers are ligated to a rhenium chromophore, as seen in Figure 3-16, the metal center forces the typically orthogonal bipyridine subunit into a planar conformation. This conformation facilitates a significant conjugation increase when compared to the uncomplexed oligomer. However, peripheral biphenyl subunits are likely still twisted as illustrated. Recall that the consequences of metal complexation was utilized by Wang and Wasielewski\(^1^8\) to create metal ion sensors with their 2,2’-bipyridine-substituted PPV polymers (Figure 1-9). Metal ion complexation to these
polymers induced absorption and fluorescence red-shifts of up to 100 nm in certain cases. With these two effects in mind, the photophysical observations can be interpreted with a greater understanding of the connection between oligomer structure and photophysical properties.

Figure 3-16: Effect of metal complexation to the conjugated segments of the oligomer.

**Electronic absorption spectra**

For the 5-L oligomers, recall that following an initial red-shift from 5-L-1 to 5-L-2, the lower-energy $\pi,\pi^*$ transition remained at a constant wavelength for oligomers 5-L-2 – 5-L-4, suggesting that the oligomer bandgap (405 nm = 3.06 eV) had been reached. The biphenyl conjugation breaks do not allow further delocalization and, consequently, additional red-shifting. However, the increased overall size of the oligomer still increases the electronic transition dipole, which in turn increases the oscillation strength of both $\pi,\pi^*$ transitions, resulting in the observed intensity increase. The $\textbf{P1}$
absorption spectrum mirrors the oligomer absorption band maxima, suggesting that these same conjugation limitations exist in the polymer.

For the 5-Re complexes, following an initial increase and red-shift from 5-Re-1 to 5-Re-2, the oscillator strength and wavelength of the lower energy $\pi,\pi^*$ transition band remains relatively constant as the oligomer size increases. The red-shifted $\pi,\pi^*$ transition with respect to the free oligomer is due to the forced oligomer bipyridine planarity and the resulting conjugation increase (Figure 3-16), in addition to potential contributions from a charge transfer band. Recall, however, that the absorptivities are exceedingly high for a solely MLCT-based absorption. Similar red-shifts are seen in the 5-ReAN complexes. The central chromophore is electronically isolated from the remainder of the oligomer due to biphenyl conjugation breaks, which leads to the observations of “constant” and “varying” portions of the absorption spectrum as described above. Since the outer sections of the oligomers do not experience any significant conjugation effect upon rhenium complexation, it continues to electronically behave as the free oligomer would. Therefore, we observe the evolution of bands that represent different segregated chromophores on the same oligomer chain. For example, 5-Re-4 is large enough to effectively isolate “all-organic” chromophores from the central section so that the absorption spectrum exhibits both the same two electronic transitions seen in unbound oligomer 5-L-4 (343 and 388 nm) along with the red-shifted $\pi,\pi^*$ absorption seen in rhenium complexes 5-Re-1 – 5-Re-3 (444 nm).

Emission spectra

As seen above, the fluorescence quantum yields decrease and triplet yields increase as oligomer size increases, which is due to greater electron delocalization in the
larger oligomers. However, the lack of significant yield variation between 5-L-2 and 5-L-3 further suggests no significant delocalization increase due to the oligomer backbone conjugation breaks. The fluorescence yield increase observed for 5-L-4 could result from concurrent emission from an electronically isolated second chromophore in the same oligomer.

The increasing spectral complexity (i.e., “blurring” of the spectra) of the 5-Re complexes (except 5-Re-1) may also have its roots in the oligomer conformation. As the complexes are confined in the solvent glass, the biphenyl units can potentially be trapped in a wide variety of rotational conformations. These various conformations lead to an effective conjugation length distribution and, consequently, multiple $^{3}\pi,\pi^{*}$ energy levels in the sample. This distribution would lead to an overall emission band broadening similar to the experimentally observed spectra.

**Oligomer triplet energies**

The photophysical characterization of the triplet excited state of P1 and the 5-L oligomers allows us to assess the effect that extended $\pi$-conjugation has on its properties. It is surprising that $E_T$ (i.e., triplet energy) is the same for the 5-L oligomers within error, but the $E_{ST}$ value (Table 3-9) increases slightly ($< 2 \text{ kcal mol}^{-1}$) as the oligomer length increases. Logic suggests that the splitting energy would decrease as the oligomer size increases as a consequence of decreased electron exchange energy, which presumably is due to the fact that the $\pi \rightarrow \pi^{*}$ transition delocalization is greater as the extended $\pi$-conjugation increases. In fact, an inverse relation between $E_{ST}$ and oligomer size is observed by Becker and coworkers for a series of oligothiophenes. The biphenyl twists in our oligomers break the potential conjugation and limit the delocalization impact on
the excited-state energies, resulting in similar $E_T$ values across the series. These same
conjugation breaks in the polymer result in the similar oligomer and P1 triplet energies.
The oligomer and polymer singlet excited state energy difference is due to the presence of
the bipyridyl subunit in the oligomers. In fact, $E_{ST}$ is almost 1000 cm$^{-1}$ lower in P1 (5600
cm$^{-1}$) compared to a biphenyl analogue of 5-L-1 (6500 cm$^{-1}$). The triplet energies for
these oligomers and polymer are significantly higher than the PPV and polythiophene
triplet energies previously reported ($29 - 35$ kcal mol$^{-1}$), which is likely a direct result of
the conjugation limitations imposed by the bipyridine and biphenyl subunits.

**Oligomer Temperature Dependence and Aggregation**

It has already been seen that in dilute solution alkyl- and alkoxy-substituted PPV,
PPE and related polymers and oligomers feature strong absorption and fluorescence
bands arising from long-axis $\pi,\pi^*$ transitions on a single polymer chain (i.e., intrachain
excitations). In contrast, the solid state photophysics of the polymers (i.e., as amorphous
films) originate from states that absorb and luminesce at a lower energy than the solution
intrachain $\pi,\pi^*$ bands.$^{21,127,128}$ Although it is clear that the photophysical properties of the
polymers in the solid state arise from “excimer-like” states created by interchain
interactions, little evidence was available until recently for the involvement of interchain
states in dilute solution polymer photophysics.$^{129-134}$ Aggregation examples include a
cyano-substituted alkoxy-PPV polymer (both in solution and in the solid state), where
aggregation was attributed to competition between luminescence from intrachain and
interchain (excimer) states arising from chromophore aggregates.$^{129-131}$ Additionally, it is
known that poly-3-alkylthiophenes exhibit thermochromism and solvatochromism that is
due in part to aggregation.$^{132-134}$ Several of the oligomers presented here exhibit these
same characteristics, which suggest that the oligomers aggregate in dilute solution at low temperatures. However, aggregate formation has not been previously reported for dilute \( \pi \)-conjugated oligomer solutions such as the 5-L oligomers.

The temperature dependence of the 5-L oligomer emission (Figure 3-3) illustrates that the \( \pi,\pi^* \) fluorescence observed from dilute solution red-shifts, broadens and decreases in intensity with decreasing temperature. The fluorescence is dominated by a broad red-shifted band, a feature typically associated with “excimer” emission from an excited state dimer. These effects are opposite to what is typically observed for aromatic fluorophores, where lowering the temperature usually induces a blue-shift with a corresponding fluorescence lifetime and quantum yield increase because \( k_{nr} \) decreases with decreasing temperature.\(^{113} \) The decay rate is proportional to the excited-state / ground-state vibrational overlap, which decreases with temperature due to a decrease in the Boltzmann excited vibronic level population and decreased electron-phonon coupling to outer-sphere solvent modes. Indeed, for the lowest temperature emission spectra in 5-L-1 the typical trend described here is observed, but only after the “sample aggregation” is apparently complete. The larger oligomer spectra do not exhibit this same blue-shift, apparently because an energy deactivation pathway more favorable than fluorescence is available to the oligomer excited state.

The oligomer temperature-dependent fluorescence data strongly suggests that the oligomers exist in an aggregated state in low temperature solution. Furthermore, the broad, red-shifted fluorescence band features a longer decay time (several ns) than the blue "monomer" emission (< 1 ns). This longer decay time is also consistent with an aggregated or “excimer-like” state, since an excimer state would have a lower \( k_c \) (and
consequently a longer decay time) compared to a monomer excited state. This rate
decrease is due to the fact that the exciplex radiative decay rate is proportional to the
square of the ground state monomer to excited state exciplex transition moment. If the
exciplex exhibits charge transfer behavior (as indicated below), the transition moment
decreases from its monomeric level, leading to the observed $k_r$ decrease.\textsuperscript{135}

The key to confirming aggregation as the probable mechanism for the
fluorescence temperature-dependence lies in the \textit{5-L-3} and \textit{5-L-4} polarization anisotropy
data. Under ordinary conditions, the polarization anisotropy of a fluorophore in dilute
solution increases with decreasing temperature.\textsuperscript{109} The increase occurs because the
primary mechanism for polarization loss in dilute solutions is rotational diffusion, which
slows with increasing solvent viscosity. An alternate depolarization mechanism is long-
range (Förster) energy transfer or exchange energy migration among aggregated
chromophores. Thus, under conditions where rotational diffusion is slow (i.e., at
cryogenic temperatures), observation of depolarization is a strong indication that energy
transfer migration within chromophore aggregates occurs.

With these facts in mind, the temperature-dependent anisotropy data for \textit{5-L-3} and
\textit{5-L-4} is examined. For \textit{5-L-3}, as temperature decreases the anisotropy slightly increases
as expected due to the rotational diffusion rate decrease (Figure 3-5). However, below
190 K there is an abrupt anisotropy decrease, suggesting that at this temperature
aggregation occurs. For \textit{5-L-4}, the anisotropy also increases slightly with decreasing
temperature then drops precipitously between 230 and 210 K, which is also due to
chromophore aggregation. Note that the anisotropy data implies that \textit{5-L-4} aggregates at
a higher temperature than \textit{5-L-3}, consistent with the fact that \textit{5-L-4} is a larger “rod” than
5-L-3 based on semi-empirical calculations (5-L-3: length = 59.1 Å, four n-C_{18}H_{37} alkyl side-chains; 5-L-4: length = 95.3 Å, eight n-C_{18}H_{37} alkyl chains).

Although it is clear that the oligomers aggregate at low temperature, two subtle features demand a more complicated model for explanation: 1) At intermediate temperatures (i.e., 298 > T > 220 K) the fluorescence is dominated by emission from the “monomeric” excited state, but the band *steadily* red-shifts and decreases in intensity with decreasing temperature; 2) An *abrupt* change in the fluorescence bandshape, decay kinetics and wavelength-dependent polarization anisotropy occurs at T \approx 220 K for 5-L-4 and T \approx 180 K for 5-L-3. This latter feature implies that a dramatic change occurs in the system properties that arise from intermolecular aggregation.

Because the polarization anisotropy remains high at intermediate temperatures (i.e., 298 > T > 190 K for 5-L-3 and 298 > T > 230 K for 5-L-4), energy transfer resulting from aggregation must not occur at these temperatures. Therefore, these spectral changes must arise from intramolecular effects. We conclude that these effects arise from variations in the oligomer backbone and side chain conformation. As temperature decreases, the oligomers may adopt conformations in which the phenylene rings for the oligomer series lie more within the same plane. A π-conjugated system planarity increase would effectively increase the conjugation length, which in turn decreases the \(^1π,π^*\) transition energy that is responsible for the red-shifting fluorescence. This energy decrease may also increase \(k_{nr}\), resulting in the observed fluorescence yield (i.e., intensity) decrease.\(^{136}\)

An important consideration in formulating this mechanism is that the oligomer backbone and n-C_{18}H_{37} alkyl side chain conformations must be correlated. Indeed, as the
oligomer π-system becomes more planar, the n-C_{18}H_{37} alkyl side chains probably tend to lie essentially in the same plane. It is possible that as temperature decreases the oligomers and side chains may adopt a planar “sheet-like” conformation that is the precursor to the formation of extended aggregates as suggested in Figure 3-17. Cooperation between side chain conformation and intermolecular interactions has been proposed to occur in “hairy-rod” π-conjugated polymers similar in structure to the oligomers, but this study may be the first example of such an effect in medium molecular weight “hairy-rod” oligomers.

![Figure 3-17: Proposed oligomer aggregation mechanism.](image)

**Excited State Photophysics of the Rhenium Complexes**

Initially, it was believed that the same excited state (the $^3$MLCT state) was responsible for both the observed emission and transient absorption spectra. However, two pieces of data could not be explained by this theory: 1) The emission decay is never single exponential, displaying a predominant rapid decay component before the assigned MLCT decay; and 2) The different emission and transient absorption lifetimes of the 5-ReAN complexes show that the same excited state cannot be responsible for both spectral results. Therefore, a new excited-state model is derived that takes these
observations into account and is illustrated in a Jablonski diagram in Figure 3-18. This model is based on the existence of an equilibrium between two excited states, $^{3}\pi\pi^*$ (oligomer-based phosphorescence) and $^{3}\text{MLCT}$ (metal-based luminescence). The $^{3}\text{MLCT}$ state is responsible for the observed emission (EM in Figure 3-18), while the $^{3}\pi\pi^*$ state is responsible for the excited-state absorption observed in the transient absorption spectrum (TA in Figure 3-18).

![Jablonski diagram of 5-Re excited state energy levels.](image)

Using this model, the unusual photophysics observed in the emission lifetime decays and disparate 5-ReAN excited-state observations can now be explained. First, the biexponential decay observed in the emission data is the result of an equilibrium that is
rapidly established between the two excited states following initial photoexcitation. The large-amplitude rapid component represents \(^3\text{MLCT}\) emission which quickly decays to the \(^3\pi,\pi^*\) state that is non-emissive at room temperature. The slower decay component is the remaining emission after equilibration, which is either \(^3\text{MLCT}\) at room temperature or a mixture of both \(^3\text{MLCT}\) and \(^3\pi,\pi^*\) at low temperature.

Following equilibration, the population remaining in the \(^3\pi,\pi^*\) state is available to be excited into a higher triplet excited state, producing the obtained transient absorption spectrum. In principle, the \(^3\text{MLCT}\) transient absorption should be seen at early delay times following laser excitation, but our instrument does not have the capability to resolve such fast decays. Preliminary investigations on a picosecond time-resolved flash photolysis system in collaboration with Professor Mike Wasielewski at Northwestern University, however, did show some spectral evolution on the timescale of the excited-state equilibrium process.\(^{99,137,138}\) The broad observed absorption seen in all the 5-Re spectra (Figure 3-9) mirrors the 5-L oligomers spectra well, further supporting this assignment. The sharp 500 nm band is believed to be a derivative remnant of the overlapping ground and excited-state absorbances at that wavelength rather than a unique excited-state absorption. The excited state equilibria result in identical decay rates of both states following equilibration, which is a common result for this equilibria.\(^{139-141}\)

The 5-ReAN complexes, however, do not have equivalent emission and transient absorption decay rates. Upon replacing the chloride ligand with an acetonitrile, the \(^3\text{MLCT}\) excited state is raised in energy due to \(\pi\) backbonding with the acetonitrile ligand, which draws electron density away from the metal center and increases the ligand field splitting.\(^{142}\) Consequently, the excited state equilibrium is disrupted, leading to a rapid
MLCT emission decay as it undergoes internal conversion to the $^3\pi,\pi^*$ state with no opportunity for reverse conversion to $^3$MLCT as seen in the 5-Re complexes. This $^3\pi,\pi^*$ state can then undergo triplet-triplet absorption and exhibit a longer decay time that is more typical of organic triplet absorptions.

To further confirm that the transient absorption originates from the $^3\pi,\pi^*$ excited state, time-resolved continuous-wave EPR (TREPR) studies were performed in a collaborative effort with Dr. Hans van Willigen and Dr. Alejandro Bussandri at the University of Massachusetts at Boston. If the transient absorption originates from a ligand-based $^3\pi,\pi^*$ state, an EPR signal should be observed. On the other hand, no signal is expected if the transient is a metal-based MLCT state because of the short spin-lattice relaxation time associated with such a state. TREPR spectra following laser excitation were recorded on a biphenyl analogue of 5-L-1 and 5-ReAN-2 at 130 K and are shown in Figure 3-19.

The biphenyl version of 5-L-1 was used to model the expected $^3\pi,\pi^*$ excited state response. A broad resonance peak (~2000 gauss centered at $g = 2$) was observed. The low-field half of this spectrum is an emission, and the high-field half is an absorption. The resonance peak is assigned to the photoexcited $^3\pi,\pi^*$ state. This assignment is based on the broad nature of the band, which occurs due to the dipole – dipole interaction between the unpaired electrons of the triplet state. The E/A polarization pattern arises from the singlet-triplet intersystem crossing process spin selectivity that populates the three levels in the triplet manifold.
A spectrum of 5-ReAN-2 at 130 K gives a similar but narrower resonance peak (700 gauss at $g = 2$) with reverse polarization characteristics with respect to the biphenyl 5-L-1 TREPR spectrum. The polarization difference suggests that even though the resonance still originates from the $^3\pi,\pi^*$ excited state, this state is reached via a different pathway (i.e., through the metal MLCT state). If the excited state is mainly MLCT in character, one would not expect to detect a signal due to very rapid spin-lattice relaxation associated with the metal center. However, the observed signal-to-noise decrease and reduction in spectral width could suggest that the $^3\pi,\pi^*$ excited state may contain a small amount of MLCT character. Nevertheless, the data support the conclusion that the observed transient absorption does have significant $^3\pi,\pi^*$ character.
The slow-component amplitude decrease as temperature decreases in the 5-Re complexes (Table 3-4) is an example of “delayed fluorescence,” which has been observed in fullerenes\textsuperscript{144} and other $\pi$-conjugated systems.\textsuperscript{115,145} Note that in the excited-state equilibrium (Figure 3-18) the $^3\text{MLCT}$ energy is slightly higher than the $^3\pi,\pi^*$ energy, as seen in the low-temperature 5-Re emission spectra (Figure 3-6). Therefore, thermal energy is needed in order to maintain equilibrium and produce the observed $^3\text{MLCT}$ luminescence. As temperature decreases, the available thermal energy decreases, driving the equilibrium more to the $^3\pi,\pi^*$ state and decreasing the observed $^3\text{MLCT}$ emission component amplitude. Eventually, hardly any population remains in the $^3\text{MLCT}$ state after equilibration, resulting in a slow decay component which is barely detectable above the instrument baseline.\textsuperscript{108,146} The 5-ReAN complexes cannot exhibit this same “delayed fluorescence” behavior due to the larger energy difference between the two excited states.

Similar biexponential emission decays were readily observed in spectra of a ruthenium-pyrene donor-acceptor complex.\textsuperscript{147,148} A series of emission decays at different temperatures for this complex are shown in Figure 3-20. The ligand-based excited state in this case is not emissive and is isoenergetic with the metal-based $^3\text{MLCT}$ state. The observed biexponential decays are due to an excited state equilibration, and the temperature dependence (i.e., the long-lived component amplitude increases with increasing temperature) illustrates $^3\text{MLCT}$ “delayed fluorescence” via thermal back-population. This data is very similar to the decays observed for the 5-Re complexes (Figure 3-8).
Figure 3-20: Luminescence decays of \([(\text{bpy})_2\text{Ru( bpy \_pyr)})]^{2+}\) in 4:1 EtOH:MeOH at various temperatures (Ref. 147). (a) 150 K; (b) 200 K; (c) 250 K.

In order to better understand the excited-state behavior of these complexes, simulations were performed using a Runge-Kutta integrator. Decays of two excited states in equilibrium were modeled with independent decay lifetimes of 150 ns (MLCT) and 9 µs \((^3\pi,\pi^*\))

It was assumed that the \(^3\text{MLCT} \) state is the initially populated state. When \(K_{\text{eq}}\), the constant for equilibrium between the two excited states defined as

\[
\frac{k_{\text{MLCT} \rightarrow \pi,\pi^*}}{k_{\pi,\pi^* \rightarrow \text{MLCT}}} = 1 - 10, \text{ results exhibit the same } ^3\text{MLCT} \text{ emission biexponential decay observed in the experimental results. Lifetimes of the two excited-state decays are also equivalent, ranging from 100 to 300 ns. However, as } K_{\text{eq}} \text{ increased beyond 10, the } ^3\text{MLCT emission decay rapidly goes to zero with very short lifetimes (} < 5 \text{ ns), while the } ^3\pi,\pi^* \text{ decay remains largely unchanged in intensity but considerably longer (5 – 6 µs). These results mirror the 5-ReAN experimental data. Further quantitative fitting of our data was not possible due to our limited time resolution in the emission lifetime and}
transient absorption experiments. Typically, the fast lifetime decay was complete within the span of just a few data points on our fastest time response settings.

Experimental

Oligomer and Complex Synthesis

The molecules and complexes in the 5-L oligomers and 5-Re complexes were previously synthesized, and their synthesis is described in detail elsewhere.99,100

5-ReAN-2. 5-Re-2 (12 mg, 6.1 µmol) was dissolved in 20 mL methylene chloride, whereupon 5 mL of CH3CN and AgOTf (12 mg, excess) was added. The solution was stirred at room temperature overnight. A TLC (1:1 hexanes:CH2Cl2) on silica showed two spots, Rf = 1 (5-ReAN-2) and Rf = 0.6 (5-Re-2). Additional stirring and addition of acetonitrile produced the final product. AgCl was removed from the sample solution by filtration through celite on a medium-porosity glass frit, and the filtrate was reduced by rotary evaporation to produce the final product as a triflate salt. Due to the small amount of material available, further purification was impractical. IR (THF soln, cm\(^{-1}\)), 1966, 2101, 2135 (ν\(\text{C=O}\)), 2278 (ν\(\text{C≡N}\)).‡ ESI-MS calcd for C\(_{131}\)H\(_{182}\)N\(_3\)O\(_7\)Re: 2096; found: 2053 (parent – CH\(_3\)CN).

5-ReAN-3. This synthesis progressed in an analogous manner to the 5-ReAN-2 synthesis except that 5-Re-3 was used as the starting material. IR (THF soln, cm\(^{-1}\)) 1967, 2097, 2133 (ν\(\text{C=O}\)), 2280 (ν\(\text{C≡N}\)). ESI-MS calcd for C\(_{149}\)H\(_{195}\)N\(_2\)O\(_{11}\)Re: 2416; found: 2414 (parent), 2372 (parent – CH\(_3\)CN).

‡ For comparison purposes, 5-Re-2 and 5-Re-3 in a KCl pellet exhibit ν\(\text{C=O}\) stretches at 1902, 1927, and 2025 cm\(^{-1}\).46
Photophysical Measurements

All sample solutions studied are in either THF, 2-methyltetrahydrofuran (2-MTHF), or CH2Cl2. All solvents were distilled according to typical laboratory practices. All photophysical studies were conducted in 1 cm square quartz cuvettes unless otherwise noted. All room temperature studies were conducted on argon bubble-degassed solutions, and all low temperature studies were conducted on solvent glasses degassed by four freeze-pump-thaw cycles (ca. 10^{-4} Torr) unless otherwise noted. For the emission and photothermal measurements, sample concentrations were adjusted to produce “optically dilute” solutions (i.e., A < 0.20 at all wavelengths; typical final concentration is ca. 1.5 x 10^{-6} M). Transient absorption measurements were routinely performed on solutions with higher concentrations (i.e., A ≈ 0.8 – 1.0, ca. 7.5 x 10^{-6} M).

