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Conjugation Length Dependent Ground and Excited State Electronic Behavior in Oligothienyl Ru Complexes

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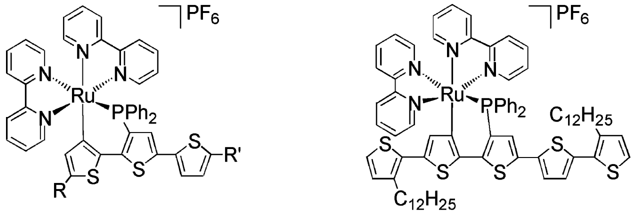
Photoexcitation of a bis(bipyridyl) Ru(II) complex bearing a phosphinopentathiophene ligand results in formation of a transient species with a lifetime of 2.2 μs. The transient is attributed to the product of an intramolecular charge transfer from the pentathiophene ligand. EPR and UV/vis spectroelectrochemistry show that the HOMO is pentathienyl-based, while corresponding complexes with shorter conjugation length ligands have a metal-based HOMO and do not exhibit long-lived transients.

Chart 1



1 R=R'=H
2 R=CH$_3$, R'=H
3 R=R'=CH$_3$

4

Molecular approaches to solar energy harvesting are being explored with renewed urgency as part of the development of sustainable energy sources.[1] Many classes of materials are under investigation, among them conjugated polymers[2,3] which may be readily fabricated into thin-film devices. Transition metal complexes have also been extensively studied due to their favorable charge-transfer (CT) characteristics and the energy content of the excited state which may be harvested by construction of donor/acceptor linked systems.[4,5] Heterogeneous electron transfer to TiO$_2$ from sensitizing Ru(II) dyes constitutes another successful approach.[6]

It would be advantageous to construct a hybrid system where charge transport through a conjugated polymer backbone occurs, while incorporating the favorable excited-state energy content of Ru(II) polypyridyl species. A key feature of this approach would be the ability to use the metal group to introduce holes into the conjugated backbone, as these are the most stable charge carriers in many conjugated polymers. Excited-state behavior of Ru(II) polypyridyl complexes typically features a metal-to-ligand charge-transfer (MLCT) state; therefore, introduction of holes on a pendant conjugated ligand may be best achieved in complexes where the HOMO is delocalized over metal and π orbitals on the conjugated ligand. Quenching of MLCT emission via intramolecular electron transfer from an oligoaniline group to Ru(II) was reported by Hirao.[7] Other groups have prepared materials in which the tris(bipyridyl) Ru(II) ([Ru(bpy)$_3$]$^{2+}$) groups are incorporated into a polythiophene backbone;[8,9] however, these materials all feature a bipyridine group embedded in the backbone. Here we demonstrate that the ground and excited state behavior in a Ru(II) complex with an unbroken oligothienyl chain are dependent on the conjugation length of the ligand.

Bis(bipyridyl) Ru(II) complexes **1**−**4** (Chart 1) were previously prepared in which the Ru(II) is bonded directly to the conjugated oligothiophene backbone via a Ru−C bond and anchored with phosphine linker groups.[10,11] These complexes have multiple absorption peaks due to bipyridyl

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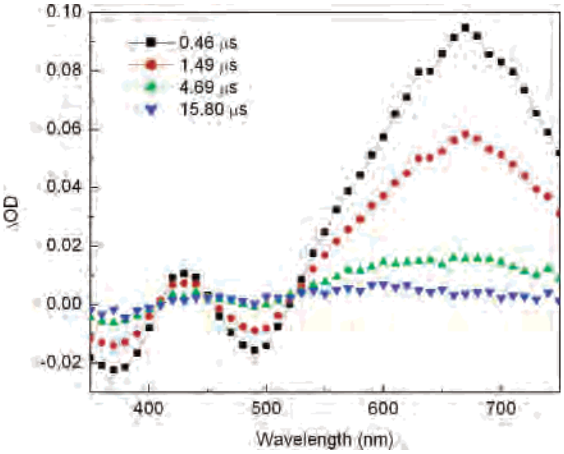

Figure 1. Transient absorption spectra of **4** in deaerated acetonitrile solution excited at 337 nm and recorded with a Luzchem LFP-111 instrument.