Steady state absorption spectra were recorded on either an HP 8452A diode-array or Varian Cary 100 dual-beam spectrophotometer. Corrected steady state emission measurements were conducted on a SPEX F-112 fluorimeter. Emission quantum yields were measured by relative actinometry (chapter 2), with 9,10-dicyanoanthracene (Φ_{em} = 0.89) and perylene (Φ_{em} = 0.89) in ethanol as actinometers. Time-resolved emission decays were observed with time-correlated single photon counting (FLT, Photochemical Research Associates; Excitation filter/source: Schott UG-11/H2 spark (350 nm maximum) or 405 nm IBH NanoLED-07 laser diode; Emission filter: 450 and 550 nm (5-L oligomers) or 600 nm (5-Re complexes) interference filters). Lifetimes were determined from the observed decays with DECAN fluorescence lifetime deconvolution software. Low temperature emission measurements were conducted in 1 cm diameter glass tubes contained in an Oxford Instruments cryostat connected to an Omega
CYC3200 automatic temperature controller. Transient absorption spectra were obtained on previously described instrumentation,\textsuperscript{150} with the third harmonic of a Nd:YAG laser (Spectra Physics GCR-14, 355 nm, 10 ns fwhm, 5 mJ pulse$^{-1}$) as the excitation source. Spectra for the 5-L oligomers were recorded on freeze-pump-thaw degassed solutions due to their long lifetimes and the high propensity for oxygen to quench organic triplet excited states. Primary factor analysis followed by first order (A $\rightarrow$ B) least square fits of the transient absorption data was accomplished with SPECFIT global analysis software.\textsuperscript{114} LIOAS and TRTL measurements were obtained with the setups described in chapter 2. LIOAS data (average of four data acquisitions on fresh sample and reference solutions) were obtained with both 1 and 5 MHz transducers, and LIOAS data deconvolution analysis was performed with Sound Analysis software.\textsuperscript{82,92}

Time-resolved EPR measurements were conducted on a Varian E-9 X-band spectrometer with a variable temperature attachment to allow data collection at 130 K. The signal from the microwave bridge was fed into a PAR 162 dual channel boxcar integrator via an HP461A high-frequency amplifier. The integrator signal was then fed into a PC via a data acquisition board for signal processing and analysis.\textsuperscript{151} Samples were excited at 355 nm with a Nd:YAG laser. Sample solutions were prepared in 1:1 toluene:chloroform and freeze-pump-thaw degassed.

**Electrochemical Measurements**

All electrochemical measurements were conducted on THF solutions with 0.1 M tetrabutylammonium hexafluorophosphate (TBAH, Aldrich) as the supporting electrolyte. Cyclic voltammetry measurements were performed on nitrogen bubble-degassed solutions with a BAS CV-27 Voltammograph and MacLab Echem software or a BAS
CV-50W Voltammetric Analyzer and accompanying software. Platinum disk and glassy carbon working electrodes, platinum wire auxiliary electrode, and silver wire quasi-reference electrode were used, and potentials were corrected to values versus SCE via an internal ferrocene standard. A scan rate of 100 mV sec\(^{-1}\) was employed in all measurements.

**Langmuir-Blodgett Film Preparation**

A KSV 2000 system (Stratford, CT) was used in combination with a homemade, double barrier Teflon trough for the LB film preparation. The surface area of the trough is 343 cm\(^2\) (36.5 cm × 9.4 cm). A platinum Wilhelmy plate, suspended from a KSV microbalance, measured the surface pressure. Subphases were pure water with a resistivity of 17-18 MΩ cm\(^{-1}\) produced from a Barnstead NANOpure (Boston, MA) purification system. LB films were prepared from premixed chloroform solutions of 5-Ru-2 and 5-L-3 (typical concentrations were 2 x 10\(^{-4}\) M). Spreading volumes of 100 to 150 µL were used, and the films were compressed to and maintained at a pressure of 20 mN m\(^{-1}\) for film transfer. Glass substrates were drawn through the monolayer at a rate of 8 mm min\(^{-1}\) during the film transfer.
5-5' MONOPHENYL OLIGOMER PHOTOPHYSICS

Introduction

The photophysical work on the 5-L oligomers and 5-Re complexes led to insight concerning the nature of the interactions between π-conjugated systems and MLCT chromophores, prompting additional oligomer synthesis and subsequent photophysical study. A series of oligomers (5-LP oligomers) were synthesized containing monophenyl subunits in the conjugated backbone in contrast to the biphenyl units used in the 5-L oligomers. These oligomers contain a “core” consisting of a 5,5’-(2,2’-bipyridyl) unit and primary repeat units on either side containing 1,4-diethynylbenzene and dialkoxybenzenes and were synthesized with similar synthetic methodologies used for the 5-L oligomers.64,99 Complexes (5-ReP complexes) were synthesized ligating these oligomers to the –ReI(CO)3Cl chromophore.99,100 The structures of the 5-LP oligomers and 5-ReP complexes are shown in Figure 4-1. Extensive photophysical and photothermal studies were conducted on these molecules, and the results are presented in this chapter.

Results

Several photophysical parameters from various measurements are presented for the 5-LP oligomers and 5-ReP rhenium complexes in Tables 4-1 and 4-2, respectively. The individual measurements are discussed below.
Figure 4-1: 5-LP oligomer and 5-ReP rhenium complex structures.

Table 4-1: 5-LP oligomer photophysics.

<table>
<thead>
<tr>
<th></th>
<th>5-LP-2</th>
<th>5-LP-3</th>
<th>5-LP-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>λ_{max} / nm</td>
<td>334 (5.45)</td>
<td>338 (7.93)</td>
<td>334 (12.7)</td>
</tr>
<tr>
<td>(ε_{max} / 10^4 M^{-1} cm^{-1})</td>
<td>396 (9.13)</td>
<td>406 (14.6)</td>
<td>414 (25.6)</td>
</tr>
<tr>
<td>Emission</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>λ_{max, 298 K} / nm</td>
<td>460</td>
<td>449</td>
<td>452</td>
</tr>
<tr>
<td>λ_{max, 80 K} / nm</td>
<td>471</td>
<td>473</td>
<td>471</td>
</tr>
<tr>
<td>φ_{em}</td>
<td>0.72</td>
<td>0.77</td>
<td>0.87</td>
</tr>
<tr>
<td>k_r / 10^8 s^{-1}</td>
<td>6.55</td>
<td>8.42</td>
<td>13.9</td>
</tr>
<tr>
<td>k_{irr} + k_{isc} / 10^8 s^{-1}</td>
<td>2.55</td>
<td>2.52</td>
<td>2.08</td>
</tr>
<tr>
<td>TA</td>
<td>375</td>
<td>410</td>
<td>277</td>
</tr>
</tbody>
</table>

Note: Measurements were conducted on freeze-pump-thaw degassed THF solutions. Additional experimental conditions are discussed in the text.
Table 4-2: **5-ReP** rhenium complex photophysics.

<table>
<thead>
<tr>
<th></th>
<th>5-ReP-2</th>
<th>5-ReP-3</th>
<th>5-ReP-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \lambda_{\text{max}} ) / nm</td>
<td>331 (6.51)</td>
<td>348 (10.8)</td>
<td>338 (14.7)</td>
</tr>
<tr>
<td>( (\epsilon_{\text{max}} / \text{10}^4 \text{ M}^{-1} \text{ cm}^{-1}) )</td>
<td>438 (6.78)</td>
<td>442 (10.2)</td>
<td>393 (18.7)</td>
</tr>
<tr>
<td>Emission</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \lambda_{\text{max, 298 K}} ) / nm</td>
<td>659</td>
<td>650</td>
<td>646</td>
</tr>
<tr>
<td>( \lambda_{\text{max, 80 K}} ) / nm</td>
<td>659</td>
<td>652</td>
<td>579, 666</td>
</tr>
<tr>
<td>TA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \tau_{298 \text{ K}} ) / ns</td>
<td>123</td>
<td>181</td>
<td>164</td>
</tr>
<tr>
<td>Electrochem</td>
<td>( E_{1/2}^{\text{red}} ) / V vs. SCE</td>
<td>-0.79(^a)</td>
<td>-0.82(^b)</td>
</tr>
</tbody>
</table>

Note: Measurements were conducted on argon bubble-degassed THF solutions. Additional experimental conditions are discussed in the text. \(^a\)Pt disc working electrode. \(^b\)GCE disc working electrode. \(^c\)No resolvable wave was obtained for **5-ReP-4**.

**Absorption Spectra**

Absorption spectra were recorded on dilute THF solutions of the various oligomers and rhenium complexes, and molar absorptivity values (\( \epsilon, \text{ M}^{-1} \text{ cm}^{-1} \)) were calculated based on (3-1). Absorption spectra for the **5-LP** oligomers and **5-ReP** complexes are shown in Figure 4-2, and absorption maxima for all oligomers and complexes are listed in Tables 4-1 and 4-2, respectively.

The oligomer spectra exhibited the same two \( \pi, \pi^* \) transitions observed in the **5-L** oligomers (Figure 3-2), and the **5-LP** absorption maxima are relatively equivalent with analogous **5-L** oligomers. Note that the band energies red-shift with increasing conjugation length, which is counter to the consistent maximum observed in the **5-L** oligomers and suggests less-efficient \( \pi \)-conjugation disruption with the monophenyl subunits compared to the twisted biphenyl subunits. The rhenium complex spectra exhibited the same two \( \pi, \pi^* \) transitions red-shifted from uncomplexed oligomer values,
and 5-Re and 5-ReP absorption maxima are equivalent. This shift reflects increased conjugation due to forced bipyridine planarity via complexation as discussed in chapter 3. The low-energy band remains constant in the complex spectra, while the high-energy band red-shifts with increasing oligomer length. As explained previously, this observation suggests the existence of isolated “central” and “peripheral” chromophores within the same molecule as a result of oligomer backbone conjugation breaks.

Furthermore, 5-ReP-4 (like 5-Re-4) exhibits absorptions seen both in the 5-LP oligomers (338 and 393 nm) and 5-ReP complexes (∼ 450 nm shoulder), further confirming the isolation of multiple chromophores in a single complex. Like the 5-Re spectra, any MLCT-based absorptions are obscured by the more intense oligomer π,π* transitions.

Emission Spectra

The 5-LP oligomer emission spectra in optically dilute 2-MTHF solutions at temperatures ranging from room temperature to 80 K are shown in Figure 4-3. Emission maxima at room temperature and 80 K are listed in Table 4-1. The oligomer room temperature fluorescence spectra exhibited the same strong band assigned to the long-axis polarized $^1\pi,\pi^*$ state in the 5-L spectra (Figure 3-3). The fluorescence maximum remains constant throughout the oligomer series and is slightly blue-shifted relative to the 5-L oligomer maxima. The (0,1) shoulder band intensity clearly decreases relative to the (0,0) band as the oligomer size increases, reflecting an electron-vibration coupling decrease with increasing oligomer length due to increased $^1\pi,\pi^*$ state delocalization. This coupling decrease is smaller than that observed for the 5-L-2, since 5-LP-2 does not exhibit the (0,1) shoulder. The difference is likely due to the smaller size of the 5-LP-2 oligomer, although the size difference is not very large. No phosphorescence was
detected at low temperatures for any of the 5-LP oligomers. Emission quantum yields were measured for the oligomers using (2-17), and calculated values are listed in Table 4-1. Note that the quantum yields increase as the oligomer size increases. While quantum yields agree well for 5-L-2 and 5-LP-2, the 5-L-3 and 5-L-4 quantum yields are smaller than their monophenyl counterparts.

![Absorbance spectra in THF](image)

Figure 4-2: Absorbance spectra in THF. (a) 5-LP oligomers; (b) 5-ReP complexes.
Figure 4-3: Emission spectra of the 5-LP oligomers in 2-MTHF (360 nm excitation) at various temperatures ranging from 298 to 80 K. Emission intensity decreases with decreasing temperature except as noted, and spectra are in 30 K increments. (a) 5-LP-2; (b) 5-LP-3; (c) 5-LP-4 (note unique low temperature trends).

All oligomer fluorescence red-shifts with decreasing temperature, exhibiting the same behavior displayed by the 5-L oligomers. This observation supports the aggregation conclusions discussed in chapter 3. One of the goals of studying the 5-LP oligomers was to see if the monophenyl subunit might lessen the initial intramolecular aggregation effect by removing the biphenyl subunit that is restricted by steric. However, the
photophysical data clearly indicates that similar aggregational effects are observed for both the biphenyl and monophenyl oligomers. Therefore, it is believed that the long alkyl side chains rather than the oligomer backbone structure provides the major impetus for the initial “intramolecular excimer” formation process (Figure 3-17), although the monophenyl-based backbone exhibits some of the same rotational flexibility observed in the biphenyl-based oligomers. One interesting difference in the 5-LP oligomers, however, was observed in the 5-LP-4 temperature-dependent behavior. After the 2-MTHF sample solution freezes (ca. 170 K), the excimer-based emission increases in intensity and remains at a constant energy. This observation is duplicated to a much lesser extent in the other 5-LP oligomers and is similar to the temperature dependence typically observed in oligomer chromophores.108

The 5-ReP complex emission spectra in optically dilute 2-MTHF solutions at temperatures ranging from 298 to 80 K are shown in Figure 4-4. Emission maxima at 298 and 80 K are listed in Table 4-2. As observed for the 5-Re complexes, a weak emission corresponding to free oligomer π,π* fluorescence was observed in the complex samples and is considered a trace free oligomer impurity. The rhenium complexes exhibited a weak, low-energy emission that increased in intensity with decreasing temperature similar to the 5-Re complexes (Figure 3-5). The emission band structure at 80 K again appears to consist of an overlapping structureless 575 – 600 nm band that blue-shifts with decreasing temperature and structured 650 nm band that remains constant with decreasing temperature. The structureless band increases in intensity with increasing oligomer size, leading to a clear resolution of the two emission components in the
5-ReP-4 spectrum. Attempts were made to measure the emission quantum yield of the 5-ReP complexes, but they were too weak to be effectively measured (< $10^{-4}$).

The superimposed emission spectra at low temperatures warranted excitation polarization studies to see if behavior similar to 5-Re-3 was observed (Figure 3-6). Spectra were collected on an 80 K 2-MTHF 5-ReP-3 solution at various emission wavelengths. Excitation spectra and $r(\lambda)$ values are shown in Figure 4-5 along with the 80 K emission spectrum that indicates the examined wavelengths. The high-energy structureless shoulder exhibits a high anisotropy value (0.3 maximum) that decreases with decreasing excitation wavelength, exhibiting a typical anisotropy behavior for similar absorbing and emitting excited states. Anisotropies recorded at the structured emission maximum exhibit a lower value (0.07) that does not vary across the excitation spectrum, indicating nearly unpolarized emission light and a large triplet phosphorescence component in the emission at that wavelength. This polarization data exhibits trends identical to those observed for 5-Re-3, so the conclusions stated earlier for the low temperature emission apply. Again, the structured emission is oligomer-based $^{3} \pi, \pi^{*}$ phosphorescence and the overlapping structureless emission is metal-based MLCT luminescence. It is clear that changing from biphenyl to monophenyl subunits does not alter the temperature-dependent emission behavior of the complex other than increasing the intensity of the MLCT luminescence. This increase may be due to the increased rigidity or planarity of the monophenyl-based oligomer backbone, which might lessen the likelihood of nonradiative decay via molecular rotation and account for the linear relationship between MLCT intensity and oligomer length.
Figure 4-4: Emission spectra of the 5-ReP complexes in 2-MTHF (450 nm excitation) at various temperatures ranging from 298 to 80 K. Emission intensity increases with decreasing temperature, and spectra are in 30 K increments. (a) 5-ReP-2; (b) 5-ReP-3; (c) 5-ReP-4.
Emission Lifetimes

Emission decay lifetimes were recorded for the 5-LP oligomers in 2-MTHF at various temperatures and emission wavelengths. Both monoexponential and biexponential decays were observed, and lifetime results are listed in Table 4-3.
Table 4-3: Variable temperature emission decay times of the 5-LP oligomers.

<table>
<thead>
<tr>
<th>Oligomer a</th>
<th>T / K</th>
<th>( \alpha_1 )</th>
<th>( \tau_1 ) / ps</th>
<th>( \alpha_2 )</th>
<th>( \tau_2 ) / ps</th>
<th>( \alpha_1 )</th>
<th>( \tau_1 ) / ps</th>
<th>( \alpha_2 )</th>
<th>( \tau_2 ) / ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-LP-2</td>
<td>298</td>
<td>1</td>
<td>1099.0</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>1138.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>1</td>
<td>967.0</td>
<td>-</td>
<td>-</td>
<td>0.997</td>
<td>352.0</td>
<td>0.003</td>
<td>7707.0</td>
</tr>
<tr>
<td>5-LP-3</td>
<td>298</td>
<td>1</td>
<td>914.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>1</td>
<td>785.5</td>
<td>-</td>
<td>-</td>
<td>0.974</td>
<td>1326.4</td>
<td>0.026</td>
<td>6701.7</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.981</td>
<td>1332.4</td>
<td>0.019</td>
<td>7863.4</td>
</tr>
<tr>
<td>5-LP-4</td>
<td>298</td>
<td>1</td>
<td>627.4</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>627.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.950</td>
<td>614.8</td>
<td>0.050</td>
<td>4529.3</td>
<td>0.970</td>
<td>881.8</td>
<td>0.030</td>
<td>4346.2</td>
</tr>
</tbody>
</table>

\(^a\)2-MTHF solutions; 405 nm excitation. Biexponential decays were calculated based on (3-3). Errors for the fit parameters are ± 5%.

On the blue side of the fluorescence (450 nm), decay kinetics are single exponential, decrease in lifetime with decreasing temperature and are roughly equivalent to the 5-L oligomer emission lifetimes (Table 3-3). On the red side of the fluorescence band (550 nm), decays are monoexponential at room temperature (except 5-ReP-4) and biexponential with a long-lived component (4 – 7 ns) at reduced temperatures. These observations duplicate the 5-L oligomer data and are reminiscent of excimer species formation in solution at reduced temperatures via extended aggregation, resulting in the longer-lived emission. Values for \( k_r \) and \( k_{nr} + k_{isc} \) at 298 K were also calculated based on (4-1) and are listed in Table 4-1.

\[
k_r = \frac{\phi_{em}}{\tau_{em}} \quad (4-1a)
\]

\[
k_{nr} + k_{isc} = \frac{k_r (1 - \phi_{em})}{\phi_{em}} \quad (4-1b)
\]
The $k_r$ values clearly increase while $k_{nt} + k_{isc}$ decreases as oligomer size increases, due to the increase in electron delocalization afforded by the size increase. These values and trends are very similar to those determined for the 5-L oligomers (Table 3-10), suggesting similar excited-state manifolds for the two oligomer series.

Emission decay lifetimes were recorded for the 5-ReP complexes in 2-MTHF at various temperatures, and lifetime results are listed in Table 4-4.

Table 4-4: Variable temperature emission decay times of the 5-ReP complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>T / K</th>
<th>$\alpha_1$</th>
<th>$\tau_1$ / ns</th>
<th>$\alpha_2$</th>
<th>$\tau_2$ / ns</th>
<th>$\alpha_1$</th>
<th>$\tau_1$ / ns</th>
<th>$\alpha_2$</th>
<th>$\tau_2$ / ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-ReP-2</td>
<td>298</td>
<td>0.999</td>
<td>0.476</td>
<td>0.001</td>
<td>375.4</td>
<td>0.996</td>
<td>0.476</td>
<td>0.004</td>
<td>255.0</td>
</tr>
<tr>
<td></td>
<td>171</td>
<td>0.999</td>
<td>0.202</td>
<td>0.001</td>
<td>56.4</td>
<td>0.996</td>
<td>4.961</td>
<td>0.004</td>
<td>2644</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.999</td>
<td>0.202</td>
<td>0.001</td>
<td>91.5</td>
<td>0.995</td>
<td>4.961</td>
<td>0.005</td>
<td>2801</td>
</tr>
<tr>
<td>5-ReP-3</td>
<td>298</td>
<td>0.999</td>
<td>0.200</td>
<td>0.001</td>
<td>86.78</td>
<td>0.995</td>
<td>1.85</td>
<td>0.005</td>
<td>754.7</td>
</tr>
<tr>
<td></td>
<td>172</td>
<td>0.999</td>
<td>0.200</td>
<td>0.001</td>
<td>48.89</td>
<td>0.995</td>
<td>10.0</td>
<td>0.005</td>
<td>3657</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.997</td>
<td>0.200</td>
<td>0.003</td>
<td>7.363</td>
<td>0.997</td>
<td>10.0</td>
<td>0.003</td>
<td>5097</td>
</tr>
<tr>
<td>5-ReP-4</td>
<td>298</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.996</td>
<td>0.736</td>
<td>0.004</td>
<td>176.9</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>1</td>
<td>1.103</td>
<td>-</td>
<td>-</td>
<td>&gt; 0.999</td>
<td>1.107</td>
<td>&lt; 0.001</td>
<td>b</td>
</tr>
</tbody>
</table>

a2-MTHF solutions; 405 nm excitation. Biexponential decays were calculated based on (3-3). Errors for the fit parameters are ±5%. bDecay component was too weak to accurately measure the lifetime.

Emission decays of the structured $\pi,\pi^*$ phosphorescence (650 nm) are biexponential at all temperatures and characterized by a large amplitude, short-lived component ($\tau \approx 1 – 4$ ns at room temperature, $\alpha > 0.95$) and a low amplitude longer-lived component ($\tau = 250 – 750$ ns at room temperature, $\alpha \approx 0.005$). Only the long-lived component shows significant temperature dependence, increasing to a lifetime of several microseconds at 80 K. As the oligomer size increases, the amplitude of the longer-lived
component decreases to the point that it is too weak to accurately measure in 5-ReP-4 at 80 K. These lifetimes (even at room temperature) are longer than the analogous 5-Re complex emission lifetimes, suggesting a lower $^3\pi,\pi^*$ energy in the monophenyl-based oligomer complexes that would draw more electronic population from the $^3$MLCT state and upset the excited-state equilibrium.

Furthermore, $^3$MLCT luminescence emission decays (550 nm) also exhibit biexponential decays, but the majority of the decay (99.9% of the total amplitude) is represented by a rapid decay component. The long-lived component is much shorter ($\tau < 100$ ns at room temperature) and is so small in amplitude that its lifetime is difficult to accurately determine. This behavior is similar to the lifetime data of the 5-ReAN complexes in chapter 3, where the shorter lifetime stemmed from the “pure” $^3$MLCT excited state after equilibrium disruption. Clearly, the monophenyl-based complexes exhibit better separation of the two excited-state emissions than the biphenyl-based complexes.* Alternatively, 5-LP impurities in the 5-ReP samples could lead to the short 550 nm lifetimes originating from free ligand fluorescence.

**Transient Absorption Spectra**

Transient absorption spectra were recorded for all the oligomers and complexes in THF solutions. Transient absorption spectra for the 5-LP oligomers are shown in Figure 4-6. Excited state lifetimes obtained from factor analysis and global decay fitting\textsuperscript{114} are listed in Table 4-1. Equivalent first order decays were observed for all features of the various transient absorption spectra. These spectra are very similar to their 5-L analogues

---

* Emission lifetimes for the 5-Re complexes were independent of the probed wavelength.
(Figure 3-8), with all oligomers exhibiting long-axis $\pi,\pi^*$ ground state absorption bleaching and a broad, long-lived excited-state absorption extending into the near-IR. Excited state lifetimes are very long (300 – 400 $\mu$s), which is typical for organic triplets. These transients, like the corresponding 5-L spectral features, are assigned to oligomer $3\pi,\pi^*$ excited states.

Transient absorption spectra for the 5-ReP complexes in THF solutions are shown in Figure 4-7. Excited state lifetimes obtained from factor analysis and global decay fitting are listed in Table 4-2. Generally, equivalent first order decays were observed for all spectral features. However, the 450 nm bleach exhibited biexponential decay in certain samples with a rapid decay component ($\tau < 1$ ns) and longer-lived decay component with lifetimes that corresponded to the other transients in the spectrum. This behavior is due to trace 5-LP free oligomer impurities as described in the previous chapter. Obtained spectra are very similar to the 5-Re complexes (Figure 3-9), with a 450 nm ground state $\pi,\pi^*$ bleach and transient absorptions at 500 and 700 nm stretching into the near-IR. The transient decay lifetimes for 5-ReP-2 and 5-ReP-3 are shorter than the room temperature 650 nm emission decay lifetime shown in Table 4-4. This observation further suggests that the 650 nm emission is mainly $3\pi,\pi^*$ phosphorescence in nature due to its longer lifetime. While the transient absorption spectra stem from this same excited state, their lifetimes may be shorter due to the influence of the excited-state equilibrium on the lifetime. Furthermore, the transient absorption may have an MLCT contribution, which would shorten the lifetime. This explanation is definitely possible for 5-ReP-4, which has equivalent TA and emission lifetimes and a different, flatter TA excited-state absorption, which may be indicative of an $3\text{MLCT}$ state. Based on these results and the
5-Re spectra, the transients are assigned to oligomer-based $^3\pi,\pi^*$ transitions (except for 5-ReP-4) with the assumption that an excited-state equilibrium exists between the $^3\pi,\pi^*$ and $^3$MLCT states as seen in the 5-Re complexes.

Electrochemistry

Cyclic voltammetry was performed on the 5-ReP complexes in THF with 0.1 M TBAH as the supporting electrolyte. Quasi-reversible reduction waves were observed in all cases (except 5-ReP-4), and reduction half-wave potentials are listed in Table 4-2. Note that the reduction potential is similar for the two complexes but about 0.1 V less negative (i.e., easier to reduce) than the analogous 5-Re complexes, which implies that the oligomer conjugation extends to a greater degree in the monophenyl-based oligomer complexes to facilitate easier electron addition to the complexed oligomer.

Discussion

For the majority of the presented photophysical measurements, the monophenyl and biphenyl subunit-based oligomers and rhenium complexes have very similar properties. However, some subtle differences warrant further consideration. Since the oligomers differ only by the presence of monophenyl instead of biphenyl subunits, the photophysical differences must stem from this change. The biphenyl subunit is more likely to be twisted due to steric interactions of the $\alpha$-hydrogens on adjacent phenyl rings, producing conjugation breaks as described in chapter 1 and involved in much of the photophysics presented in chapter 3. While the monophenyl-based oligomers would not have this same steric hinderance, some flexibility and rotational ability remains in the monophenyl-based backbone to produce some of the results described in this chapter.
Figure 4-6: Transient absorption spectra of the 5-LP oligomers in freeze-pump-thaw degassed THF solutions. Arrows show the spectral trend with increasing time after laser excitation. (a) 5-LP-2 (Transients are 80 µs increments after laser excitation; (b) 5-LP-3 (Transients are 40 µs increments after laser excitation); (c) 5-LP-4 (Transients are 40 µs increments after laser excitation).
Figure 4-7: Transient absorption spectra of the 5-ReP complexes in argon bubble-degassed THF solutions. Arrows show the spectral trend with increasing time after laser excitation. (a) 5-ReP-2 (Transients are 160 ns increments after laser excitation; (b) 5-ReP-3 (Transients are 80 ns increments after laser excitation); (c) 5-ReP-4 (Transients are 80 ns increments after laser excitation).
The 5-LP oligomer absorption spectra (Figure 4-2) exhibit red-shifting with increasing oligomer length, indicating that the monophenyl subunit is less effective in restricting backbone delocalization. The twisted biphenyl subunits in the 5-L oligomers prevent this extended delocalization and lead to the constant absorption maxima across the oligomer series (Figure 3-2). However, the 5-Re and 5-ReP complexes share similar absorption spectral trends, suggesting the isolation of organic and metal-based chromophores in the same oligomer. It is possible that the forced planarity of the central bipyridine upon complexation may induce oligomer twisting in the 5-LP oligomers that does not exist in the unligated oligomer.

In order to better understand the differences between the two oligomer series, literature precedents are investigated with an interesting result. The absorption spectrum of didodecoxy-substituted poly(phenyleneethynylene) in THF solution (Figure 1-3) exhibited a 425 nm maximum.5 Furthermore, model trimer and pentamer oligomers with the same repeat structure feature absorption maxima at 376 and 418 nm, respectively.25 Clearly, a red-shift is observed with increasing oligomer size, which is replicated in our oligomers to a lesser degree. The smaller red-shift in the 5-LP oligomers compared to the PPE work may be due to the alkyl side-chain size increase to an eighteen-carbon chain. This increase, coupled with the presence of alkyl chains on only half the phenyl rings in the 5-LP oligomer backbone, may provide a thermodynamic impetus for backbone twisting. The alkyl-substituted phenyl rings may twist in unison, while the non-substituted rings may resist this movement and twist independently (or vice versa). Unfortunately, very little precedent is found that addresses this PPE backbone twisting issue.
Note that the 5-LP fluorescence maximum is blue-shifted 5 nm from analogous 5-L values and remains fairly constant across the oligomer series, suggesting that the $^1\pi,\pi^*$ excited state is higher in energy for the 5-LP oligomers. The different conclusions presented by the absorption (more delocalized excited state) and emission (higher excited state energy) spectra suggest that the initial photoexcited state probed by the absorption spectra and the lower-energy emitting state are structurally different, perhaps due to a change in oligomer conformation (i.e., twisting or canting of the various phenyl rings).

The higher 5-LP oligomer $^1\pi,\pi^*$ energy should result in a higher emission quantum yield based on the energy gap law. The quantum yields for 5-L-2 and 5-LP-2 are identical, which is not surprising since these two oligomers have identical chromophores if the 5-L-2 biphenyl subunits are twisted. For 5-LP-3 and 5-LP-4, higher quantum yields are observed than their biphenyl analogues, confirming this conclusion. Recall also that the emission quantum yield increases with increasing oligomer size in the 5-LP oligomers, which is opposite of the trend observed in the 5-L oligomers. The reversed trend is surprising, since the greater delocalization in the 5-LP oligomers should increase $\phi_{isc}$ and decrease $\phi_{em}$. The propensity of these oligomers to aggregate in solution might lead to the increased quantum yields, since aggregates would erroneously increase the measured value.

The unique temperature-dependent emission of 5-LP-4 (Figure 4-3) is interesting, as the excimer exhibited spectral trends (intensity increase with decreasing temperature) typically observed for organic molecules in the 2-MTHF glass. This same trend is observed for the other 5-LP oligomers, but the intensity increase is very small compared to 5-LP-4. The greater response observed for this oligomer could also be due to the
increased rigidity of the oligomer backbone due to the monophenyl subunits, which might inhibit efficient aggregate formation and impair the non-radiative energy transfer decay pathway. The mixed alkyl chain lengths of 5-LP-4 might further contribute to this effect, as solvent pockets could be trapped within the aggregate and lessen its ability to quench the monomer fluorescence.

The 5-ReP-4 complex is unique in the sense that it has a different transient absorption spectrum (Figure 4-7). The “flatter” nature of the excited-state absorption is less indicative of the $^3\pi,\pi^*$ excited-state absorption observed for all the other biphenyl and monophenyl-based free oligomers and rhenium complexes, which leads to the conclusion that this transient may originate from the $^3$MLCT state.† It is unclear why 5-ReP-4 would have this different excited-state behavior, as 5-Re-4 did not exhibit results counter to the trends set forth by the rest of its complex series in chapter 3. The differing sidechain structure of 5-ReP-4 is not likely to alter the metal-based excited state energetics, but this is the only structural difference in this complex. Further studies, including time-resolved infrared spectroscopy, will hopefully better elucidate this excited-state behavior.

Experimental

Oligomer and Complex Synthesis

The 5-LP oligomers and 5-ReP complexes were previously synthesized, and their synthesis is described in detail elsewhere.99,100

† A similar TA spectrum is seen for P4-Os in chapter 6 (Figure 6-12), which assists in the 5-ReP-4 assignment.
Photophysical Measurements

All sample solutions studied were in either THF or 2-MTHF. All solvents were distilled according to typical laboratory practices. All photophysical studies were conducted with the same instrumentation and techniques described in chapter 3.

Electrochemical Measurements

All electrochemical measurements were conducted on THF solutions with TBAH as the supporting electrolyte. Cyclic voltammetry measurements were performed with the same procedures on the same instrumentation described in chapter 3.
4,4’ OLIGOMER PHOTOPHYSICS

Introduction

After extensive photophysical work with the linear 5,5’-substituted oligomers, a different oligomer geometry which could significantly affect its photophysics was considered. A “bent” oligomer series, where the ethynylene substitutions on the central 2,2’-bipyridine occur at the 4,4’ positions was chosen for experimentation. This position change is significant in the sense that the conjugated oligomer periphery is now in line with the rhenium bipyridine MLCT dipole. Also, the overall dipole moment and wavefunction of the oligomer itself will change by this structural shift, which might allow better ligand and metal based excited state resolution than the 5,5’ oligomer rhenium complexes presented in chapters 3 and 4. Previous studies\textsuperscript{16,152} on \(\pi\)-conjugated polymers showed that backbone structure can have a large effect on the excited state energy manifold. Therefore, three “bent” PPE-type oligomers (4-L-1, 4-L-2, and 4-L-3) were synthesized,\textsuperscript{99} along with complexes made with the Re\(\text{I}(\text{CO})_3\text{Cl}\) (4-Re-1, 4-Re-2, 4-Re-3) and Re\(\text{I}(\text{CO})_3(\text{NCCH}_3)^+\) (4-ReAN-3) chromophores. All the structures discussed in this chapter are illustrated in Figure 5-1.

Results

Various photophysical parameters from many different measurements for the 4-L oligomers and 4-Re rhenium complexes are listed in Tables 5-1 and 5-2, respectively.
All the oligomers and rhenium complexes were soluble in THF, 2-MTHF, and CH₂Cl₂ to similar degrees as the 5,5’-substituted oligomers and complexes. No solubility improvement was observed in more polar solvents.

Figure 5-1: 4-L oligomer and 4-Re complex structures.
### Table 5-1: 4-L oligomer photophysics.

<table>
<thead>
<tr>
<th></th>
<th>4-L-1</th>
<th>4-L-2</th>
<th>4-L-3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Absorption</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda_{\text{max}}$ / nm</td>
<td>296 (4.56)</td>
<td>320 (9.84)</td>
<td>332 (9.51)</td>
</tr>
<tr>
<td>($\varepsilon_{\text{max}}$ / 10$^4$ M$^{-1}$ cm$^{-1}$)</td>
<td>346 (2.67)</td>
<td>384 (10.4)</td>
<td>388 (12.9)</td>
</tr>
<tr>
<td><strong>Emission</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda_{\text{max, 298 K}}$ / nm</td>
<td>415</td>
<td>422</td>
<td>426</td>
</tr>
<tr>
<td>$\lambda_{\text{max, 80 K}}$ / nm</td>
<td>430, 614</td>
<td>427, 614</td>
<td>433</td>
</tr>
<tr>
<td>$\phi_{\text{em}}$</td>
<td>0.77</td>
<td>(0.91)$^{a}$</td>
<td>(0.96)$^{a}$</td>
</tr>
<tr>
<td>TA $\tau_{298 \text{K}}$ / $\mu$s</td>
<td>166.4</td>
<td>231.3</td>
<td>348.1</td>
</tr>
</tbody>
</table>

Note: Measurements were conducted on freeze-pump-thaw degassed THF solutions. Additional experimental conditions are discussed in the text. $^{a}$Values are erroneously high, see text for details.

### Table 5-2: 4-Re rhenium complex photophysics.

<table>
<thead>
<tr>
<th></th>
<th>4-Re-1</th>
<th>4-Re-2</th>
<th>4-Re-3</th>
<th>4-ReAN-3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Absorption</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda_{\text{max}}$ / nm</td>
<td>314 (4.31)</td>
<td>324 (7.30)</td>
<td>340 (11.1)</td>
<td>343 (7.70)</td>
</tr>
<tr>
<td>($\varepsilon_{\text{max}}$ / 10$^4$ M$^{-1}$ cm$^{-1}$)</td>
<td>378 (2.25)</td>
<td>408 (5.00)</td>
<td>408 (8.25)</td>
<td>425 (4.92)</td>
</tr>
<tr>
<td><strong>Emission</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda_{\text{max, 298 K}}$ / nm</td>
<td>670</td>
<td>678</td>
<td>615</td>
<td>620</td>
</tr>
<tr>
<td>$\lambda_{\text{max, 80 K}}$ / nm</td>
<td>610</td>
<td>609</td>
<td>621</td>
<td>617</td>
</tr>
<tr>
<td>$\phi_{\text{em}}$</td>
<td>0.0032</td>
<td>0.0044</td>
<td>0.0046</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>TA $\tau_{298 \text{K}}$ / ns</td>
<td>37</td>
<td>183.4</td>
<td>329.7</td>
<td>33800</td>
</tr>
<tr>
<td><strong>Electrochem</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_{1/2}^{\text{red}}$ / V vs. SCE</td>
<td>-0.94$^{a}$</td>
<td>-0.91$^{b}$</td>
<td>-0.89$^{a}$</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Note: Measurements were conducted on argon bubble-degassed THF solutions (except 4-ReAN-3 transient absorption measurements, which were CH$_2$Cl$_2$ solutions). Additional experimental conditions are discussed in the text. $^{a}$GCE disc working electrode. $^{b}$Pt disc working electrode.

### Absorption Spectra

Absorption spectra of the 4-L oligomers and 4-Re rhenium complexes in THF solutions, with absorptivity values calculated based on (3-1), are shown in Figure 5-2. Absorption maxima are listed for the oligomers and complexes in Tables 5-1 and 5-2, respectively.
The ligand absorption spectra exhibited two intense $\pi,\pi^*$ absorption bands that are similar to those observed in the 5-L and 5-LP oligomers (Figures 3-2 and 4-2). However, the 4-L oligomers are blue-shifted by 20 nm with respect to the “linear” oligomers. The absorptivity values remain high, which is expected for conjugated organic systems. The lowest energy band experiences a significant red-shift from 4-L-1 to 4-L-2 but does not exhibit further significant shifting in 4-L-3. This trend mirrors the 5-L spectral data, so it can be concluded that conjugation breaks also occur in the 4-L oligomers. This
conclusion is not surprising since the structural repeat units do not change from the “linear” species.

The rhenium complex absorption spectra exhibited two strong bands that red-shift about 20 nm from the free ligand spectra. These bands are the $\pi,\pi^*$ oligomer absorptions observed in the 4-L spectra, and the red-shift is due to complexation of the rhenium chromophore and the subsequent conjugation increase. This observation is similar to the 5-Re and 5-ReP spectra, but the shift is smaller for the 4-Re complexes. In the 4-Re-1 spectrum, a distinct shoulder is observed on the red side of the low-energy absorption band. This shoulder is the singular evidence of an unobscured MLCT absorption seen for the PPE-type oligomer complexes, as the $\pi,\pi^*$ transitions in the remaining complexes are too intense to permit its observation. Note that the 4-Re complex low-energy absorption band continues to increase in intensity and red-shift with increasing oligomer size. The 5-Re complexes, however, exhibit constant low-energy absorptions, suggesting a “constant” chromophore in the middle of the oligomer (Figure 3-2). Obviously, the 4-Re central chromophore is not efficiently isolated from the “peripheral” chromophores at the oligomer ends, which may influence the additional red-shift seen in the 4-L spectra.

Another possibility is that the 4-L oligomer is now in line with the MLCT transition dipole, which may influence the transition energy.

**Emission Spectra**

The 4-L oligomer emission spectra in optically dilute 2-MTHF solutions at temperatures ranging from room temperature to 80 K are shown in Figure 5-3, and the emission maxima at room temperature and 80 K are listed in Table 5-1.
The spectra exhibit strong $\pi,\pi^*$ fluorescence that is analogous to the $5$-$L$ and $5$-$LP$ spectra (Figures 3-3 and 4-3). The emission maxima do not vary across the oligomer series, suggesting that the $^1\pi,\pi^*$ energy remains constant with increasing oligomer size. The (0,1) shoulder also decreases in intensity relative to the (0,0) band as oligomer size increases, which duplicates the $5$-$L$ results and again suggests increased $^1\pi,\pi^*$
delocalization in the larger oligomers. However, unlike the 5-L and 5-LP oligomers, phosphorescence was observed at low temperatures for oligomers 4-L-1 and 4-L-2 as a structured emission with a 614 nm maximum. Note that the position of this emission is very similar to that observed in the 5-Re and 5-ReP complexes, which was assigned to the oligomer $^3\pi,\pi^*$ state (Figures 3-5 and 4-4). The phosphorescence observed for 4-L-1 and 4-L-2 is clearly due to a different excited-state wavefunction and possible spin-orbit coupling increase resulting from the “bent” geometry.

The oligomer fluorescence red-shifts with decreasing temperature and decreases in intensity, resulting in a broad low temperature emission. Oligomer 4-L-1, however, exhibits a unique intensity increase concurrent with the red-shift from 298 to 200 K before a dramatic fluorescence quenching at 190 K coinciding with phosphorescence initiation. This photophysical trend is identical to the observations for the 5-L and 5-LP oligomers that was concluded to be a combination of intra- and inter-molecular energy transfer through conformation changes and aggregation. This process, however, appears to be superceded in 4-L-1 and 4-L-2 by the phosphorescence emission decay, since the fluorescence almost entirely disappears in 4-L-1 and is greatly reduced in 4-L-2 at 80 K. Furthermore, the initial appearance of phosphorescence occurs at a higher temperature in 4-L-1 (190 K) than 4-L-2 (160 K). These observations suggest that the competition between excited state decay through either phosphorescence or nonradiative energy transfer is dependent upon the oligomer size. In 4-L-1, phosphorescence is the most favorable decay pathway, leading to the pronounced emission at reasonably high temperatures. The larger size and introduction of long alkyl side chains in 4-L-2 increases the favorability of energy transfer deactivation, leading to a weaker
phosphorescence that does not appear until lower temperatures. The oligomer size is further increased in \textbf{4-L-3}, where aggregation and conformation-induced energy transfer is now the favored decay pathway and phosphorescence is no longer observed.

Emission quantum yields were measured for the oligomers, and calculated values are listed in Table 5-1. The quantum yields are again very high, which is typical of rigid organic chromophores.\textsuperscript{108} However, the high values were difficult to accurately measure, and several attempts were made to achieve consistent results. This problem may result from oligomer aggregation in solution. The reported values are averages of several data sets, but it will be clear in calculations below that the \textbf{4-L-2} and \textbf{4-L-3} yields are erroneously high.

The \textbf{4-Re} complex emission spectra in optically dilute 2-MTHF solutions at temperatures varying from 298 to 80 K are shown in Figure 5-4. The emission maxima at room temperature and 80 K are listed in Table 5-2. Again, very weak emission was observed in all the rhenium complex samples that corresponded to the free oligomer fluorescence. This emission was considered to be a trace impurity. The \textbf{4-Re} complexes exhibited a weak, broad emission that increases in intensity with decreasing temperature, which repeats to the \textbf{5-Re} and \textbf{5-ReP} spectral trends. Emission intensities were high enough to successfully measure their quantum yield, and calculated values are listed in Table 5-2. The yields are rather low, but these are typical of (bipyridine)Re\textsuperscript{I}(CO)\textsubscript{3}Cl complexes.\textsuperscript{41} The ability to measure the “bent” complex quantum yields may stem from higher \textbf{4-L} excited-state energy levels, which increases the MLCT energy gap.
Figure 5-4: Emission spectra of the 4-Re rhenium complexes in 2-MTHF (400 nm excitation) from 298 to 80 K. The emission intensity decreases as temperature increases, and individual spectra are in 20 K increments for all complexes except 4-Re-3, which is in 30 K increments. (a) 4-Re-1; (b) 4-Re-2 (inset spectra are recorded from 204-264 K); (c) 4-ReAN-3; (d) 4-Re-3.
The low temperature spectrum for 4-Re-1 is broad and blue-shifted, but the larger oligomer complexes acquire a highly structured emission with a 615 nm maximum (0,0) band and 680 nm (0,1) shoulder.* Note that this emission maximum is very similar to the 614 nm phosphorescence maximum observed in the 4-L emission spectra (Figure 5-3). Also, no overlapping spectral elements are apparent in these spectra, which is quite different than the 5-Re and 5-ReP spectra (Figures 3-6 and 4-4). A clear transition between the broad MLCT emission and structured $^3\pi,\pi^*$ emission can be seen for 4-Re-2 in the Figure 5-4b inset at 240 K. This same transition is not seen in 4-Re-3 and 4-ReAN-3 spectra, where the structure is retained at all temperatures. These observations suggest that the observed emission in the 4-Re complexes (except 4-Re-1) is $\pi,\pi^*$ phosphorescence at low temperature and $^3$MLCT luminescence (or a mixture of the two excited states) at room temperature.

To further prove the conclusion that the low-temperature emission is ligand-based $\pi,\pi^*$ phosphorescence, excitation polarization studies were conducted on 2-MTHF solutions at 80 K of 4-Re-3 at various emission wavelengths. Excitation spectra and $r(\lambda)$ values are shown in Figure 5-5, along with an emission spectrum that indicates the studied wavelengths. For all the recorded excitation spectra, the anisotropy value is low ($\approx 0$) and does not vary across the excitation spectrum. The observation of unpolarized light that is excitation wavelength independent confirms the emission band assignment as oligomer $\pi,\pi^*$ phosphorescence, as seen in the 5-Re and 5-ReP polarized excitation

* The odd high-temperature emission spectra recorded for 4-Re-3 are due to a significant 4-L-3 impurity in the studied sample.
spectra (Figures 3-7 and 4-5). However, the 80 K 4-Re emission spectrum is *entirely* phosphorescence, with no evidence of an overlapping MLCT state as seen in the “linear” oligomer complexes. Furthermore, the anisotropy values are higher for the 5-Re-3 and 5-ReP-3 polarization data (∼ 0.05), suggesting excited-state mixing in these complexes that is not observed in the 4-Re-3 polarization data. Surprisingly, polarization measurements on 4-Re-1 returned anisotropy values very similar to those observed for 5-Re-3, with a low value (0.07) that is excitation wavelength independent. This observation suggests for 4-Re-1 that at low temperature a ligand-based phosphorescence might be mixed with the observed MLCT emission.

The 4-ReAN-3 emission spectra and temperature response are practically identical to the 4-Re-3 spectra, which is not surprising if the majority of the emission is ligand-based. The room temperature emission quantum yield, however, decreases dramatically upon ligand substitution, which is counter to expected results for acetonitrile-substituted complexes. These observations, which are very similar to those observed for 5-ReAN-2 and 5-ReAN-3, suggest that ligand substitution alters the excited-state equilibria for the 4-Re complexes to a similar degree as that observed for the 5-Re complexes (Figure 3-17).

**Emission Lifetimes**

Emission lifetime decays were recorded for two different emission wavelengths on the 4-L oligomers in 2-MTHF at room temperature and 80 K. Both monoexponential and biexponential decays were observed, and lifetime results are listed in Table 5-3.
Figure 5-5: Excitation (dashed line) and excitation polarization (solid line) $r(\lambda)$ spectra at 80 K of 4-Re-3 2-MTHF solution at various emission wavelengths.
Table 5-3: Variable temperature emission decay times of the 4-L oligomers.

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>T / K</th>
<th>α_1</th>
<th>τ_1 / ns</th>
<th>α_2</th>
<th>τ_2 / ns</th>
<th>α_1</th>
<th>τ_1 / ns</th>
<th>α_2</th>
<th>τ_2 / ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-L-1</td>
<td>298</td>
<td>1</td>
<td>1.317</td>
<td>-</td>
<td>-</td>
<td>0.995</td>
<td>1.573</td>
<td>0.005</td>
<td>46.82</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.989</td>
<td>1.275</td>
<td>0.011</td>
<td>12.28</td>
<td>1</td>
<td>84100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4-L-2</td>
<td>298</td>
<td>1</td>
<td>1.461</td>
<td>-</td>
<td>-</td>
<td>0.986</td>
<td>1.374</td>
<td>0.014</td>
<td>8.167</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.889</td>
<td>0.909</td>
<td>0.111</td>
<td>2.184</td>
<td>1</td>
<td>153000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4-L-3</td>
<td>298</td>
<td>1</td>
<td>1.153</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.903</td>
<td>0.887</td>
<td>0.097</td>
<td>1.897</td>
<td>0.946</td>
<td>1.691</td>
<td>0.054</td>
<td>9.407</td>
</tr>
</tbody>
</table>

^2-MTHF solutions; 405 nm excitation. Biexponential decays were modeled based on (3-3). Errors for the fit parameters are ± 5%.

Fluorescence emission lifetimes (450 nm) are short at room temperature (around 1 ns) and become biexponential at low temperature with the addition of a low amplitude, longer lived (7 ns) component. This photophysical behavior is identical to the “excimer-like” behavior observed in the 5-L and 5-LP oligomers (Tables 3-3 and 4-3), again confirming the presence of aggregation in the 4-L oligomers. The phosphorescence (600 nm) observed in 4-L-1 and 4-L-2 exhibited monoexponential decay with a very long lifetime (> 80 µs) at 80 K, which is typical for organic phosphorescence.\(^{108}\)

Emission decay lifetimes were recorded for the 4-Re complexes in 2-MTHF at various temperatures. Biexponential decays were observed at all temperatures, and results are listed in Table 5-4. At room temperature, the emission decays are biexponential and characterized by a large amplitude, short-lived component (τ = 1 ns) and a low-amplitude component with a longer lifetime (τ = 50 – 150 ns). In contrast, at reduced temperatures the long-lifetime component dramatically increases in both amplitude and lifetime (τ > 40 µs). These observations reflect the domination of
phosphorescence in the low-temperature emission spectra. However, the presence of a biexponential decay still signifies an excited state equilibrium similar to that previously described for the 5-Re and 5-ReP complexes. This equilibrium results in a phosphorescence lifetime that is shorter than those recorded for 4-L-1 and 4-L-2 under the same degassing conditions. Alternatively, a small free oligomer impurity could result in the biexponential behavior.

Table 5-4: Variable temperature emission decay times of the 4-Re complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Temp. / K</th>
<th>α₁</th>
<th>τ₁ / ns</th>
<th>α₂</th>
<th>τ₂ / ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Re-1</td>
<td>298</td>
<td>0.824</td>
<td>1.604</td>
<td>0.176</td>
<td>47.99</td>
</tr>
<tr>
<td></td>
<td>171</td>
<td>0.723</td>
<td>155.77</td>
<td>0.277</td>
<td>626.2</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>0.588</td>
<td>1286.7</td>
<td>0.412</td>
<td>3734.5</td>
</tr>
<tr>
<td>4-Re-2</td>
<td>298</td>
<td>0.928</td>
<td>1.931</td>
<td>0.072</td>
<td>151.8</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>0.968</td>
<td>10.00</td>
<td>0.032</td>
<td>16485</td>
</tr>
<tr>
<td></td>
<td>91</td>
<td>0.870</td>
<td>10.35</td>
<td>0.130</td>
<td>49222</td>
</tr>
<tr>
<td>4-Re-3</td>
<td>298</td>
<td>0.954</td>
<td>1.025</td>
<td>0.046</td>
<td>168.74</td>
</tr>
<tr>
<td></td>
<td>181</td>
<td>0.984</td>
<td>5.832</td>
<td>0.016</td>
<td>14489</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>0.948</td>
<td>6.235</td>
<td>0.052</td>
<td>34565</td>
</tr>
<tr>
<td>4-ReAN-3</td>
<td>298</td>
<td>0.935</td>
<td>8.289</td>
<td>0.065</td>
<td>4461</td>
</tr>
<tr>
<td></td>
<td>169</td>
<td>0.992</td>
<td>0.860</td>
<td>0.008</td>
<td>159.8</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.965</td>
<td>1.720</td>
<td>0.035</td>
<td>385.3</td>
</tr>
</tbody>
</table>

Note the decreasing phosphorescence decay amplitude with increasing oligomer size. The trend is similar to the 4-L oligomer phosphorescence, which decreases in efficiency with increasing oligomer size due to the increasing availability of a competing nonradiative pathway. The 4-ReAN-3 low temperature emission lifetimes are nearly two
orders of magnitude smaller than 4-Re-3. This trend is the opposite of what is expected
for the acetonitrile-substituted chromophore, which should increase the emission lifetime.
This trend further supports an excited-state equilibrium in the 4-Re complexes.
Furthermore, the longer room temperature lifetime for 4-ReAN-3 compared to 5-ReAN-2
and 5-ReAN-3 illustrates the influence of the $^3\pi,\pi^*$ phosphorescence on the “bent”
oligomer complex emission.

**Transient Absorption Spectra**

Transient absorption spectra for the 4-L oligomers in THF solutions are shown in
Figure 5-6. Excited state lifetimes obtained from factor analysis and global decay
fitting\(^{114}\) are listed in Table 5-1. Equivalent first order decays were observed for all
features of the various transient absorption spectra.

The spectra show bleaching of the lowest energy $\pi,\pi^*$ ground state absorption
(Figure 5-2) at 400 nm and a broad long-lived excited-state absorption. The excited state
lifetimes are all very long and similar to the phosphorescence lifetimes obtained for 4-L-1
and 4-L-2. The transient absorption spectra for the 4-L oligomers are very similar to the
5-L and 5-LP spectra (Figures 3-8 and 4-6) except that the absorption maximum is blue-
shifted by 50 nm. It is interesting to note that 4-L-1 exhibits excited-state absorptions
that do not correspond with the larger oligomer spectra. In fact, the prominent 390 nm
transient is more similar to a bipyridine radical anion transient absorption.\(^{153}\) This
difference may be due to the lack of extended conjugation in 4-L-1, which may give rise
to higher-energy excited state transitions similar to 2,2′-bipyridine.
Figure 5-6: Transient absorption spectra of the **4-L** oligomers in freeze-pump-thaw degassed THF solutions. Arrows indicate the spectral trend with increasing time after laser excitation. (a) **4-L-1** (Transients are 40 µs increments after laser excitation); (b) **4-L-2** (Transients are 40 µs increments after laser excitation); (c) **4-L-3** (Transients are 80 µs increments after laser excitation).
Transient absorption spectra of the 4-Re complexes in THF solutions are shown in Figure 5-7. Excited state lifetimes obtained from factor analysis and global decay fitting\textsuperscript{114} are listed in Table 5-2. Spectra were recorded in CH\textsubscript{2}Cl\textsubscript{2} for 4-ReAN-3 to prevent photosubstitution of the CH\textsubscript{3}CN ligand. Generally, equivalent first order decays were observed for all features of the various transient absorption spectra. However, the 450 nm bleach transient exhibited biexponential decay in certain samples with a rapid (\(\tau < 1\) ns) component followed by a slower decay lifetime that corresponded to the other decay lifetimes in the transient absorption spectrum. This result is due to trace 4-L oligomer impurities in the examined samples and is similar to behavior observed for the 5-Re and 5-ReP complexes discussed in previous chapters.

Ground state bleaching is observed similar to the 4-L spectra but red-shifted to reflect the red-shifted ground state \(\pi,\pi^*\) absorption. A broad excited-state absorption is also observed with maxima around 520 nm for 4-Re-1 and 650 nm for 4-Re-2 and 4-Re-3. The excited-state absorptions are very similar for the 4-L oligomers and the 4-Re-2 and 4-Re-3 complexes, suggesting that they all originate from similar \(\pi,\pi^*\) excited states. The 4-Re-1 spectrum, however, with its 350 and 520 nm absorptions is more similar to (bipyridine)Re\textsuperscript{I}(CO\textsubscript{3})Cl spectra and 4-L-1, suggesting that the 4,4'-substitutions do not exert a significant effect on the excited state behavior until 4-Re-2.\textsuperscript{94,154} The transient decay lifetime for the 4-Re complexes (except 4-ReAN-3) is much shorter than the 4-L oligomers and very similar to the observed emission decay long-lifetime component, suggesting that an excited-state equilibrium exists to cause the similar lifetimes originating from different excited-states. For 4-ReAN-3, a longer transient lifetime was observed, exhibiting the same trend seen in 5-ReAN-2 and
5-ReAN-3 and confirming an excited-state equilibrium disruption in the acetonitrile-substituted complexes.

Figure 5-7: Transient absorption spectra of the 4-Re rhenium complexes in argon bubble-degassed THF solutions (except 4-ReAN-3, which is in CH$_2$Cl$_2$). Arrows show the spectral trend with increasing time after laser excitation. (a) 4-Re-1 (Transients are 40 ns increments after laser excitation); (b) 4-Re-2 (Transients are 80 ns increments after laser excitation); (c) 4-Re-3 (Transients are 80 ns increments after laser excitation); (d) 4-ReAN-3 (Transients are 4000 ns increments after laser excitation).
**Photothermal Measurements / Triplet Yields**

LIOAS measurements were performed on THF solutions of the 4-L oligomers and 4-Re complexes with the 5 MHz transducer. For the 4-L oligomers, a single fast component was observed, resulting in a single amplitude with an insignificant lifetime. Results of multiple 4-L oligomer measurements are listed in Table 5-5. For the 4-Re complexes, two components (one fast and one intermediate lifetime) were observed. Measurements of 4-Re-1 are impractical due to its short excited state lifetime. Results of multiple 4-Re complex measurements are listed in Table 5-6.

Table 5-5: 4-L oligomer LIOAS data.

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>φ₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-L-1</td>
<td>0.2743 ± 0.02</td>
</tr>
<tr>
<td>4-L-2</td>
<td>0.2934 ± 0.03</td>
</tr>
<tr>
<td>4-L-3</td>
<td>0.3105 ± 0.02</td>
</tr>
</tbody>
</table>

*aTHF solutions, 298 K. LIOAS deconvolution parameters are averages of four measurements on fresh sample solutions with a reported error of ± σ. τ₁ fixed at 1 ns.

Table 5-6: 4-Re complex LIOAS data.

<table>
<thead>
<tr>
<th>Complex</th>
<th>φ₁</th>
<th>φ₂</th>
<th>τ₂ / ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Re-2</td>
<td>0.3564 ± 0.020</td>
<td>0.5719 ± 0.054</td>
<td>129.8 ± 3.76</td>
</tr>
<tr>
<td>4-Re-3</td>
<td>0.4793 ± 0.030</td>
<td>0.4056 ± 0.025</td>
<td>196.4 ± 10.6</td>
</tr>
</tbody>
</table>

*aTHF solutions, 298 K. LIOAS deconvolution parameters are averages of four measurements on fresh sample solutions with a reported error of ± σ. τ₁ fixed at 1 ns.
The LIOAS data measured on the 4-L oligomers and 4-Re complexes can be used to calculate the excited-state triplet yields. The 4-L-1 and 4-L-2 phosphorescence provides the triplet energy needed for the triplet yield calculation (614 nm = 46.6 kcal mol$^{-1}$) if the assumption is made that the triplet energy does not vary across the oligomer series. The triplet yields can subsequently be calculated using (3-6) as before, and the results are listed in Table 5-7. Recall that for 4-L-2 and 4-L-3 emission quantum yields were very difficult to accurately measure, and the numbers reported in Table 5-1 give erroneous results in this calculation. Therefore, the emission quantum yield for these oligomers was assumed to be greater than 0.7, producing the reported “upper bound” triplet yields.

### Table 5-7: 4-L oligomer triplet yields.

<table>
<thead>
<tr>
<th>Oligomer$^a$</th>
<th>$\Phi_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-L-1</td>
<td>0.12</td>
</tr>
<tr>
<td>4-L-2</td>
<td>$\leq$ 0.20</td>
</tr>
<tr>
<td>4-L-3</td>
<td>$\leq$ 0.18</td>
</tr>
</tbody>
</table>

$^a$THF solutions, 298 K. Errors for the triplet yield are ±15%.

The 4-Re-2 and 4-Re-3 triplet yields can also be calculated from the LIOAS data by assuming the same triplet energy used for the 4-L data. Recall that the transient absorption spectra for both the 4-L oligomers and 4-Re complexes are similar, suggesting that the same excited state (oligomer $^3\pi,\pi^*$) is populated in both cases. Therefore, this excited state is the lowest-energy excited state that would be responsible for the
deconvolution component. The triplet yield can then be calculated by independently using each decay component in (5-1).

\[
\phi_1 = \frac{E_{hu} - \phi_T E_T}{E_{hu}} \quad (5-1a)
\]

\[
\phi_2 = \frac{\phi_T E_T (1 - \phi_{cm})}{E_{hu}} \quad (5-1b)
\]

Calculated 4-Re-2 and 4-Re-3 triplet yields are listed in Table 5-8.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\phi_T^a)</th>
<th>(\phi_T^b)</th>
<th>(\phi_T^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Re-2</td>
<td>(\approx 1.00)</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>4-Re-3</td>
<td>0.90</td>
<td>0.70</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)THF solutions, 298 K. \(^b\)Triplet yield based on the first deconvolution amplitude (5-1a). \(^c\)Triplet yield based on the second deconvolution amplitude (5-1b).

It is clear from the calculations that the triplet yields are much higher in the 4-Re complexes than the 4-L oligomers. While intersystem crossing yields for rhenium complexes are commonly close to unity,\(^7^6\) the data in this case are indicative that the triplet yield is enhanced by the presence of the metal chromophore (i.e., the \(^3\)MLCT excited state serves as a conduit for \(^3\pi,\pi^*\) excited state formation). The triplet yield decrease observed for 4-Re-3 is surprising but likely originates from errors in the triplet yield measurements.

**Decay Rate Calculations**

Sufficient data is now available to calculate the radiative, intersystem crossing, and nonradiative decay rate constants for the 4-L oligomers based on (3-6).
Berg equation (3-7) can also be used to calculate the radiative rate constant in a similar manner to the 5-L oligomer calculations. The experimental and calculation results are listed in Table 5-9. Note that for 4-L-2 and 4-L-3 limits are given for the rate constants due to the emission quantum yield assumption used in the LIOAS calculations.

### Table 5-9: Decay rates of the 4-L oligomers.

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>( k_r / 10^8 \text{ s}^{-1} )</th>
<th>( k_{nr} / 10^7 \text{ s}^{-1} )</th>
<th>( k_{isc} / 10^7 \text{ s}^{-1} )</th>
<th>( k_r^{SB} / 10^8 \text{ s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-L-1</td>
<td>6.35</td>
<td>9.07</td>
<td>9.89</td>
<td>0.978</td>
</tr>
<tr>
<td>4-L-2</td>
<td>≥ 4.79</td>
<td>≤ 6.84</td>
<td>≤ 13.7</td>
<td>4.17</td>
</tr>
<tr>
<td>4-L-3</td>
<td>≥ 6.07</td>
<td>≤ 10.4</td>
<td>≤ 15.6</td>
<td>4.12</td>
</tr>
</tbody>
</table>

Several observations stem from this data. Of course, the limitations of drawing any decisive conclusions from these numbers are obvious since exact values are not obtained for 4-L-2 and 4-L-3. First, note that \( k_r \) does not increase with increasing oligomer size as readily as observed with the 5-L oligomers (Table 3-10). This trend suggests a marked difference in the ability of the “bent” oligomer extended \( \pi \)-conjugation to influence its excited-state photophysics. Second, the calculated \( k_r^{SB} \) values still agree with the experimental values (except for 4-L-1), suggesting that the fluorescence originates from the lowest-energy absorption band and is strongly allowed. Third, the \( k_{nr} \) values are larger for the 4-L oligomers than the 5-L oligomers, while the \( k_{isc} \) values are smaller. Since it is likely that radiative and intersystem crossing pathways are the major deactivation pathways of the \( ^1\pi,\pi^* \) state (i.e., \( \phi_{em} + \phi_{isc} \approx 1 \)), the actual \( k_{nr} \) values are certainly much lower than the upper bounds reported here.
Electrochemistry

Cyclic voltammetry was performed on the $4\text{-Re}$ complexes in THF with 0.1 M TBAH as the supporting electrolyte. Again, the limited THF potential window prevented the measurement of oxidation potentials. Quasi-reversible reduction waves of the organic oligomer were observed in all cases, and half-wave potentials are listed in Table 5-1. The reduction potential (and, subsequently, excited state energy) does not change much as the oligomer size increases. The potentials are slightly more negative than the $5\text{-Re}$ complexes (Table 3-1), suggesting that the PPE-type oligomer is harder to reduce when the aryl-ethynyl moieties are substituents at the 4,4’ positions on the ligated bipyridine.

Electroabsorption Spectroscopy

In order to investigate the differences between the transition dipoles associated with the ligand $\pi,\pi^*$ and metal MLCT transitions, electroabsorption spectroscopy (also known as stark effect spectroscopy) was employed in a collaboration with Dr. Linda Peteanu and Lavanya Premvardhan at Carnegie Mellon University. This technique has been used to investigate dipole moment changes associated with MLCT transitions in ruthenium complexes with a high degree of success. Electroabsorption spectroscopy involves monitoring the ground-state absorption spectrum change as the sample is subjected to a rapidly oscillating electric field. The resulting field-induced effects are modeled as a combination of the zeroth, first, and second derivatives of the original absorption spectrum to allow the extraction of information on the transition dipole moment and polarizability changes associated with the optical transition. The fit equations are specified in (5-2).
\[ \Delta A(\nu) = \left\{ A_x \, A(\nu) + \frac{B_x}{15hc} \frac{\nu d[A(\nu)\nu]}{d\nu} + \frac{C_x}{30h^2c^2} \frac{\nu d^2[A(\nu)/\nu]}{d\nu^2} \right\} F_{\text{int}}^2 \]  

(5-2a)

\[ B_x = \frac{5}{2} \text{Tr}\Delta\alpha + \left( 3 \cos^2 \chi - 1 \right) \left( \frac{3}{2} \hat{g} \cdot \Delta\alpha \cdot \hat{g} - \frac{1}{2} \text{Tr}\Delta\alpha \right) \]  

(5-2b)

\[ C_x = \left| \Delta \mu \right|^2 \left[ 5 + \left( 3 \cos^2 \xi - 1 \right) \left( 3 \cos^2 \chi - 1 \right) \right] \]  

(5-2c)

In (5-2), \( A(\nu) \) is the absorption spectrum, \( \nu \) is the absorption spectrum frequency, \( F_{\text{int}}^2 \) is the internal electric field, \( \text{Tr}\Delta\alpha \) is the trace of the molecular polarizability change, \( \chi \) is the angle between the electric field and optical axis, \( \hat{g} \cdot \Delta\alpha \cdot \hat{g} \) is the molecular polarizability change along the transition moment, \( \Delta \mu \) is the dipole moment change, and \( \xi \) is the angle between the transition dipole moment and the “change in dipole” moment (i.e., difference between ground and excited-state dipole moments). To fit electroabsorption data, the original absorption spectrum is modeled with combinations of Gaussian peaks that best reproduce the data and mathematically separate the different transitions of interest. After taking the zeroth, first, and second derivatives of the model, (5-2a) is used to yield the best fits for parameters \( A_x, B_x, \) and \( C_x \). If data is acquired for two different \( \chi \) values (typically 0° and 54.7°), the dipole moment and polarizability changes can readily be extracted for the various components of the absorption spectrum.\(^{155}\)

The **4-Re-1** complex was selected for these experiments since it is the only complex that exhibited an MLCT absorption shoulder not completely obscured by the...

\(^{‡}\) Note that \( A_x \) contains information regarding transition moment polarizability and is usually zero for MLCT electroabsorption measurements, so it is not considered here.
more intense \( \pi, \pi^* \) absorptions. Electroabsorption spectroscopy for **4-Re-1** in a polymethylmethacrylate (PMMA) matrix at 77 K is shown in Figure 5-8. Although three Gaussians were needed to properly model the absorption spectrum, the electroabsorption response is fit to a sum of only Gaussians 1 and 3 as shown in Figure 5-8a. The use of Gaussian functions to model the two observed absorption bands in the **4-Re-1** spectrum (Figure 5-2) allows the expansion of (5-2a) to a six-parameter fit and the extraction of \( \Delta \mu \) and \( \Delta \alpha \) values for each transition.\(^\text{159} \) For the low-energy band, three independent measurements produced an average \( \Delta \mu \) of \( 8.7 \pm 0.5 \) Debye and \( \Delta \alpha \) of \( 60 \) Å\(^3 \), while the higher-energy band returned an average \( \Delta \mu \) of \( 8.0 \pm 0.5 \) Debye and \( \Delta \alpha \) of \( 31 \) Å\(^3 \). Therefore, within experimental error the two bands have the same \( \Delta \mu \) value, both at room temperature and 77 K. These results are similar to those previously reported by Oh and Boxer\(^\text{158} \) for Ru(bpy)\(_3\)\(^{2+}\), where the MLCT \( \Delta \mu \) was 8.8 Debye.

The positive \( \Delta \alpha \) values indicate that the excited state exhibits a greater propensity for polarization than the ground state, and the higher \( \Delta \alpha \) value for the lower-energy band is likely a contribution from the overlapping MLCT absorption within the more intense \( \pi, \pi^* \) band.\(^*\) The similar \( \Delta \mu \) values for both transitions suggest that the two transitions populate very similar excited states. That is, the \( \pi, \pi^* \) absorption dominates both bands as previously concluded from the high absorbptivity values. However, the slightly higher \( \Delta \mu \) value for the lower-energy transition may result from additional contribution from the

\(^*\) Hupp obtained a \( \Delta \alpha \) of \( 570 \pm 100 \) Å\(^3 \) for the MLCT absorption of ruthenium(II) tris(phenanthroline), which is considerably larger than our results and likely due to the lack of overlapping organic and metal-based transitions.\(^\text{155} \)
overlapping MLCT transition that would constructively interfere with the $\pi,\pi^*$ transition $\Delta \mu$.

Figure 5-8: Electroabsorption spectroscopy of 4-Re-1 in a PMMA matrix at 80 K. (a) Absorption spectrum illustrating Gaussians utilized in data fitting; (b) Electroabsorption signal and fitting results using (5-2) and (Gaussian 1 + 3) as the model.

Discussion

**Excited-State Energetics**

The 4-Re photophysics requires a slight alteration of the excited-state model presented for the 5-Re complexes in chapter 3. Therefore, the model illustrated in the Jablonski diagram shown in Figure 5-9 is proposed.
Figure 5-9: Jablonski diagram of 4-Re complexes.

The general construction of this diagram is very similar to that presented for the 5-Re complexes (Figure 3-18), except for a slight raising of the oligomer $^1\pi,\pi^*$ energy, a slight lowering of the oligomer $^3\pi,\pi^*$ energy and the introduction of oligomer phosphorescence (EM1 in Figure 5-9). The same excited-state equilibrium exists between the oligomer-based $^3\pi,\pi^*$ and metal-based $^3$MLCT states, but the lowered $^3\pi,\pi^*$ energy alters the temperature-dependence of the emission behavior. At room temperature, the equilibrium results in the observation of $^3$MLCT emission (EM2 in Figure 5-9), since the oligomer phosphorescence is superceded by nonradiative decay at these temperatures. As the temperature is lowered, the thermal energy necessary to maintain equilibrium between the excited states is no longer present, and the electronic population collects in the $^3\pi,\pi^*$ state. Furthermore, the nonradiative decay pathway
favorable at room temperature gradually gives way to phosphorescence, which is the only emission observed at low temperatures. The biexponential emission decays obtained at 80 K, however, suggest that the $^3$MLCT excited state still has some small effect on the decay through the aforementioned equilibrium. Alternatively, an impurity could be responsible for the fast component of the emission decay.

The transient absorption spectra, due to their similarity to the 5-Re spectra (Figure 3-10), still originate from the oligomer $^3\pi,\pi^*$ state (TA in Figure 5-9) following equilibration. The presence of the acetonitrile ligand in 4-ReAN-3 raises the $^3$MLCT energy, disrupting the excited-state equilibrium as before and producing the shortened emission and increased TA room temperature lifetimes. No changes are observed in the emission and TA spectral bandshapes upon acetonitrile substitution, however, since the oligomer is responsible for the observed spectra.

**How Does the Substitution Position Alter the Photophysics?**

As illustrated above, there are subtle differences between the photophysics of the “linear” and “bent” oligomers and rhenium complexes. Namely, the excited-state singlet energy is higher while the triplet energy is slightly lower for the “bent” oligomers with respect to the “linear” systems. In order to better understand these differences, literature precedents were investigated to see if similar substitution trends have been observed. Extensive photophysics have been conducted on stilbazoles (styrylpyridines), both by themselves and incorporated into –Re(CO)$_3$Cl chromophores (Figure 5-10). Some of these results are considered here for comparison to our systems. Note that 3-SA structurally corresponds to the 5-L and 5-LP oligomers while 4-SA structurally corresponds to the 4-L oligomers.
Photophysics of 2-SA, 3-SA and 4-SA were studied by Bartocci\textsuperscript{160} and Görner\textsuperscript{,161} and fluorescence quantum yields and triplet energies are listed in Table 5-10.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\Phi_\text{f}$</th>
<th>$E_T$ / kcal mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-SA</td>
<td>0.002</td>
<td>49.0</td>
</tr>
<tr>
<td>3-SA</td>
<td>0.065</td>
<td>48.8</td>
</tr>
<tr>
<td>4-SA</td>
<td>0.003</td>
<td>49.2</td>
</tr>
</tbody>
</table>

Note that the triplet energy remains constant, but 3-SA is more emissive by an order of magnitude. The major excited-state deactivation pathway for stilbazoles is photoisomerization, but for 3-SA this capability is clearly hampered. Bartocci and
coworkers explain this difference based upon the heteroatom position, which significantly alters the excited state molecular orbital nodal structure and inhibits the internal conversion needed to induce photoisomerization. The 2-SA and 4-SA equivalency illustrates the lack of a node at these atom positions. While the stilbazole photochemistry is different than our PPE-type oligomers, the idea that heteroatom positioning affects the excited-state photophysics is highly relevant. Note that the increased $\phi_{em}$ for the 4-L oligomers is the opposite observed for the stilbazoles, where 3-SA has a higher fluorescence quantum yield.

Wrighton and coworkers synthesized rhenium complexes Re-3-SA and Re-4-SA as part of a photoassisted reactions study. While they did not embark on detailed photophysical studies, an interesting trend was observed. First, the lowest-energy absorption (associated with the $\pi,\pi^*$ transition of the styrylpyridine ligands) is 30 nm blue-shifted for Re-3-SA (297 nm) compared to Re-4-SA (328 nm). Note that this trend is opposite that observed for the 5-Re and 4-Re complexes, where the 4-Re complexes have higher-energy absorptions. Of course, stilbazole complexes might not be the best model for these oligomers since they lack the rigidity of the acetylene linkages (i.e., no possibility of photoisomerization) and a bipyridine moiety.

One additional study by Zhou and Swager examined the photophysics of “linear” and “bent” PPE-type polymers SP1 and SP2, as shown in Figure 5-11. Absorption measurements on these polymers showed that SP2 (388 nm) is blue-shifted with respect to SP1 (428 nm), agreeing with the 5-L / 4-L spectral trends. This observation shows that the “bent” polymer excited states are higher in energy than the “linear” polymer due to the different structure. While the authors did not speculate why
the excited state energies change, it clearly is due to the differing polymer substitutional
gallery.††

**Figure 5-11: “Linear” and “bent” PPE-type polymers. (Ref. 16)**

**Semi-Empirical Calculations**

In order to better understand the trends observed between the “linear” and “bent”
oligomers, semi-emperical calculations were performed on 4-arylethynylpyridine (4-M)
and 5-arylethynylpyridine (5-M) with Hyperchem and the PM3 / ZINDO basis sets, as
shown in Figure 5-12. The molecular axis was oriented such that the planar molecule
rests in the xy plane, with the y axis corresponding to the long molecular axis. Calculated
excited-state energies and spectroscopic parameters‡‡ are listed in Table 5-11.

†† Of course, the differing phenyl ring substituents might contribute to the observed
absorptions. However, the electron-withdrawing amide substituents on **SP1** would draw
electron density from the polymer backbone and blue-shift the absorption,⁵ which is
counter to the reported observations.

‡‡ Note that the absorption transitions calculated by Hyperchem indicate a single
molecular orbital for the responsible ground and excited-states. This is a simplification
of the configurational interaction output internally performed by the software, as several
different molecular orbitals are mixed in this method to arrive at the electronic transition.
Nevertheless, the simplification is reported here.
Figure 5-12: Arylethynylpyridine model compounds.

Table 5-11: Semi-empirical calculations for 5-M and 4-M

<table>
<thead>
<tr>
<th>Parameter</th>
<th>5-M</th>
<th>4-M</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_S$ / kcal mol$^{-1}$</td>
<td>105.6</td>
<td>106.4</td>
</tr>
<tr>
<td>$E_T$ / kcal mol$^{-1}$</td>
<td>71.1</td>
<td>71.7</td>
</tr>
<tr>
<td>Dipole moment / Debye</td>
<td>3.09</td>
<td>3.78</td>
</tr>
<tr>
<td>Absorption (HOMO – 1 → LUMO) / nm</td>
<td>N/A</td>
<td>238</td>
</tr>
<tr>
<td>Absorption (HOMO → LUMO) / nm</td>
<td>272</td>
<td>268</td>
</tr>
<tr>
<td>Absorption (HOMO → LUMO + 1) / nm</td>
<td>245</td>
<td>N/A</td>
</tr>
</tbody>
</table>

*Parameters obtained from ZINDO/CI single point calculations following PM3 geometry optimizations as described in the experimental section.

For both molecules, two major absorption bands were obtained, corresponding to the two major $\pi,\pi^*$ absorptions observed in all PPE-type oligomer reported spectra. The 5-M molecule exhibited slightly lower excited-state energies, reflected in the red-shifted absorption bands. Molecular orbital diagrams for the states involved in the absorption bands are shown in Table 5-13. Particular attention is paid to the energy of the molecular
orbital that represents the non-bonding electrons on the nitrogen atom (i.e., the molecular orbital with significant N p$_x$ character). For 5-M, the highest energy non-bonding molecular orbital is number 21 A’, with an energy of –14.46 eV and N p$_x$ coefficient of +0.263. The 4-M molecule, however has non-bonding molecular orbital 15 A1, with an energy of -10.06 eV and N p$_x$ coefficient of +0.377. Therefore, the 4-M non-bonding molecular orbital is 4 eV closer to the HOMO molecular orbital energy than 5-M (2.01 eV versus 6.70 eV). This observation suggests that the 4-M HOMO $\rightarrow$ LUMO transition exhibits more (n $\rightarrow$ $\pi^*$) character than 5-M, which is a ($\pi$ $\rightarrow$ $\pi^*$) transition. Transitions involving an isolated non-bonding orbital are typically higher in energy than those involving a delocalized $\pi$ cloud, and this trend is reflected in the model molecules.

Another interesting trend observed in the calculations is the ratio of oscillator strengths of the two primary absorptions, which is larger for 5-M (6.73) than 4-M (3.84). This trend is reflected in the experimental absorption spectra, where the absorption bands in the 4-L spectra are more equivalent in intensity than the analogous 5-L spectra (Figures 3-2 and 5-2).

Following the model calculations, the larger 5-L-1 and 4-L-1 molecules were considered using the same procedure. Both planar and “twisted” (e.g., the outlying phenyl rings are rotated 90° to the central bipyridine) versions (5-L-1T and 4-L-1T) of the oligomers were studied. The molecular axis was configured such that the planar oligomer is in the xy plane, with the y axis corresponding to the long “oligomer” axis. Observed and calculated excited-state energies and absorption maxima of the most intense bands are compared in Table 5-12.
Table 5-12: Semi-empirical calculations for 5-L-1 and 4-L-1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>5-L-1</th>
<th>4-L-1</th>
<th>5-L-1T</th>
<th>4-L-1T</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_S$ / kcal mol$^{-1}$</td>
<td>81.1 (62.9)</td>
<td>97.0 (68.9)</td>
<td>87.6</td>
<td>104.5</td>
</tr>
<tr>
<td>$E_T$ / kcal mol$^{-1}$</td>
<td>61.9 (52.3)</td>
<td>69.1 (46.6)</td>
<td>60.7</td>
<td>71.6</td>
</tr>
<tr>
<td>Dipole moment / Debye</td>
<td>4.98</td>
<td>6.27</td>
<td>5.14</td>
<td>6.18</td>
</tr>
<tr>
<td>Absorption (HOMO – 2 → LUMO) / nm</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>268</td>
</tr>
<tr>
<td>Absorption (HOMO – 1 → LUMO) / nm</td>
<td>N/A</td>
<td>274</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Absorption (HOMO → LUMO) / nm</td>
<td>342</td>
<td>286</td>
<td>317</td>
<td>N/A</td>
</tr>
<tr>
<td>Absorption (HOMO → LUMO + 2) / nm</td>
<td>258</td>
<td>N/A</td>
<td>N/A</td>
<td>256</td>
</tr>
</tbody>
</table>

$^a$Parameters obtained from ZINDO/CI single point calculations following PM3 geometry optimizations as described in the experimental section. Experimental values are shown in parenthesis following the calculated values.

When examining the calculation results, keep in mind that semi-empirical calculations typically return energies that are erroneously high, presumably due to overestimation of electron-electron repulsion for the $E_S$ values. Several trends are apparent from this data. First, the calculated $E_S$ value is higher for 4-L-1 by 16 kcal mol$^{-1}$ compared to 5-L-1, which is greater than the experimental energy difference but reflects the correct trend. Second, the calculated $E_T$ values exhibit the same trend but with a smaller increase, which is counter to the experimental trend. Third, the calculated spectroscopic maxima are all higher in energy than experimental values but exhibit blue-shifted absorption bands for 4-L-1 compared to 5-L-1. Finally, the “twisted” oligomers exhibit increased $E_S$ and absorption maxima energies compared to the coplanar geometries, while the $E_T$ values do not significantly change. This observation supports
the argument that breaking the extended conjugation of the oligomer \( \pi \)-backbone can exhibit significant effects on its excited-state photophysics.

Diagrams illustrating molecular orbitals of interest for the planar and twisted oligomers are shown in Tables 5-14 and 5-15, respectively. The molecular orbitals illustrate some interesting trends. For 4-L-1, the HOMO and HOMO – 1 orbitals are very close in energy (< 0.01 eV) and exhibit delocalization across the entire oligomer with the molecular orbitals both in and out of phase across the central bipyridine. The LUMO is also delocalized across the entire oligomer. For 5-L-1, delocalization is exhibited across the entire oligomer for each molecular orbital. Further investigation of the ZINDO output uncovers the molecular orbitals associated with the bipyridine nitrogen non-bonding electrons. For 5-L-1, this orbital is 24 A1, with an energy of –10.25 eV and nitrogen \( p_x \) coefficients of +0.395 and +0.392 for the two atoms, while the corresponding 4-L-1 molecular orbital is 81 A, with an energy of –9.80 eV and coefficients of +0.249 and +0.471. The energy differences between these non-bonding molecular orbitals and the HOMO are 3.1 and 1.97 eV for 5-L-1 and 4-L-1, respectively. Therefore, these energy differences suggest that the HOMO \( \rightarrow \) LUMO transition exhibits more \((n \rightarrow \pi^*)\) character in 4-L-1 than 5-L-1, which would result in the observed absorption blue-shift and follows the trend observed in 4-M and 5-M above.

The twisted oligomer molecular orbitals support previous suggestions that electronic isolation occurs due to conjugation breaks in the oligomer backbone. For 5-L-1T, the HOMO and LUMO orbitals are isolated to the central bipyridine. The 4-L-1T absorption transitions stem from molecular orbitals isolated on the central bipyridine (HOMO – 2 and LUMO) and one of the peripheral segments (HOMO – 1 and
LUMO + 1), both of which are higher in energy than the planar 4-L-1 transitions.§§

These calculations confirm the possibility of having electronically isolated chromophores within the same oligomer, which can account for some of the photophysical behavior exhibited in previous chapters (e.g., the presence of oligomer and complex absorptions in 5-Re-4).

The semi-empirical calculations presented here shed some light on the differing photophysics of the two oligomer series. Clearly, the wavefunctions for the 4,4′-substituted bipyridine are dramatically altered by the geometry change, presumably by the position of the nitrogen atoms relative to the peripheral conjugated arms of the oligomer, which alters the relative energy of the molecular orbitals corresponding to the nitrogen non-bonding electrons. Furthermore, the nature of the electronic transition appears to change between the two oligomer geometries, as the 4-Re oligomers exhibit more (n → π*) character. It is interesting that no other literature precedents for substitution effects exhibit the same trends found here, but the large bulk of our “substitutions” must be kept in mind when making literature comparisons.

**Mulliken Theory Calculation of 4-Re-1 MLCT Dipole Moment**

To further support the electroabsorption measurements of ∆µ, calculations based on Mulliken theory were performed to determine the MLCT transition moment, µ_{DA}, based on (5-3).\(^{163-165}\)

\[
\mu_{DA} = -e\lambda_{ad} R_{aa} \tag{5-3a}
\]

§§ Some of the odd behavior of the 4-Re-1T calculations may stem from the inability to design a symmetric molecule in the Hyperchem editor.
\[ \lambda_{ad} = \frac{-\beta_{ad}}{E_{MLCT}} \]  

(5-3b)

\[ R_{aa} = \sum_{j} C_{ja}^2 z_j + \sum_{(j<k)} \sum_{k} C_{ja} C_{ka} S_{jk} \left( z_j + z_k \right) \]  

(5-3c)

In (5-3), \( e \) is the charge of an electron \((-1.60 \times 10^{-19} \text{ C})\), \( \lambda_{ad} \) is the donor-acceptor mixing coefficient, \( \beta_{ad} \) is the off-diagonal interaction energy of the donor (Re \( d_{yz} \)) and acceptor (N \( p_y \)) orbitals, \( E_{MLCT} \) is the charge transfer energy, \( C_{ja} \) is the LUMO \( \pi^* \) molecular orbital \( p_y \) orbital coefficient of atom \( j \), \( z_j \) is the z-axis distance from the rhenium atom center to atom \( j \), and \( S_{jk} \) is the overlap integral of the \( p_y \) orbitals on atoms \( j \) and \( k \). All non-hydrogen atoms in the acceptor orbital ligand are considered when calculating \( R_{aa} \). The parameters needed for \( \beta_{ad}, S_{jk}, \) and \( C_{ja} \) were determined by an Extended Hückel calculation performed with Hyperchem 5.0 on 4-Re-1. The 4-Re-1 model was built with a planar oligomer geometry and octahedral rhenium center, with the oligomer contained in the xz plane, the z axis running along the oligomer center of symmetry, and the rhenium center at the origin. The LUMO molecular orbital obtained from the calculation is shown in Figure 5-13.

Using (5-3c), the calculated \( R_{aa} \) value for 4-Re-1 is 2.53 Å, and the \( \beta_{ad} \) value extracted from the program output is \(-1.66 \text{ eV}\). This interaction energy, when considered with an \( E_{MLCT} \) value of 2.76 eV (based on the assumption that the 4-Re-1 MLCT absorption is 450 nm), gives a \( \lambda_{ad} \) value of 0.60. This mixing coefficient is slightly high for MLCT transitions (0.25 – 0.50), which is probably a symptom of the extended \( \pi \) delocalization in the complexed oligomer. Final calculation of \( \mu_{DA} \) with (5-3a) yields a value of 7.30 Debye, which is very close to the \( \Delta\mu \) values measured by electroabsorption.
spectroscopy (8.0 and 8.7 Debye for the two $\pi,\pi^*$ transitions). It is intriguing that the calculated dipole moment for the MLCT transition is closer to the experimentally-determined $\pi,\pi^*$ dipole moments than expected, which might suggest that a larger fraction of the low-energy absorption is actually MLCT-based than previously concluded.

Figure 5-13: 4-Re-1 calculated LUMO molecular orbital.

Mulliken theory can be taken a step further to determine the molar absorptivity values of the charge transfer transition based on (5-4).

$$\nu_{av} \int \varepsilon(\nu)d\nu = KC_{Na}^2S_{ReN}^2R_{aa}^2$$

(5-4)

In (5-4), $\nu_{av}$ is the average transition energy, $\varepsilon(\nu)$ is the molar absorptivity at frequency $\nu$, $K$ is an experimental constant, $C_{Na}$ is the LUMO molecular orbital coefficient of the nitrogen $p_y$ orbitals, and $S_{ReN}$ is the overlap integral between the nitrogen $p_y$ and rhenium $d_{yz}$ atomic orbitals. In order to determine $K$, similar calculations were performed on (4,4’-dimethyl-2,2’-bipyridine)rhenium(I)triscarbonyl chloride, which has known molar absorptivity values. Extended Hückel calculations on a model placed on the same molecular axis used for 4-Re-1 produced the following parameters: $R_{ij} = 1.445 \text{ Å}, \beta =$
1.67 eV, \(E_{\text{MLCT}} = 3.41\) eV, \(\lambda_{\text{ad}} = 0.49\), \(\mu_{\text{DA}} = 3.40\) Debye, \(C_{\text{Na}} = -0.2986\), and \(S_{\text{ReN}} = -0.0735\). An absorption spectrum of the rhenium model, where only the MLCT absorption band is integrated, yields a \(\mu_{\text{av}} \int \varepsilon(\upsilon) d\upsilon\) value of \(4.79 \times 10^{32}\) M\(^{-1}\) cm\(^{-1}\) s\(^{-2}\).

Substituting all the appropriate values into (5-4) results in a \(K\) value of \(4.758 \times 10^{51}\) M\(^{-1}\) cm\(^{-3}\) s\(^{-2}\).

If we use the empirically-derived \(K\) value in (5-4) with the 4-Re-1 parameters \((C_{\text{Na}} = -0.31162, S_{\text{ReN}} = -0.0723, \text{and } R_{ii} = 2.533\) Å\), a \(\mu_{\text{av}} \int \varepsilon(\upsilon) d\upsilon\) value of \(1.50 \times 10^{33}\) M\(^{-1}\) cm\(^{-1}\) s\(^{-2}\) is obtained. This value is roughly half the experimental value of \(3.28 \times 10^{33}\) M\(^{-1}\) cm\(^{-1}\) s\(^{-2}\), which further supports the conclusion that the low-energy absorption band has a higher contribution from an MLCT transition than previously believed. While it is difficult to assign the band as entirely MLCT in nature due to its high absorptivity values, these calculations suggest that the MLCT transition is not merely being covered up by the oligomer-based \(\pi,\pi^*\) transition. Rather, the MLCT transition is mixed with the \(\pi,\pi^*\) transition to such a degree that it exerts a significant effect on the observed absorption band.
Table 5-13: Singlet ground state molecular orbitals for 5-M and 4-M.

<table>
<thead>
<tr>
<th>Molecular Orbital&lt;sup&gt;a&lt;/sup&gt;</th>
<th>5-M</th>
<th>4-M</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO – 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HOMO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LUMO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LUMO + 1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Parameters obtained from ZINDO/CI single point calculations following PM3 geometry optimizations as described in the experimental section. The pyridine is the aromatic ring on the right side of the molecule as indicated.
Table 5-14: Singlet ground state molecular orbitals for 5-L-1 and 4-L-1.

<table>
<thead>
<tr>
<th>Molecular Orbital</th>
<th>5-L-1</th>
<th>4-L-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO - 1</td>
<td></td>
<td>88 A  -7.84 eV</td>
</tr>
<tr>
<td>HOMO</td>
<td>9 A2  -7.15 eV</td>
<td>89 A  -7.83 eV</td>
</tr>
<tr>
<td>LUMO</td>
<td>10 B1 + 0.69 eV</td>
<td>90 A  -0.60 eV</td>
</tr>
<tr>
<td>LUMO + 2</td>
<td>11 B1 -0.40 eV</td>
<td></td>
</tr>
</tbody>
</table>

*Parameters obtained from ZINDO/CI single point calculations following PM3 geometry optimizations as described in the experimental section.*
Table 5-15: Singlet ground state molecular orbitals for 5-L-1T and 4-L-1T.

<table>
<thead>
<tr>
<th>Molecular Orbitala</th>
<th>5-L-1T</th>
<th>4-L-1T</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO – 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HOMO</td>
<td>87 A -8.27 eV</td>
<td>86 A -7.94 eV</td>
</tr>
<tr>
<td>LUMO</td>
<td>33 A -7.43 eV</td>
<td>35 B -0.49 eV</td>
</tr>
<tr>
<td>LUMO + 2</td>
<td>89 A -0.43 eV</td>
<td>92 A -0.26 eV</td>
</tr>
</tbody>
</table>

aParameters obtained from ZINDO/CI single point calculations following PM3 geometry optimizations as described in the experimental section.
Experimental

Oligomer and Complex Synthesis

The 4-L oligomers and 4-Re complexes were previously synthesized, and their synthesis is described in detail elsewhere. The 4-ReAN-3. 4-Re-3 (18 mg, 7.47 µmol) was dissolved in 20 mL methylene chloride, whereupon 6 mL of CH₃CN and AgOTf (20 mg, excess) was added. The solution was stirred at room temperature overnight. A TLC (1:1 hexanes:CH₂Cl₂) on silica showed two spots, Rᵣ = 1 (4-ReAN-3) and Rᵣ = 0.5 (4-Re-3). Additional stirring and addition of CH₃CN produced the final product. AgCl was removed from the sample solution by filtration on a medium-porosity glass frit through celite, and the filtrate was reduced by rotary evaporation to produce the final product as a triflate salt. Due to the small amount of material available, further purification was impractical. IR (THF soln, cm⁻¹), 1966, 2097, 2134 (υC≡O), 2281 (υC≡N). ESI-MS calcd for C₁₅₁H₁₉₈N₃O₁₁Re: 2411; found: 2372 (parent – CH₃CN).

Photophysical Measurements

All sample solutions studied were in either THF, 2-methyltetrahydrofuran (2-MTHF), or CH₂Cl₂. All solvents were distilled according to typical laboratory practices. All photophysical studies were conducted with the same instrumentation and techniques described in chapter 3.

Electroabsorption spectra were recorded on PMMA films doped with 4-Re-1 at room temperature and 77 K on an in-house apparatus. An Oriel 150 W xenon arc lamp coupled to a Spex monochromator and polarizer provided horizontally polarized
excitation light. A Joe Rolfe high-voltage AC power supply was used to apply a field of approximately 3.0 kV at 440 Hz to the thin film sample. Transmitted light was detected with a silicon photodiode, and the electroabsorption response was extracted from the signal with a Stanford Research Systems 850 lock-in amplifier\textsuperscript{159}. Three measurements at each temperature were recorded on two different polymer samples, and each experiment returned nearly identical results, confirming their validity.

**Electrochemical Measurements**

All electrochemical measurements were conducted on THF solutions with TBAH as the supporting electrolyte. Cyclic voltammetry measurements were performed with the same procedures and the same instrumentation described in chapter 3.

**Semi-Empirical Calculations**

All calculations were performed with Hyperchem version 5.0\textsuperscript{166}. 4-L-1 and 5-L-1 models were built within the program editor with an initial planar geometry. Polak-Ribiere geometry optimizations were performed with successive UHF/PM3 calculations and no imposed molecular restraints. All molecules retained an essentially planar form (< 2° torsion) after optimization. Finally, a single-point RHF/ZINDOs CI calculation was performed to obtain the final energies, spectroscopic parameters and molecular orbitals. A single-point Extended Hückel calculation was performed on the 4-Re-1 model described above with a K factor of 1.75, and relevant information was extracted from the program output file.
In a collaborative research effort with Dr. Stephan Guillerez and Lise Trouillet at CEA-Grenoble, the photophysics of MLCT-incorporated π-conjugated polymers with a poly-3-alkylthiophene backbone were studied. The group in Grenoble has been involved in synthesizing regiospecific (HT-HT) polythiophenes with integrated 2,2’-bipyridine subunits spaced after every four or six thiophene rings that serve as inorganic MLCT chromophore coordination sites.37,167,168 The focus of the investigation is on the properties of organic polymer P4 \((M_n = 111 \text{ kg mole}^{-1}, M_w = 244 \text{ kg mole}^{-1}, \text{PDI} = 2.20)\) and the three metal-organic polymers, P4-Ru \((M_n = 29 \text{ kg mole}^{-1}, M_w = 70 \text{ kg mole}^{-1}, \text{PDI} = 2.41)\), P6-Ru and P4-Os (Figure 6-1). Each of these polymers contains a repeat unit structure consisting of a tris-bipyridine Ru(II) or Os(II) complex flanked by a regioregular 3-octylthiophene tetramer or hexamer. Both \(-\text{Ru(bpy)}_3^{2+}\) and \(-\text{Os(bpy)}_3^{2+}\) chromophores were integrated into the polymers due to the inherent differing electronic structure of these two chromophores. Specifically, compared to their ruthenium(II) analogues, osmium(II) complexes have larger d orbital splittings and lower oxidation potentials (leading to higher-energy dd excited states and lower-energy MLCT excited states), “larger” d orbitals (leading to metal-ligand π back-bonding enhancement), and greater spin-orbit coupling.169
Although the 3-octylthiophene oligomers used in the synthesis are regioregular, due to the constraints of the polymerization reaction the polymers are not regioregular. Specifically, there exist three types of substituted bipyridines in the backbone: (1) 2,2’-bipyridine substituted at the 5,5’-positions with two 3-octylthiophene units linked through the 2-positions (the two “heads” of the oligomers); (2) 2,2’-bipyridine substituted at the 5,5’-positions with two 3-octylthiophene units linked through the 5-positions (two oligomer “tails”); and (3) 2,2’-bipyridine substituted with the “head” of one and the “tail” of another 3-octylthiophene oligomer. Despite the mixed structure of the polymer backbones, there is no evidence that the heterogeneity has an influence on its photophysical characteristics, and therefore we will not consider the point further.

The model complexes Ru(tpbpy)(bpy)$_2^{2+}$ and Ru(tpbpy)$_3^{2+}$ (where tpbpy = 5,5’-bis(3-octylthiophene)-2,2’-bipyridine) were examined to provide insight concerning the effect of thiophene substitution on the electrochemistry, photophysics and photoinduced electron transfer reactivity of the Ru(II)-bipyridine chromophore. Note that Swager and co-workers in a recent study$^{60}$ reported details concerning the electrochemical and optical absorption properties of the structurally related complexes, Ru(dtpbpy)(bpy)$_2^{2+}$ and Ru(dtpbpy)$_3^{2+}$ (where dtpbpy = 5,5’-bis(5-(2,2’-bithienyl))-2,2’-bipyridine) and the resulting polymers produced by oxidative electropolymerization. In general, the electrochemical and UV-Visible absorption properties of these complexes are in direct accord with these results.
Results

Photophysical parameters from various measurements for the thiophene model complexes and polymers are listed in Tables 6-1 and 6-2, respectively. All photophysical work was done in acetonitrile solutions under an inert atmosphere except for \( \text{P4} \), where THF solutions were used.

\[
\text{Ru(tpbpy)(bpy)}_2^{2+}
\]

\[
\text{Ru(tpbpy)}_3^{2+}
\]

\[
\begin{align*}
\text{P4} & : M = - \\
\text{P4-Ru} & : M = [\text{Ru}(\text{bpy})_2]PF_6_2 \\
\text{P4-Os} & : M = [\text{Os}(\text{bpy})_2]PF_6_2
\end{align*}
\]

\[
\text{P6-Ru}
\]

Figure 6-1: Thiophene model complex and polymer structures.
Table 6-1: Thiophene model complex photophysics.

<table>
<thead>
<tr>
<th></th>
<th>Ru(tpbpy)(bpy)$_2^{2+}$</th>
<th>Ru(tpbpy)$_3^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Absorption</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda_{\text{max}}$ / nm</td>
<td>291 (7.74)</td>
<td>275 (4.89)</td>
</tr>
<tr>
<td>($\varepsilon_{\text{max}}$ / 10$^4$ M$^{-1}$ cm$^{-1}$)</td>
<td>331 (3.44)</td>
<td>337 (6.71)</td>
</tr>
<tr>
<td></td>
<td>373 (4.08)</td>
<td>377 (8.33)</td>
</tr>
<tr>
<td></td>
<td>459 (1.41)</td>
<td>473 (1.12)</td>
</tr>
<tr>
<td><strong>Emission</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda_{298\ K}$ / nm</td>
<td>639</td>
<td>630</td>
</tr>
<tr>
<td>$\phi_{\text{em}}$</td>
<td>0.16</td>
<td>0.18</td>
</tr>
<tr>
<td>$\tau_{600\ nm, 298\ K}$ / $\mu$s</td>
<td>2.24</td>
<td>2.85</td>
</tr>
<tr>
<td>$\tau_{600\ nm, 80\ K}$ / $\mu$s</td>
<td>5.02</td>
<td>-</td>
</tr>
<tr>
<td>$k_{r, 298\ K}$ / 10$^4$ s$^{-1}$</td>
<td>7.0</td>
<td>6.2</td>
</tr>
<tr>
<td>$k_{nr, 298\ K}$ / 10$^5$ s$^{-1}$</td>
<td>3.8</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Note: Measurements were conducted on argon bubble-degassed acetonitrile solutions prepared in a drybox. Additional experimental conditions are discussed in the text.

Table 6-2: Thiophene polymer photophysics.

<table>
<thead>
<tr>
<th></th>
<th>P4</th>
<th>P4-Ru</th>
<th>P4-Os</th>
<th>P6-Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Absorption</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda_{\text{max}}$ / nm</td>
<td>437 (3.35)</td>
<td>476 (5.70)</td>
<td>477 (4.80)</td>
<td>464 (6.95)</td>
</tr>
<tr>
<td>($\varepsilon_{\text{max}}$ / 10$^4$ M$^{-1}$ cm$^{-1}$)</td>
<td>290 (7.05)</td>
<td>294 (6.39)</td>
<td>287 (7.91)</td>
<td></td>
</tr>
<tr>
<td><strong>Emission</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda_{298\ K}$ / nm</td>
<td>541</td>
<td>629</td>
<td>797</td>
<td>770</td>
</tr>
<tr>
<td>$\phi_{\text{em}}$</td>
<td>$\approx 10^4$</td>
<td>2.57</td>
<td>0.099</td>
<td>0.495</td>
</tr>
<tr>
<td>$\tau_{298\ K}$ / $\mu$s</td>
<td>0.33</td>
<td>$&lt; 10^{-3}$</td>
<td>$&lt; 10^{-3}$</td>
<td>$&lt; 10^{-4}$</td>
</tr>
<tr>
<td><strong>TA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\tau_{298\ K}$ / $\mu$s</td>
<td>19.7</td>
<td>2.07</td>
<td>0.106</td>
<td>4.52</td>
</tr>
</tbody>
</table>

Note: Measurements were conducted on argon bubble-degassed acetonitrile solutions prepared in a drybox for all polymers except TP1, where THF solutions were used. Additional experimental conditions are discussed in the text.

**Electrochemistry**

Cyclic voltammetry was performed on CH$_3$CN / 0.1 M TBAH solutions of the model thiophene-bipyridine complexes and polymers, and relevant oxidation and
reduction half-wave potentials are listed in Table 6-3. For comparison, redox potentials for Ru(bpy)$_3^{2+}$ and Os(bpy)$_3^{2+}$ in the same solvent medium are also included.

Comparison of the two tpbpy-substituted model complex redox potentials reveals that their first oxidation and reduction potentials are shifted to more positive potentials relative to Ru(bpy)$_3^{2+}$ redox potentials. The shifts are consistent with the thiophene substituents on the bpy ligands acting as π-electron acceptors. The positive shift is greater for Ru(tpbpy)$_3^{2+}$, indicating that the three tpbpy ligands have a combined effect on both the metal center oxidation and tpbpy ligand reduction. Swager and coworkers$^{60}$ observed similar anodic shifts for the first reduction potentials of the mono- and tris-bithiophene complexes (Ru(dtpbpy)(bpy)$_2^{2+}$ and Ru(dtpbpy)$_3^{2+}$) but they did not report the oxidations, apparently due to the propensity of their complexes to electropolymerize at anodic potentials.

The model complex electrochemical data reveals that the first reduction of both tpbpy complexes is localized on the tpbpy ligand, while the first oxidation wave corresponds to the Ru(II/III) couple as shown in (6-1) and (6-2), respectively.

$$
\text{Ru}^{II}(\text{tpbpy})(\text{bpy})_2^{2+} + e^- \rightarrow \text{Ru}^{II}(\text{tpbpy}^*)(\text{bpy})_2^{2+} \quad (6-1)
$$

$$
\text{Ru}^{II}(\text{tpbpy})(\text{bpy})_2^{2+} - e^- \rightarrow \text{Ru}^{III}(\text{tpbpy})(\text{bpy})_2^{3+} \quad (6-2)
$$

The electrochemical properties of polymers P4, P4-Ru and P6-Ru were analyzed in a previous report.$^{170}$ However, features pertinent to the photophysical investigations are summarized below. Comparision of the electrochemical data for the various polymers allows assignment of the first two oxidation and first reduction waves observed for both of the ruthenated polymers to redox processes centered on the thiophene-bipyridine.
polymer backbone. For example, the first oxidation and reduction process for P4-Ru can be represented as shown in (6-3) and (6-4), respectively.

\[
\text{Ru}^{II}(\text{P4bpy})(\text{bpy})_2^{2+} + e^- \rightarrow \text{Ru}^{II}(\text{P4bpy}^-)(\text{bpy})_2^{+} \quad (6-3)
\]

\[
\text{Ru}^{II}(\text{P4bpy})(\text{bpy})_2^{2+} - e^- \rightarrow \text{Ru}^{II}(\text{P4bpy}^+)(\text{bpy})_2^{3+} \quad (6-4)
\]

In (6-3) and (6-4), P4bpy\(^-\) and P4bpy\(^+\) represent a radical anion and polaron (radical cation) localized on the \(\pi\)-conjugated polymer backbone, respectively. In polymer P6-Ru, the increased oligo(3-octylthiophene) segment length induces a cathodic (i.e., less positive) shift in the first two oxidation and reduction waves. However, the assignment remains the same. The Ru(II/III) wave occurs for P4-Ru at +1.40 V and for P6-Ru at +1.34 V in CH\(_3\)CN solution versus SCE.

For cathodic sweeps, the properties of P4-Os are similar to those of P4-Ru, where the first reduction is centered on the P4bpy polymer backbone and the second is localized on one of the “ancillary” osmium bipyridine ligands. However, anodic sweeps reveal an important difference, where three closely-spaced oxidation waves were observed. Careful comparison of the electrochemistry of the various polymers and model complexes as shown in Figure 6-2 leads us to assign the first oxidation wave to the Os(II/III) couple as shown in (6-5).

\[
\text{Os}^{II}(\text{P4bpy})(\text{bpy})_2^{2+} + e^- \rightarrow \text{Os}^{III}(\text{P4bpy})(\text{bpy})_2^{3+} \quad (6-5)
\]

The second and third oxidations are located on the thiophene segments of the P4bpy backbone.
Table 6-3: Electrochemistry of thiophene complexes and polymers

<table>
<thead>
<tr>
<th>Compound</th>
<th>( E_{1/2, \text{red}} )</th>
<th>( E_{1/2, \alpha} )</th>
<th>( \Delta E_{1/2} )^b</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ru(bpy)}_3^{2+} )</td>
<td>-1.26 (bpy(^0))(^{(*)})</td>
<td>+1.30 (Ru(^{II/III}))</td>
<td>2.57</td>
</tr>
<tr>
<td></td>
<td>-1.45 (bpy(^0))(^{(*)})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Os(bpy)}_3^{2+} )</td>
<td>-1.22 (bpy(^0))(^{(*)})</td>
<td>+0.88 (Os(^{II/III}))</td>
<td>2.10</td>
</tr>
<tr>
<td></td>
<td>-1.42 (bpy(^0))(^{(*)})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Ru(tpbpy)(bpy)}_2^{2+} )</td>
<td>-0.99 (tpbpy(^0))(^{(*)})</td>
<td>+1.57 (Ru(^{II/III}))</td>
<td>2.56(^c)</td>
</tr>
<tr>
<td></td>
<td>-1.31 (bpy(^0))(^{(*)})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Ru(tpbpy)}_3^{2+} )</td>
<td>-0.89 (tpbpy(^0))(^{(*)})</td>
<td>+1.73 (Ru(^{II/III}))</td>
<td>2.62(^c)</td>
</tr>
<tr>
<td></td>
<td>-1.18 (tpbpy(^0))(^{(*)})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{P4}^d )</td>
<td>-1.78 (P4bpy(^0))(^{(*)})</td>
<td>+0.97 (P4bpy(^0))(^{(*)})</td>
<td>2.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+1.35 (P4bpy(^0))(^{(*)})</td>
<td></td>
</tr>
<tr>
<td>( \text{P4-Ru} )</td>
<td>-0.99 (P4bpy(^0))(^{(*)})</td>
<td>+0.97 (P4bpy(^0))(^{(*)})</td>
<td>1.96</td>
</tr>
<tr>
<td></td>
<td>-1.27 [Ru(bpy)(bpy(^0)](^{(*)})</td>
<td>+1.13 (P4bpy(^0))(^{(*)})</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>+1.40 (Ru(^{II/III}))</td>
<td></td>
</tr>
<tr>
<td>( \text{P6-Ru} )</td>
<td>-0.99 (P6bpy(^0))(^{(*)})</td>
<td>+0.82 (P6bpy(^0))(^{(*)})</td>
<td>1.81</td>
</tr>
<tr>
<td></td>
<td>-1.30 [Ru(bpy)(bpy(^0)](^{(*)})</td>
<td>+0.98 (P6bpy(^0))(^{(*)})</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>+1.34 (Ru(^{II/III}))</td>
<td></td>
</tr>
<tr>
<td>( \text{P4-Os} )</td>
<td>-0.91 (P4bpy(^0))(^{(*)})</td>
<td>+0.92 (Os(^{II/III}))</td>
<td>1.83</td>
</tr>
<tr>
<td></td>
<td>-1.14 [Os(bpy)(bpy(^0)](^{(*)})</td>
<td>+1.01 (P4bpy(^0))(^{(*)})</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>+1.21 (P4bpy(^0))(^{(*)})</td>
<td></td>
</tr>
</tbody>
</table>

^aMeasurements performed in CH\(_3\)CN solution (0.1 M TBAH supporting electrolyte) with a Pt working electrode, Pt auxiliary electrode, and Ag/Ag\(^+\) (10\(^{-2}\) M) reference electrode. Potentials are referenced against a ferrocene internal standard, and reported in V vs. SCE along with their assigned redox couple.

^bDifference between lowest oxidizing and reducing waves. ^cCH\(_2\)Cl\(_2\)/ 0.2 M TBAH solution measurements. ^dThin film immersed in CH\(_3\)CN / 0.1 M TBAH solution. ^eCoulometry indicates that the first and second oxidations correspond to 0.5 and 1.5 electrons, respectively. See reference \(^{170}\) for details.

Absorption Spectra

Absorption spectra of the thiophene model complexes and polymers, with absorptivity values calculated based on (3-1), are shown in Figure 6-3. Note that the polymer absorptivity values are based on the formula weight of the repeat unit.

Absorption maxima are listed for the model complexes and polymers in Tables 6-1 and 6-2, respectively.
Figure 6-2: Cyclic voltammetry in CH₃CN solution / 0.1 M TBAH, with a Pt working electrode, Pt auxiliary electrode, and Ag/Ag⁺ (10⁻² M) reference electrode.

(a) [Os(bpy)₃][PF₆]₂; (b) P₄-Os; (c) P₄-Ru; (d) [Ru(bpy)₃]Cl₂.
The model complex absorption spectra feature two strong tpbpy-based intraligand $\pi,\pi^*$ bands at 325 and 370 nm along with a weaker 450 nm MLCT band. The strong 370 nm intraligand band, which is considerably enhanced in the tris-tpbpy complex, is due to the long axis-polarized $\pi,\pi^*$ optical transition on the tpbpy ligand. The large oscillator strength in this transition is consistent with the extended $\pi$-conjugation produced by the linear array of four heteroaromatic rings. The absorption maximum for the MLCT
transition is red-shifted \( \approx 14 \text{ nm} \) for \( \text{Ru(tpbpy)}_3^{2^+} \) compared to that for the heteroleptic complex \( \text{Ru(tpbpy)(bpy)}_2^{2^+} \). However, the red side of the MLCT bands match well. In the heteroleptic complex, the MLCT band contains contributions from \( \text{Ru} \rightarrow \text{bpy} \) and \( \text{Ru} \rightarrow \text{tpbpy} \) transitions, while in the homoleptic complex the band arises from the \( \text{Ru} \rightarrow \text{tpbpy} \) transition only. Since the electrochemical results indicate that the tpbpy ligand is \( \approx 200 \text{ mV} \) easier to reduce than bpy, the \( \text{Ru} \rightarrow \text{tpbpy} \) MLCT transition occurs at a lower energy than the \( \text{Ru} \rightarrow \text{bpy} \) MLCT transition. Consequently, the low energy side of the MLCT band for both complexes is due to the \( \text{Ru} \rightarrow \text{tpbpy} \) transition. The intensity increase on the higher energy side of the MLCT band for \( \text{Ru(tpbpy)(bpy)}_2^{2^+} \) is due to the higher energy \( \text{Ru} \rightarrow \text{bpy} \) transitions.

Another point of interest is the fact that the extended conjugation present in tpbpy does not increase its MLCT transition oscillator strength. Mulliken theory\textsuperscript{163-165} indicates that the intensity of a charge transfer transition is proportional to the transition dipole, which increases with the excited state dipole moment. Therefore, the similar oscillator strength for the MLCT transitions in the tpbpy complexes compared to \( \text{Ru(bpy)}_3^{2^+} \) signals that the MLCT excited state dipole moments are similar. Consequently, the extended conjugation in the tpbpy ligand does not increase the excited state dipole moment. This conclusion may not be a surprise, given that tpbpy has a “linear” geometry imposed by the 5,5’-substitution pattern of the thiophene rings on the bpy unit. Indeed, an increase in excited state dipole moment might be anticipated if the thiophene rings were present in the 4,4’-positions as shown for the PPE-type oligomers in chapter 5. This idea is further supported in the work by Swager and coworkers on bis(bithienyl)-substituted bipyridine complexes.\textsuperscript{60} Specifically, when the bithienyl units are at the 4,4’-positions on the
bipyridine ligand, the MLCT band extinction coefficient is increased by > 50% relative to Ru(bpy)$_3^{2+}$.

The absorption spectra of the thiophene-bipyridine polymers all feature a single broad absorption with a shoulder on the blue side of the band (Figure 6-1b). Polymer **P4** exhibits a broad 437 nm absorption band that is due to the long-axis polarized $\pi,\pi^*$ transition.$^5,26,103,167$ The molar absorptivity value, which is based on a repeat unit consisting of four thiophene rings and one bipyridine, is very similar to that of a head-to-tail 3-octyl(thiophene) hexamer ($\varepsilon_{\text{max}} \approx 3.80 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$).$^37$

Coordination of –Ru(bpy)$_2^{2+}$ to the P4bpy bipyridine unit (polymer **P4-Ru**) induces a red-shift and intensity increase in the predominant low-energy absorption band. This change in the band energy and intensity arises for several reasons. First, while the low-energy band is clearly dominated by the $\pi,\pi^*$ transitions localized on the polymer backbone, the Ru $\rightarrow$ bpy and Ru $\rightarrow$ P4bpy MLCT transitions must augment the oscillator strength of the band, possibly contributing as much as 25% of the total intensity. Second, the $\pi,\pi^*$ transition energy is decreased relative to the **P4** value due to the fact that the ruthenium coordination forces the bipyridine subunit into a planar conformation, which increases the effective conjugation length of the polymer backbone and reduces the LUMO energy. This trend is the same photophysical phenomena observed in the PPE-type oligomer presented in previous chapters. Third, it is also possible that metal coordination increases the electron-accepting capability of the bipyridine unit, which in turn increases the thiophene $\rightarrow$ bipyridine charge transfer contribution to the observed $\pi,\pi^*$ optical transition. In addition to the prominent low-energy band, the **P4-Ru** absorption features enhanced absorptivity in the 300 – 400 nm region and an additional
intense 290 nm band. This new band clearly arises from a $\pi,\pi^*$ transition localized on the remote bipyridines, while the weaker broad features in the 300 – 400 nm region may arise from metal-centered (dd) and/or higher-energy MLCT transitions localized on the –Ru(bpy)$_2^{2+}$ chromophore.$^{40}$

The P6-Ru absorption spectrum exhibits many of the same features as the P4-Ru spectrum, but the dominant low-energy band in P6-Ru displays an enhanced molar absorptivity and increased bandwidth. The absorptivity increase arises from the increase in the number of thiophene rings in the repeat unit. The increased bandwidth may also be due to the longer thiophene segment, which may allow a greater number of backbone conformations and an increased distribution of $\pi,\pi^*$ transition energies.

The P4-Os absorption spectrum is generally similar to P4-Ru with some subtle yet significant differences. First, the red edge of the dominant low-energy absorption band is shifted to slightly lower energy. This small shift may arise from allowed Os $\rightarrow$ bpy singlet-singlet MLCT transitions that are at a lower energy compared to the Ru $\rightarrow$ bpy transitions. This MLCT transition energy shift is anticipated since the osmium center is considerably easier to oxidize than ruthenium ($+0.89$ vs. $+1.37$ V). By comparison, the singlet-singlet MLCT transitions in acetonitrile solution of Os(bpy)$_3^{2+}$ and Ru(bpy)$_3^{2+}$ arise at 479 and 450 nm, respectively.$^{40,171,172}$ Second, a weak band is clearly observed for P4-Os in the 600 – 700 nm region, which is due to singlet-triplet Os $\rightarrow$ bpy and Os $\rightarrow$ P4bpy MLCT transitions.

**Emission Spectra and Decay Kinetics**

Emission spectra of Ru(tpbpy)(bpy)$_2^{2+}$ and Ru(tpbpy)$_3^{2+}$ in optically dilute acetonitrile solutions are shown in Figure 6-4, and the emission maxima are listed in
Table 6-1. The emission spectra were fitted by Franck-Condon emission bandshape analysis based on (2-14) as shown in the figure, and fit parameters are listed in Table 6-4.

Figure 6-4: Thiophene model complex emission spectra in acetonitrile (380 nm excitation). Points are experimentally-determined data, while the lines are Franck-Condon bandshape analysis fits as described in the text. (a) Ru(tpbpy)(bpy)$_2$$^{2+}$; (b) Ru(tpbpy)$_3$$^{2+}$.

Table 6-4: Franck-Condon emission bandshape fitting parameters for model complexes.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ru(tpbpy)(bpy)$_2$$^{2+}$</th>
<th>Ru(tpbpy)$_3$$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_0$ / cm$^{-1}$</td>
<td>15,795</td>
<td>15,925</td>
</tr>
<tr>
<td>$h\nu_m$ / cm$^{-1}$</td>
<td>1,300</td>
<td>1,350</td>
</tr>
<tr>
<td>$S_m$</td>
<td>0.91</td>
<td>0.86</td>
</tr>
<tr>
<td>$\Delta\nu_{0,1/2}$ / cm$^{-1}$</td>
<td>1,420</td>
<td>1,370</td>
</tr>
</tbody>
</table>

Note: Emission fitting based on (2-14) and room temperature emission spectra recorded in dilute acetonitrile solutions.
Both complexes feature broad emission bands with well-defined (0,0) and (0,1) vibronic components. The spacing of the individual vibronic components ($\Delta \nu_{0,1/2} \approx 1400 \text{ cm}^{-1}$) is consistent with C-C stretching modes centered on the bpy and tpbpy ligands. The emission bands for the two complexes are slightly red-shifted relative to the emission of Ru(bpy)$_3^{2+}$ ($\lambda_{\text{max}} = 615 \text{ nm}$). However, the overall similarity of the emission bandshape and energies for the thiophene-substituted complexes and the parent complex strongly suggests that the emission emanates from a MLCT-based excited state for the model complexes. The decreased emission energy for the tpbpy complexes is consistent with the decreased tpbpy reduction potential compared to bpy and signals that for both Ru(tpbpy)(bpy)$_2^{2+}$ and Ru(tpbpy)$_3^{2+}$ the lowest lying MLCT excited state is based on the Ru $\rightarrow$ tpbpy transition as shown in (6-6) for Ru(tpbpy)(bpy)$_2^{2+}$.

\[
\text{Ru}^{II}(\text{tpbpy})(\text{bpy})_2^{2+} + h\nu \rightarrow \text{Ru}^{III}(\text{tpbpy}^*)(\text{bpy})_2^{2+*} \quad (6-6)
\]

The emission energy is slightly higher for Ru(tpbpy)$_3^{2+}$ than for Ru(tpbpy)(bpy)$_2^{2+}$, consistent with the electrochemistry results. The MLCT state energy ($E_{\text{MLCT}}$) is proportional to the difference in the metal center oxidation potential and the acceptor ligand reduction potential ($\Delta E_{1/2} = E_{1/2}(\text{Ru}^{II/III}) - E_{1/2}(\text{tpbpy}^{0/\cdot})$), and examination of the entries in Table 6-3 indicates that $\Delta E_{1/2}$ is larger for Ru(tpbpy)$_3^{2+}$ than Ru(tpbpy)(bpy)$_2^{2+}$.

The photoluminescence spectrum of Ru(tpbpy)(bpy)$_2^{2+}$ was also examined in a 4:1 EtOH/MeOH solvent mixture over a 80 K – 298 K temperature range (data not shown). As temperature decreases, the emission intensity increases, the emission maximum blue-shifts ($\lambda_{\text{max}} = 595 \text{ nm at } 80 \text{ K}$), and the vibronic progression becomes better defined. The 0.14 eV anti-Stokes shift that occurs upon cooling is consistent with a
“rigidochromic” effect observed in MLCT emission of other d⁶ polypyridine metal complexes* and further supports the assignment of the luminescence to the Ru → tpbpy MLCT excited state.⁴¹

Emission quantum yields and decay lifetimes were measured for Ru(tpbpy)(bpy)₂²⁺ and Ru(tpbpy)₃²⁺ at 298 K, and the values are listed in Table 6-1. Radiative and apparent non-radiative decay rates (kᵣ and kᵦ) were computed for both complexes using the φₑ and τₑ values and (4-1), and these parameters are also listed in the above table. The apparent kᵦ value represents the sum of the rates of the intrinsic non-radiative decay process and internal conversion to a dd excited state that is energetically accessible via thermal activation at 298 K. In addition, there may be further complications in the excited state decay kinetics arising from the close energetic proximity of a tpbpy ligand-centered 3π,π* state.

The quantum yields and lifetimes for both tpbpy complexes are larger than those for Ru(bpy)₃²⁺ (φₑ = 0.062 and τₑ = 840 ns in acetonitrile).⁴⁰,⁷⁶ The enhanced values for the model thiophene-bipyridine complexes arise mainly due to a decrease in the apparent non-radiative decay rate. The reduced apparent kᵦ values for the tpbpy complexes likely originate from a combination of two effects. First, the MLCT energy decrease in the tpbpy complexes increases the energy gap between the MLCT and dd states, thereby decreasing the rate of internal conversion. Second, the extended π-conjugation in the tpbpy ligand increases the delocalization of the photoexcited electron which is likely to reduce the excited state electron-vibration coupling. In recent studies¹⁷⁴,¹⁷⁵ it has been demonstrated that delocalization in the acceptor ligand effectively decreases kᵦ.

* Ru(bpy)₃²⁺ features a 0.17 eV blue-shift on cooling.⁴⁰
Emission and excitation spectra of the thiophene-bipyridine polymers in optically dilute room temperature solutions are illustrated in Figure 6-5 and emission maxima, quantum yields and decay lifetimes are listed in Table 6-2. The emission spectrum of P4 in THF features a relatively intense 541 nm band and a 569 nm shoulder, with a quantum yield of 0.32. Unfortunately, the emission decay lifetime is too short to measure accurately with our instrumentation, so we conclude that $\tau \leq 200$ ps. The small Stokes shift, large quantum yield and short lifetime all suggest that photoluminescence from P4 emanates from a $^1\pi,\pi^*$ exciton that is energetically located near the material band edge. The overall fluorescence properties of P4 do not differ substantially from that of a regioregular head-to-tail poly(octylthiophene), indicating that the bipyridine unit has a relatively minor effect on its lowest excited state properties. Although phosphorescence was not observed from P4, in view of the similarity of the $^1\pi,\pi^*$ photophysics of this polymer to that of head-to-tail poly(octylthiophene), the P4 $^3\pi,\pi^*$ state can be estimated at approximately 1.6 ± 0.1 eV. This estimate is based on a recent study of thiophene oligomers that suggests the singlet-triplet splitting in polythiophenes is $\approx 5200$ cm$^{-1}$.30

The P4-Ru photoluminescence (Figure 6-5b) has a similar energy and bandshape compared to Ru(tpbpy)(bpy)$_2^{2+}$ and Ru(tpbpy)$_3^{3+}$ (Figure 6-4). This feature strongly implies that the P4-Ru photoluminescence emanates from the Ru $\rightarrow$ P4bpy MLCT excited state. However, the P4-Ru emission quantum yield is at least two orders of magnitude lower than the model complexes (Tables 6-1 and 6-2). In spite of the dramatically reduced quantum yield, the P4-Ru emission lifetime (2.57 $\mu$s) is comparable to that of the model complexes. This combination of very low quantum yield and large
lifetime suggests an apparent radiative decay rate for \textbf{P4-Ru} that is unusually low compared to other polypyridine Ru(II) complexes ($k_r \approx 10^3$ s$^{-1}$ vs. $10^5$ s$^{-1}$). This situation has been observed by Schmehl and coworkers\cite{112,147} in styryl-bipyridine and pyrene-bipyridine Ru(II) complexes where there is an intraligand $3\pi,\pi^*$ excited state that lies close in energy to the emitting MLCT excited state. By inference, we believe that the unusually weak \textbf{P4-Ru} MLCT luminescence arises because the energy of the P4bpy “ligand” $3\pi,\pi^*$ state ($E_T^{P4}$) is 0.3 – 0.4 eV less than the MLCT energy ($E_{MLCT}$) and consequently is the dominant excited state species present at long times after photoexcitation.\cite{28-30} If this scenario is correct, the MLCT emission arises via thermally-activated internal conversion from the P4bpy $3\pi,\pi^*$ state. This situation is analogous to the observation of delayed fluorescence in organic chromophores.\cite{108}

Polymer \textbf{P6-Ru} features an exceedingly weak 760 nm emission (Figure 6-5c). This emission is red-shifted and considerably weaker ($= 20$-fold weaker, $\phi_{em} < 10^{-4}$) than the \textbf{P4-Ru} emission. Unfortunately, the emission is too weak to obtain reliable decay lifetime data. Given the energy and bandshape of this emission, it is safe to conclude that \textbf{P6-Ru} does not luminesce from a Ru $\rightarrow$ P6bpy based MLCT state. MLCT emission is absent in \textbf{P6-Ru} because the $\textbf{P6}$ $3\pi,\pi^*$ state energy ($E_T^{P6}$) is even lower than the \textbf{P4} triplet energy (i.e., $E_T^{P6} < E_T^{P4}$). This idea is supported by a recent study which demonstrated that the triplet energy in $\alpha$-oligothiophenes decreases by approximately 0.06 eV per thiophene unit (for $n = 3$ to 7).\cite{30} Based on this study, we anticipate $E_T^{P6}$ may be at least 0.1 eV less than $E_T^{P4}$. The decreased \textbf{P6-Ru} triplet energy may preclude significant population of the ruthenium-based MLCT state via thermally activated internal
conversion, and consequently MLCT emission is not observed. Finally, it is tempting to consider the fact that the weak emission observed from P6-Ru may emanate directly from the \( ^3\pi,\pi^* \) manifold (i.e., the emission is phosphorescence). Based on the emission energy, this would place \( E_T^{\text{P6}} \approx 1.5 – 1.6 \) eV. This phosphorescence conclusion is based on its similarity to an 826 nm phosphorescence band observed for poly(3-hexylthiophene) at 18 K.\(^{38}\)

Polymer P4-Os features a relatively weak 797 nm emission (Figure 6-5d). This emission is red-shifted \( \approx 0.45 \) eV compared to the P4-Ru MLCT emission. However, based on the difference in the emission energies of the parent complexes (Ru(bpy)\(_3\))\(^{2+}\) and Os(bpy)\(_3\))\(^{2+}\), \( 0.35 \) eV,\(^{171}\) the P4-Os emission energy is in accord with expected results if the luminescence emanates from the Os \( \rightarrow \) P4bpy MLCT state. The MLCT assignment is also supported by the lifetime \( (\tau_{\text{em}} = 100 \) ns), which is consistent with MLCT state lifetimes in osmium polypyridyl complexes that have emission energies similar to that of P4-Os.\(^{76}\) Since the luminescence properties are similar to those observed for osmium polypyridine complexes, we conclude that in P4-Os the MLCT state is not significantly “perturbed” by the P4 \( ^3\pi,\pi^* \) state. Therefore, in P4-Os \( E_{\text{MLCT}} < E_T^{\text{P4}} \). In summary, the P4-Ru and P4-Os observations imply that \( E_T^{\text{P4}} \) is less than \( E_{\text{MLCT}} \) for the -Ru(bpy)\(_2\))\(^{2+}\) chromophore but greater than \( E_{\text{MLCT}} \) for the –Os(bpy)\(_2\))\(^{2+}\) chromophore (i.e., \( 2.0 \) eV > \( E_T^{\text{P4}} > 1.55 \) eV). Note that this implication agrees with the estimated P4bpy “ligand” triplet energy given above \( (\approx 1.6 \pm 0.1 \) eV).
Figure 6-5: Thiophene polymer emission (solid line) and excitation (dashed line) spectra in optically dilute acetonitrile solution (except P4, which is in THF solution).
(a) P4 (400 nm excitation; 540 nm emission); (b) P4-Ru (380 nm excitation; 630 nm emission); (c) P6-Ru (460 nm excitation; 760 nm emission); (d) P4-Os (475 nm excitation; 800 nm emission).
An important feature that is shared by all metal-organic polythiophenes is the absence of any significant $^1\pi,\pi^*$ fluorescence from the polymer backbone. Fluorescence emission is not observed despite the fact that 1) the absorption spectra of the polymers are dominated by the $^1\pi,\pi^*$ bands and 2) the radiative decay rate of the $^1\pi,\pi^*$ state is large. These observations suggest that the $^1\pi,\pi^*$ exciton produced by light absorption in the metal-organic polymers diffuses to and becomes trapped by the metal complex units very rapidly with a rate in excess of $10^{11}$ s$^{-1}$. This conclusion is in accord with recent studies of intra- and inter-strand energy migration in conjugated polymers discussed in chapter 1 which suggest that $^1\pi,\pi^*$ excitons are highly mobile in $\pi$-conjugated assemblies.

**Transient Absorption Spectra**

Transient absorption spectra were recorded for the thiophene-bipyridine model complexes and polymers following 355 nm excitation.Transient absorption decay lifetimes obtained from global factor analysis$^{114}$ of the time-resolved absorption data are listed in Table 6-1 for the model complexes and Table 6-2 for the polymers.

The transient absorption difference spectra for Ru(tpbpy)(bpy)$_2^{2+}$ and Ru(tpbpy)$_3^{2+}$ are illustrated in Figures 6-6a and 6-7a, respectively. Transient absorption decay lifetimes for both complexes are in approximate agreement with the MLCT luminescence decay lifetimes, suggesting that the transient absorptions arise from the MLCT excited state. The similarity of the transient absorption difference spectra for the two complexes suggests similar MLCT excited state electronic structures. By contrast, the excited state difference spectra of the tpbpy complexes are very different from the difference spectrum of Ru(bpy)$_3^{2+}$, where a 360 nm absorption and 440 nm MLCT bleach
is observed.\textsuperscript{176} Therefore, we conclude that the long-lived MLCT state in the tpbpy complexes is based on the Ru $\rightarrow$ tpbpy transition shown in (6-6) above.

Figure 6-6: Transient absorption spectra of Ru(tpbpy)(bpy)$_2^{2+}$ in acetonitrile. Arrows indicate progression of the transients with time after 355 nm laser excitation. (a) complex only (transients are 800 ns increments after laser excitation); (b) complex with 20 mM MV$^{2+}$ (transients are 80 ns increments after laser excitation).
Several points are of interest with respect to the transient absorption spectra of the model complexes. First, given that tpbpy is the MLCT state “acceptor ligand”, the excited-state transient absorption spectrum is dominated by features associated with the one-electron reduced state of the ligand (i.e., tpbpy$^\ast$). This conclusion is clearly the case since the most pronounced feature in the difference spectrum is the 380 nm bleach that...
corresponds to the ground-state $\pi,\pi^*$ absorption of the tpbpy ligand. In addition, two strong excited-state absorption bands are observed in the visible region which likely arise from allowed $\pi \to \pi^*$ and $\pi^* \to \pi^*$ transitions localized on tpbpy*. Furthermore, the lack of an observable bleach of the ground state MLCT absorption band in the 400 – 450 nm region ($\varepsilon = 15,000 \text{ M}^{-1}\text{cm}^{-1}$) seen in the Ru(bpy)$_3^{2+}$ difference spectrum qualitatively indicates that the oscillator strength of the excited state absorption bands seen in the visible region are large ($\varepsilon > 20,000 \text{ M}^{-1}\text{cm}^{-1}$). These large oscillator strengths also correspond to the visible transient absorption bands arising from transitions associated with tpbpy*.

The transient absorption difference spectrum of $\textbf{P4}$ in THF is shown in Figure 6-7. The spectrum features bleaching at 440 nm that corresponds to the ground-state $\pi,\pi^*$ absorption and a broad excited-state 740 nm absorption band that extends into the near-IR. The transient absorption decays with $\tau \approx 20 \mu$s,† which is a strong indication that the transient is the $^3\pi,\pi^*$ state. In accord with the triplet assignment, the transient absorption difference spectrum of $\textbf{P4}$ is remarkably similar to the triplet-triplet difference spectra of poly(3-octylthiophene) ($\lambda_{\text{max}} = 820 \text{ nm}$)$^{132}$, $\alpha$-septithiophene (Figure 1-8, $\lambda_{\text{max}} = 740 \text{ nm}$)$^{28,29}$ and the PPE-type oligomers previously discussed (Figure 3-9). The transient absorption of $\textbf{P4}$ is comparatively weak ($\Delta A_{\text{max}} \approx 0.02$), which is a qualitative indication that the triplet yield following direct excitation of the polymer is low (likely < 20%).

† The $\textbf{P4}$ transient lifetime is likely limited by the presence of residual oxygen after argon bubble-degassing.
Figure 6-8: Transient absorption spectra of P4 in argon bubble-degassed THF. Arrows indicate progression of the transients with time after laser excitation, and transients are 1600 ns increments after laser excitation.

Transient absorption difference spectra for P4-Ru and P6-Ru are illustrated in Figures 6-9a and 6-10a, respectively. The difference spectra of the ruthenated polymers are qualitatively similar to the P4 difference spectrum, which suggests that the P4-Ru and P6-Ru transient absorption arises from the thiophene-bipyridine polymer backbone $^3\pi,\pi^*$ excited state. However, despite the triplet assignment, the transient absorption decay lifetimes of P4-Ru and P6-Ru are considerably shorter than the P4 triplet state. Furthermore, there is good agreement in P4-Ru between the transient absorption and photoluminescence decay lifetimes. This correlation is surprising given that the photoluminescence of P4-Ru has been assigned to the Ru $\rightarrow$ P4bpy MLCT state. These features suggest that the $^3\pi,\pi^*$ decay dynamics may be modified in P4-Ru and P6-Ru due
to its close energetic proximity to the MLCT state. This point will be discussed in more detail below.

Figure 6-9: Transient absorption spectra of P4-Ru in acetonitrile. Arrows indicate progression of the transients with time after 355 nm laser excitation. (a) polymer only (transients are 800 ns increments after laser excitation); (b) polymer with 20 mM MV$^{2+}$ (transients are 4000 ns increments after laser excitation).
Figure 6-10: Transient absorption spectra of P6-Ru in acetonitrile. Arrows indicate progression of the transients with time after 355 nm laser excitation. (a) polymer only (transients are 1600 ns increments after laser excitation); (b) polymer with 20 mM MV$^{2+}$ (transients are 8000 ns increments after laser excitation).

The P4-Os transient absorption difference spectrum is shown in Figure 6-11a.

The spectrum exhibits a 490 nm ground-state bleach similar to that observed in P4-Ru and P6-Ru. However, the excited-state absorption of P4-Os in the 600 – 800 nm region is much less prominent than the corresponding ruthenated polymer (i.e., the absorption of P4-Os is relatively “flat” without any discernible maximum in the 600 – 800 nm region).
Furthermore, the **P4-Os** transient absorption decay lifetime is in excellent agreement with the emission decay lifetime (Table 6-2). These features point to the possibility that for **P4-Os** the transient absorption arises from the Os → P4bpy MLCT state and not the polymer backbone $\pi,\pi^*$ state.

![Figure 6-11: Transient absorption spectra of **P4-Os** in acetonitrile. Arrows indicate progression of the transients with time after laser excitation. (a) polymer only (transients are 24 ns increments after laser excitation); (b) polymer with 20 mM MV$^{2+}$ (transients are 48 ns increments after laser excitation).](image-url)
Discussion

Excited-State Energetics

Based on the luminescence and transient absorption spectroscopy of the various thiophene-bipyridine polymers, it is possible to assemble a relatively concise scheme that explains the experimental observations. This scheme is summarized in the Jablonski diagrams shown in Figure 6-12, where the energies of the various states are defined as accurately as possible.

First, consider the situation for the two ruthenated polymers, P4-Ru and P6-Ru, which are shown on the left side of the figure. Photoexcitation in the near-UV and visible region primarily populates the $^1\pi,\pi^*$ state of the Pnbpy polymer (path 1). This state rapidly decays to the $^3\pi,\pi^*$ state of the Pnbpy backbone, which is the lowest excited state.
in the “supermolecule”. It is unknown whether this process occurs via heavy atom promoted direct intersystem crossing (path 3) or the $^3\text{MLCT}$ state (path 2 followed by path 4). However, it is certain that the process occurs rapidly and efficiently, given the complete absence of $^1\pi,\pi^*$ fluorescence and the comparatively high yield of the long-lived excited state based on the strength of the transient absorption signal. For both P4-Ru and P6-Ru, the long-lived excited state observed by ns-μs transient absorption spectroscopy is the $^3\pi,\pi^*$ state. Although the population of the excited state polymer molecules predominantly exists in the $^3\pi,\pi^*$ state, the $^3\text{MLCT}$ state can be repopulated via a thermally-activated internal conversion process (step 5). In this way, an equilibrium is established between the two states.\textsuperscript{147,148} In P4-Ru, the energy gap between the $^3\pi,\pi^*$ and $^3\text{MLCT}$ states is small enough so that at equilibrium there is a sufficient population of $^3\text{MLCT}$ to observe its characteristic emission (path 6). However, in P6-Ru the energy gap separating these states is apparently large enough to suppress the MLCT emission. Nonetheless, in both P4-Ru and P6-Ru the dominant pathway for $^3\pi,\pi^*$ state decay is via the $^3\text{MLCT}$ state (i.e., path 5 followed by path 7). Note that the increased $^3\pi,\pi^*$ state lifetime in P6-Ru relative to P4-Ru is consistent with the larger energetic deficit that needs to be overcome to return to the MLCT state. This excited-state equilibrium is identical to that observed in the PPE-type oligomers presented in previous chapters.

The P4-Os excited state scheme is outlined in the Jablonski diagram on the right side of Figure 6-12. Near-UV and visible excitation of this polymer (path 1) affords the P4bpy backbone $^1\pi,\pi^*$ state. This state rapidly relaxes to the Os $\rightarrow$ P4bpy $^3\text{MLCT}$ state (path 2), which is the lowest excited state of the “supermolecule”. The $^3\text{MLCT}$ state then relaxes by normal radiative and non-radiative decay pathways (paths 3 and 4), giving rise
to the luminescence spectrum and lifetime that are typical for the Os(bpy)$_3^{2+}$ chromophore.

**Electron Transfer Energetics**

In an effort to investigate the propensity of the excited state polymers to undergo photoinduced electron transfer (ET) and to characterize the spectroscopic properties of the oxidized and/or reduced forms of the polymers, transient absorption studies were carried out on the model complexes and P4-Ru, P6-Ru and P4-Os in the presence of N,N'-dimethylaniline (DMA, a reductive quencher) and N,N'-dimethyl-4,4'-bipyridinium (MV$^{2+}$, an oxidative quencher).

Addition of 20 mM DMA did not result in excited state quenching (as assessed by transient absorption) for any of the complexes or polymers. The lack of quenching is consistent with free energy estimates for ET (calculated below) that indicate reductive quenching by DMA is endothermic by at least 0.1 eV for all of the materials. By contrast, MV$^{2+}$ quenches the transient absorption of all of the ruthenium complexes and metallated polymers. Furthermore, in almost every case quenching leads to the production of long-lived transient absorptions that clearly arise from the products of bimolecular photoinduced ET. The ET rate constant ($k_{et}$) for these model complexes and polymers are calculated based on (6-7).

\[
-k_{0} \frac{d[M^*]}{dt} + k_{et} ^ {\*} \frac{d[M^{\*\*}]}{dt} = \left( k_{et} ^ {\* \*} [MV^{2+}] + k_{d} ^ {\*} [M^*] \right) = k_{obs} [M^*]
\]  

(6-7)

In (6-7), $k_{d} ^ {0}$ is the M* decay rate constant without the presence of the methyl viologen quencher and $k_{et}$ is the decay rate constant at a specific viologen concentration.

Calculated electron transfer rate constants are listed in Table 6-5.
Table 6-5: Electron transfer rate constants for thiophene-bipyridine models and polymers.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k_d / 10^5$ s$^{-1}$</th>
<th>$k_{obs} / 10^6$ s$^{-1}$</th>
<th>[MV$^{2+}$] / mM</th>
<th>$k_{et} / 10^7$ M$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(tpbpy)(bpy)$_2$$^{2+}$</td>
<td>8.40</td>
<td>5.90</td>
<td>20</td>
<td>25.3</td>
</tr>
<tr>
<td>Ru(tpbpy)$_3$$^{2+}$</td>
<td>3.12</td>
<td>1.19</td>
<td>22</td>
<td>3.99</td>
</tr>
<tr>
<td>P4-Ru</td>
<td>4.83</td>
<td>5.25</td>
<td>30</td>
<td>15.9</td>
</tr>
<tr>
<td>P6-Ru</td>
<td>2.21</td>
<td>1.60</td>
<td>21</td>
<td>6.57</td>
</tr>
<tr>
<td>P4-Os</td>
<td>100</td>
<td>15.3</td>
<td>20</td>
<td>26.5</td>
</tr>
</tbody>
</table>

$^a$Argon bubble-degassed acetonitrile solutions, 298 K. $^b$Transient absorption decay rate in the absence of quencher. $^c$Transient absorption decay rate in the presence of the specified methyl viologen concentration.

Figures 6-6b and 6-7b illustrate the evolution of the transient absorption spectra when a solution of Ru(tpbpy)(bpy)$_2$$^{2+}$ or Ru(tpbpy)$_3$$^{2+}$ and 20 mM MV$^{2+}$ is subjected to 355 nm excitation. At early times after excitation, the MLCT excited state absorption is apparent. However, over the course of $\approx 1 \mu$s the spectrum evolves into one that is characterized by bleaching for $\lambda < 380$ nm, a strong 395 nm absorption with a 400 nm shoulder, weak bleaching between 440 and 480 nm and a broad 605 nm band. This difference spectrum is clearly due to a superposition of absorption bands characteristic of the oxidized Ru(III) complex and the viologen radical cation, MV$^{+\bullet}$. These species are produced by the photoinduced ET described in (6-8).

$$\text{Ru}^{III}(\text{tpbpy}^{•\bullet})(\text{bpy})_2^{2+\bullet} + \text{MV}^{2+} \rightarrow \text{Ru}^{III}(\text{tpbpy})(\text{bpy})_2^{3+} + \text{MV}^{+\bullet} \quad (6-8)$$

The transient absorption decays on a longer timescale ($\tau = 50 \mu$s) consistent with the disappearance of radical ions via diffusion-controlled back ET. The excited state quenching rate for Ru(tpbpy)$_3$$^{2+}$ is approximately six times lower than Ru(tpbpy)(bpy)$_2$$^{2+}$ (Table 6-5).
There are several significant features with respect to the ET quenching experiments on the model complexes. First, although both complexes are quenched by MV$^{2+}$, the quenching rates are an order of magnitude less than the rate that MV$^{2+}$ quenches Ru(bpy)$_3^{2+}$ ($k_{eq} = 2.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$). The reduced quenching rates are easily explained by the fact that the excited state oxidation potentials for the tpbpy complexes are considerably less negative than Ru(bpy)$_3^{2+}$ ($E_{1/2}(M^{2+*/M^{3+}}) \approx -0.81 \text{ V vs SCE}$). The excited state tpbpy complexes are less powerful reducing agents because the π-acceptor nature of the tpbpy ligand 1) renders the ground complexes harder to oxidize and 2) lowers $E_{MLCT}$. Next, it is clear that the difference absorption spectrum corresponding to the ET products in (6-8) is dominated by the MV$^{2+*}$ absorption, indicating that the absorption difference between Ru$^{II}$(tpbpy)(bpy)$_2^{2+}$ and Ru$^{III}$(tpbpy)(bpy)$_2^{3+}$ is relatively small. However, there is one feature worth noting: the λ $<$ 380 nm bleach coupled with the 410 nm shoulder implies that the tpbpy ligand long-axis polarized π,π* absorption is slightly red-shifted in Ru$^{III}$(tpbpy)(bpy)$_2^{3+}$. This red-shift likely occurs because the more electrophilic Ru(III) metal center increases the π-acceptor nature of the bipyridine unit, thereby slightly increasing the thiophene $\rightarrow$ bipyridine CT contribution to the π,π* transition.

The transient absorption difference spectra of P4-Ru and P6-Ru in the presence of 20 mM MV$^{2+}$ are illustrated in Figures 6-9b and 6-10b, respectively. Methyl viologen efficiently quenches the excited state absorption of both complexes (Table 6-5), and the quenching is accompanied by very significant changes in the transient absorption spectra. Specifically, for P4-Ru the quenching products feature the 395 nm MV$^{2+*}$ absorption along with a very strong 735 nm absorption band and a 600 nm shoulder. For P6-Ru, the
395 nm band due to MV'' is also observed, but the strong absorption band in the red is shifted to 800 nm (or above). The very strong absorption bands in the red that are produced by oxidative quenching of P4-Ru and P6-Ru correspond remarkably well with the absorption bands of the cation radicals of quaterthiophene (λ_{max} = 650 nm, shoulder to the blue) and sexithiophene (λ_{max} = 780 nm, shoulder at 690 nm). Therefore, it is clear that oxidative quenching of the two ruthenated polymers affords the corresponding oxidized polymers where the charge resides on the thiophene oligomer segments (i.e., Ru^{II}(P4bpy^{+•})(bpy)_{2}^{3+} and Ru^{II}(P6bpy^{+•})(bpy)_{2}^{3+}). By comparing the intensity of the MV'''' band at 395 nm (ε = 30,000 M^{-1} cm^{-1}) and the red bands due to P4bpy^{+•} and P6bpy^{+•}, the molar absorptivity of the thiophene-based polarons can be estimated, ε ≈ 70,000 M^{-1} cm^{-1}.

Figure 6-11b shows the transient absorption spectrum of P4-Os in the presence of 20 mM MV^{2+}. In this case, MV^{2+} clearly quenches the excited state (∼ 50% quenching is achieved at [MV^{2+}] = 20 mM). However, only weak absorption due to MV'''' at 395 nm is observed, along with ground-state bleaching between 400 – 500 nm and weak absorption above 500 nm. Although it is clear that photoinduced ET occurs when P4-Os is quenched by MV^{2+}, the lack of a strong absorption band due to the P4bpy^{+•} polaron state is significant. Consideration of the electrochemical data provides an explanation for this apparent anomaly. In P4-Os, the first oxidation occurs at the metal center, and consequently the one-electron oxidized state of the material has the hole on the metal center rather than on the P4bpy backbone (i.e., Os^{III}(P4bpy)(bpy)_{2}^{3+}). Because of this situation, the difference absorption spectrum of the oxidized polymer is not very
pronounced because the Os(III) ion induces only a small perturbation in the polymer backbone electronic structure.

The final point that must be considered concerns the correlation between the observed ET quenching rates and the ET driving force. Table 6-6 summarizes the excited state oxidation potentials and free energy for photoinduced ET to MV$^{2+}$ and DMA ($\Delta G^{\text{ET}}$) as calculated in (6-9).

$$\Delta G^{\text{ET}} = E_{\text{ox}} - E_{\text{red}}$$  \hspace{1cm} (6-9)

In order to obtain the proper redox potentials for the metal complex excited state, the excited state energy must be included with the redox measurements as described in (6-10).

$$E_{\text{M}^*/\text{M}^-} = E_{\text{M}^+ / \text{M}^-} + E_{00}$$  \hspace{1cm} (6-10a)

$$E_{\text{M}^+ / \text{M}^*} = E_{\text{M}^+ / \text{M}} - E_{00}$$  \hspace{1cm} (6-10b)

In (6-10), $E_{00}$ is the zero-zero excitation energy of the excited-state transition (i.e., the MLCT transition). If we consider the electrochemistry and spectroscopy data above along with the dimethylaniline oxidation half-wave potential (+0.88 V vs. SCE)$^{181}$ and methyl viologen reduction half-wave potential (-0.46 V vs. SCE) in acetonitrile,$^{97}$ the free energy changes can be calculated.
Table 6-6: Electron transfer free energy changes for thiophene-bipyridine models and polymers.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>E(M / M⁻)</th>
<th>E(M⁺ / M⁻)</th>
<th>E(P / P⁺)</th>
<th>E₀₀</th>
<th>E(M⁺ / M⁺)</th>
<th>E(P⁺ / P⁺)</th>
<th>∆G° ET (DMA)</th>
<th>∆G° ET (MV²⁺)</th>
<th>∆G° ET (MV²⁺)</th>
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</thead>
<tbody>
<tr>
<td>Ru(tpbpy)(bpy)$_2$²⁺</td>
<td>-1.16</td>
<td>+1.36</td>
<td>-</td>
<td>1.96</td>
<td>+0.80</td>
<td>-0.60</td>
<td>-</td>
<td>+0.08</td>
<td>-0.14</td>
</tr>
<tr>
<td>Ru(tpbpy)$_3$²⁺</td>
<td>d</td>
<td>+1.40</td>
<td>-</td>
<td>1.97</td>
<td>d</td>
<td>-0.57</td>
<td>-</td>
<td>d</td>
<td>-0.11</td>
</tr>
<tr>
<td>P4-Ru</td>
<td>-0.99</td>
<td>+1.40</td>
<td>+0.97</td>
<td>1.97</td>
<td>+0.98</td>
<td>-0.57</td>
<td>-1.00</td>
<td>-0.10</td>
<td>-0.11</td>
</tr>
<tr>
<td>P6-Ru</td>
<td>-0.99</td>
<td>+1.34</td>
<td>+0.82</td>
<td>(1.97)$^e$</td>
<td>+0.98</td>
<td>-0.63</td>
<td>-1.15</td>
<td>-0.10</td>
<td>-0.17</td>
</tr>
<tr>
<td>P4-Os</td>
<td>-0.91</td>
<td>+0.92</td>
<td>-</td>
<td>1.56</td>
<td>+0.65</td>
<td>-0.64</td>
<td>-</td>
<td>+0.23</td>
<td>-0.18</td>
</tr>
</tbody>
</table>

$^a$All values are in volts versus SCE except for $\Delta G^o$, which is in eV. All measurements were made in acetonitrile solutions. $E_{00}$ values are taken from Franck-Condon emission bandshape fitting or the emission band maximum. $^b$Thermodynamic driving force based on metal oxidation potential. $^c$Thermodynamic driving force based on Pnbpy oxidation potential. $^d$No reduction observed due to absorption on the working electrode. $^e$Since no MLCT emission was observed for P6-Ru, the P4-Ru value is used in the calculation. $^f$The slight exothermic value may be due to errors in determining $E_{00}$. 
In each case, the excited state oxidation potentials for the complexes and polymers are computed using the first oxidation potential and the observed emission energies. In addition, a second set of entries is listed for P4-Ru and P6-Ru. These entries are computed using the Ru$^{II/III}$ potentials rather than the first oxidation potential that is based on P4bpy backbone oxidation. In effect, P4-Ru and P6-Ru have significantly higher reducing power in the excited state than the model complexes if the polymer-based oxidation is used in the free energy calculation. The implication of this result is clear: photoinduced ET with P4-Ru and P6-Ru must occur in a step-wise fashion involving the sequence illustrated in Figure 6-13. Thus, we suggest that the reactive excited state for ET from these polymers to MV$^{2+}$ is the Ru $\rightarrow$ P4bpy MLCT state (this state is present in an equilibrium with the Pnbpy-based $^3\pi,\pi^*$ state). Photoinduced ET (step 1) affords the oxidized polymer in a state where the hole is centered on the metal. In a second (thermal) intramolecular ET reaction (step 2), the hole is transferred from the metal center to the P4bpy backbone affording the long-lived polaron state. Note that the driving force for the overall ET reaction written in (6-8) is given by the sum of the free energies for the two individual steps ($\Delta G_{ET1} + \Delta G_{ET2}$); however, the driving force for photoinduced ET calculated with the Ru$^{II/III}$ oxidation is given by $\Delta G_{ET1}$ only. This discrepancy accounts for the higher than expected photoinduced ET rate when $\Delta G$ is computed using the first (polymer-based) oxidation potentials.

A final point of interest concerns the application of Figure 6-13 to photooxidation of P4-Os by MV$^{2+}$. In this case, since the stable redox isomer of the oxidized polymer has the hole on the Os center, photoinduced ET (step 1) directly affords the stable redox
isomer of the oxidized polymer. This species persists until back ET occurs (step 4) to re-generate the ground state polymer.

Figure 6-13: Photoinduced electron transfer process from M(P4bpy)(bpy)$_2^{2+}$ to MV$_2^{2+}$.

**Implications of this Work**

A detailed electrochemical and photophysical investigation has been carried out on a novel series of metal-organic polymers that contain d$^6$ transition metal polypyridine complexes interspersed within a poly(3-octylthiophene) π-conjugated network. The properties of these metal-organic materials clearly indicate that the metal centers interact strongly with the π-conjugated system. This interaction gives rise to properties that are not simply predictable based on the sum of the component molecular electronic systems.

A central objective of this study was to prepare soluble π-conjugated materials that display strong, long-lived MLCT photoluminescence characteristic of Ru(II)- and Os(II)-bipyridine complexes. Although in most cases these polymers feature MLCT luminescence, the efficiency is relatively low due to the “intrusion” of the energetically
low-lying $^3\pi,\pi^*$ state of the $\pi$-conjugated thiophene-bipyridine system. Although the objective of producing materials that are strongly photoluminescent was not achieved, the work provides good insight into the steps that need to be taken in order to produce strongly photoluminescent metal-organic materials. Specifically, it is clear that to produce metal-organic materials that display efficient MLCT emission it is necessary to keep the $^3\pi,\pi^*$ states of the $\pi$-conjugated system above the energy of the MLCT states. The PPE-based oligomers in previous chapters exhibit this same energetic trend. Given the singlet-triplet splitting that is typical of PPV, PPE and polythiophenes (i.e., 0.6 – 0.7 eV), and the energies typical of strongly photoluminescent MLCT states (2.0 eV or above), the $\pi$-conjugated system bandgap must be ≥ 2.6 eV (475 nm) to have efficient $^3$MLCT emission. This concept has been demonstrated in recent work from our laboratories in which efficient MLCT photoluminescence has been observed from PPE-type oligomers and polymers that contain the –Ru(bpy)$_2$$^{2+}$ chromophore which fluoresce at 440 nm.

Finally, another important finding in this study is that despite the fact that the MLCT states are not strongly luminescent, the metal-organic materials feature the photoredox activity characteristic of MLCT chromophores. This finding is significant, because strong photoredox activity is necessary to produce materials that perform well in photoconductivity applications.
Experimental

Model Complex and Polymer Synthesis

The thiophene model complexes and polymers were synthesized by Lise Trouillet and Stephan Guillerez at CEA-Grenoble, and all synthesis has been published.\textsuperscript{167,170,182}

\textbf{Methyl viologen synthesis.} 1.6 g (0.01 mol) of 4,4’-dipyridine and 3.6 g (0.025 mol) of methyl iodide were added to a pyrex tube, which was sealed after freeze-pump-thaw degassing. The sealed tube was heated in a 90 °C sand bath for two days. The resulting brownish solid was dissolved in 100 ml of deionized water. A 50 ml water solution containing 4.5 g (0.027 mol) of ammonium hexafluorophosphate was added to the reaction mixture, immediately producing a yellow precipitate. The precipitate was collected by filtration on a medium-porosity glass frit and air dried. The product precipitate was purified by recrystallization from hot ethanol, isolating 4.5 g of pure product.

Photophysical Measurements

All sample solutions studied were in distilled acetonitrile unless otherwise noted. Note that all samples and solutions were handled under an inert atmosphere shielded from light to avoid sample decomposition. Additional argon sample degassing was performed after the initial sample preparation to ensure consistent sample degassing. All photophysical studies were conducted with the same instrumentation and techniques described in chapter 3.
**Electrochemical Measurements**

Electrochemical measurements were performed using PAR 173, 175, and 179 units from EG&G Princeton Applied Research connected to a SEFRAM TGM 164 or a KIPP&ZONNEN BD 91 recorder. Methylene chloride and acetonitrile solutions were used with 0.2 and 0.1 M TBAH, respectively, as a supporting electrolyte. A three-electrode cell was used with a Ag / Ag⁺ (AgNO₃, 10⁻² M) nonaqueous reference electrode, platinum disk working electrode (0.07 cm²) and platinum wire auxiliary electrode. Reference electrodes were calibrated with a ferrocene (Fc) internal standard, and all potentials are listed versus SCE (+0.425 V vs. Fc / Fc⁺).
CONCLUSIONS

In the previous chapters, the extensive photophysics of three series of PPE-type oligomers and one series of polythiophenes, each containing a central 2,2’-bipyridine unit to allow MLCT chromophore incorporation into the \( \pi \)-backbone, have been presented. Several trends and conclusions can be made when examining these data:

1. **Metal chromophore coordination to the oligomer or polymer increases the \( \pi \)-conjugation.** As discussed in chapter 1, the twisted bipyridine serves as a break in the oligomer/polymer backbone \( \pi \)-conjugation. When the MLCT chromophore is ligated to this bipyridine, the geometry is forced to a planar configuration. This geometric change increases the backbone conjugation and alters the observed photophysics, as seen in the oligomer/polymer ground-state absorption bands that red-shift upon coordination. This shift is due to a lowering of the LUMO as a result of the increased delocalization. The MLCT chromophore also serves as an effective “exciton trap” in the PPE and polythiophene systems, as the organic fluorescence is readily quenched after chromophore incorporation and replaced by an MLCT-based emission.

2. **The 2,2’-bipyridine subunits prevent complete delocalization in the \( \pi \)-backbone and limit its effect of the observed photophysics.** The same twisted bipyridine subunits discussed above along with the biphenyl subunits limit the effective delocalization of the PPE-type oligomers. This limit is observed in the lack of additional red-shifting of the ground-state absorption spectra (Figure 3-2) or emission spectra.
(Figure 3-3) of the 5-L oligomers and 5-Re complexes with increasing oligomer size. This effect is most pronounced in the largest oligomer (5-Re-4), where both oligomer- and metal-based transitions are observed, signifying isolation of multiple chromophores in the same molecule. The monophenyl-based 5-LP oligomers and 5-ReP complexes, however, do exhibit red-shifting absorption bands with increasing oligomer size, since they do not have these same conjugation breaks. The 4-L oligomers and 4-Re complexes also exhibit spectral red-shifting to a lesser degree, as the “bent” oligomer does not appear to restrict the delocalization as effectively. This conclusion is further supported by the semi-empirical calculations in chapter 5, which showed that “twisted” oligomers had higher excited-state energies than planar analogues due to a restriction in possible \(\pi\)-delocalization.

3. An excited-state equilibrium exists between ligand- and metal-based states \((^3\pi,\pi^* \leftrightarrow ^3\text{MLCT})\) that control the observed photophysics. It is clear after our experiments that the observed emission band for the PPE and polythiophene complexes is a metal-based MLCT transition, while the transient absorption spectra is assigned to an oligomer/polymer-based \(^3\pi,\pi^*\) transition. An equilibrium exists between these two excited states, leading to the equivalent decay lifetimes for the two spectroscopic techniques in the PPE and polythiophene (P4-Ru) systems. However, when the equilibrium is disrupted by either changing the \(^3\text{MLCT}\) energy via ligand substitution in the PPE oligomers or the \(^3\pi,\pi^*\) energy via increasing the repeat unit length in the polythiophenes, the decay lifetimes are dramatically altered. The \(^3\text{MLCT}\) emission decay lifetime significantly decreases, while the \(^3\pi,\pi^*\) transient absorption decay lifetime increases. Furthermore, when the variable temperature emission is examined in the PPE-
type oligomers, a transition between $^3\text{MLCT}$ luminescence and $^3\pi,\pi^*$ phosphorescence is observed. Both emissions are present at low temperature in the $5\text{-Re}$ and $5\text{-ReP}$ complexes, while only phosphorescence is observed in the $4\text{-Re}$ complexes.

4. The structure and geometry of the oligomer/polymer exerts a dramatic effect on the observed photophysics. As noted above, the monophenyl-based $5\text{-LP/5-ReP}$ series exhibit different photophysics than the $5\text{-L/5-Re}$ series due to their inability to attenuate delocalization. The monophenyl-based series also exhibits a slightly higher $^1\pi,\pi^*$ energy, as exhibited in the blue-shifted fluorescence spectra. The reason for this energy difference is not clear. The alteration of the oligomer geometry from “linear” $5,5'$-substitution to “bent” $4,4'$-substitution in the $4\text{-L/4-Re}$ series brings altered photophysics, including lower $^3\pi,\pi^*$ energies and the presence of $^3\pi,\pi^*$ phosphorescence at reduced temperatures in both the oligomers and rhenium complexes as described above. This difference is attributed to the differing dipole moments of the two oligomer geometries, an altered excited state ordering that increases the $(n \rightarrow \pi^*)$ nature of the $4\text{-L}$ electronic transitions and possibly increased metal orbital mixing into the orbitals involved in the optical transition. The repeat unit length increase in the polythiophenes from $\text{P4-Ru}$ to $\text{P6-Ru}$, as mentioned above, varies the $^3\pi,\pi^*$ energy and precludes the observation of $^3\text{MLCT}$ luminescence by creating a more favorable non-radiative decay pathway.

5. The oligomers and polymers exhibit properties favorable for materials development. The PPE-type systems are fabricated into thin films with the Langmuir-Blodgett technique and exhibit photophysical results similar to solution studies. Furthermore, photoinduced energy transfer is observed both in solution and thin films.
containing mixtures of the oligomer and MLCT complex, suggesting their potential use in photonics applications. The thiophene polymers and model complexes exhibit oxidative electron transfer to methyl viologen, illustrating their potential use in photonics and supramolecular photochemistry. The polythiophenes could serve a dual role as both a light harvesting complex and molecular wire in photosynthetic model systems, which is a rare component in such designs.

6. The use of photothermal techniques can serve as a valuable aid in determining excited-state energetics. The implementation of thermal lensing followed by photoacoustic calorimetric techniques added an additional tool that, in conjunction with other optical spectroscopic measurements, can obtain excited-state energies and/or yields. While our results have definite flaws, this technique can be successfully utilized so long as its limitations are kept in mind when the data is interpreted.

When the PPE-based oligomers are compared to their polymer counterparts, it is clear that the oligomers are excellent models of their photophysical behavior. With this research in mind, the focus can shift back to polymeric systems, and the knowledge obtained in the oligomer research can be applied to better anticipate and interpret the polymer photophysical results. The alteration of the MLCT chromophores and oligomer/polymer structures exhibited above permits the controlled, predictable variation of the observed photophysics, making these systems ideal foundations for constructing more complex and novel π-conjugated polymer systems. The polythiophene research also lays the groundwork for the incorporation of more novel, substituted MLCT chromophores into the polythiophene backbone with the hope of boosting the materials properties of these polymers, such as photoconductivity or non-linear optical effects.
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BIOGRAPHICAL SKETCH

Keith Walters was born in 1975 in Asheville, North Carolina, at the foot of the Great Smoky Mountains, the only child of Marianne and Joe, an elementary school teacher and professor of education at Western Carolina University. He spent his childhood in nearby Waynesville, a quiet rural community of 6,000. Throughout his youth, Keith was active in drama, playing such roles as Michael in *Peter Pan*, the Mad Hatter in *Alice in Wonderland*, and the title roles in *Oliver!*, *Willy Wonka and the Chocolate Factory*, and *Dr. Doolittle*. He also played the violin in the local youth orchestra and solo handbells in his church. Keith was also involved in many academic activities, including the math and science clubs and serving as the captain of the high school quiz bowl team.

After graduating valedictorian of his senior class at Tuscola High School in 1993, Keith attended Furman University in Greenville, South Carolina, where he received a B.S. in chemistry in 1996. During his time in Greenville, Keith spent time in the labs of his undergraduate mentor, Dr. Noel A.P. Kane-Maguire, and on the big couch at Coffee Underground discussing chemistry and philosophy with other Furmanites. Somehow between the two, he received the ACS outstanding senior award from the chemistry department and graduated *magna cum laude*.

During his time at the University of Florida, Keith has expanded beyond his duties in the lab to involve church activities. He is an active member of Trinity United
Methodist Church, where he has served on various musical committees and directs the handbell choir. He still tries to do solo handbells when he has time. Upon graduation, Keith will serve as a postdoctoral fellow for Dr. Joe Hupp at Northwestern University with the ultimate goal of attaining an academic position somewhere in the south.