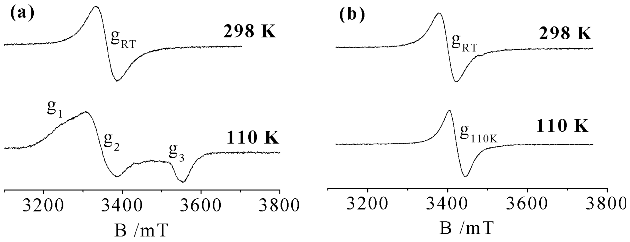

Figure 2. EPR spectra at 298 and 110 K of the first oxidized species of (a) **2** and (b) **4** in CH_3CN/0.1 M [*n*-Bu_4N]PF_6.

(295 nm) and oligothienyl (347−380 nm) $\pi \rightarrow \pi^*$ transitions and Ru(dπ) → bpy(π^*) MLCT (456−485 nm) transitions. Complexes **1**−**4** are very weakly emissive or nonemissive;[11] however, excitation of **4** at 337 nm reveals absorption due to a transient species at 430 and 670 nm and bleaching of the transitions at 370 and 485 nm (Figure 1). The transient decays monoexponentially with a lifetime of 2.2 μs monitored at 630 nm. Interestingly, the transient absorption (TA) spectra of **1**−**3** did not show the formation of an absorbing species even at short time scales (<1 μs). In these spectra, negative peaks with fast decays were observed at time scales of <0.02 μs that are likely due to transient photobleaching of the terthienyl $\pi \rightarrow \pi^*$ transitions. The difference in the TA behavior between **1**−**3** and **4** suggests significant differences in the excited states for these complexes, dependent on the conjugation length of the oligothienyl ligand.

Two oxidation waves are observed for each of **1**−**4** which have been previously attributed to oligothienyl and $Ru^{II/III}$ oxidation processes.[11] First oxidation waves of **1**−**4** are reversible, enabling investigations of the oxidized species that assist in understanding the TA results. X-band electron paramagnetic resonance (EPR) measurements of one-electron oxidized samples of **1**−**3** displayed broad unresolved signals at 298 K in fluid solution and partially separated *g*-factor components in frozen solution at 110 K in CH_3CN/0.1 M [*n*-Bu_4N]PF_6 (Figures 2 and S1). The *g*-factor anisotropy observed at low temperatures (Table S1) indicates significant contributions of the metal with its high spin−orbit coupling constant to the singly occupied MO (SOMO) in the oxidized complexes. Cation $\mathbf{1}^+$ exhibits the most pronounced *g*-factor anisotropy $\Delta g = g_1 - g_3 = 0.2505$, whereas $\mathbf{2}^+$ and $\mathbf{3}^+$ display smaller Δg values and thus diminished metal contribution to the SOMO. In contrast to $\mathbf{1}^+$−$\mathbf{3}^+$, the EPR spectra of $\mathbf{4}^+$ at both 298 and 110 K show single signals closer to the free electron value of $g = 2.0023$ which suggests an organic radical with bound Ru(II).[12−14]

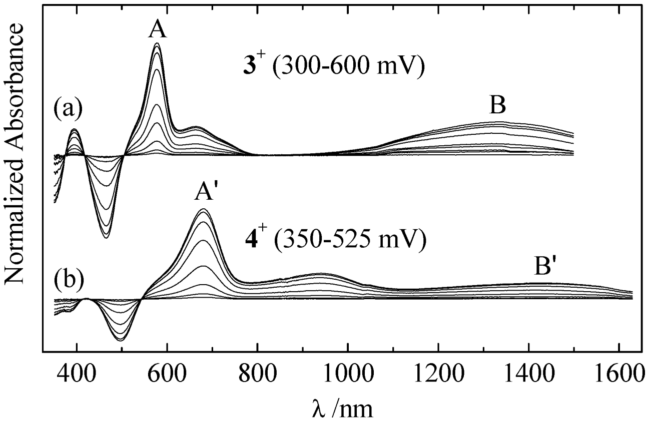

Figure 3. Absorption spectra of (a) $\mathbf{3}^+$ and (b) $\mathbf{4}^+$ in deaerated acetonitrile solution with 0.1 M [*n*-Bu)$_4$N]PF_6 supporting electrolyte at progressively higher oxidation potentials. The spectra of the neutral species of **3** and **4** have been subtracted.

These results from the EPR analysis of the SOMO suggest that the HOMO of **1**−**4** loses metal character with increasing methyl substitution and especially with extension of the conjugation length of the ligand from three to five thiophene rings. In light of these results, it would be most correct to assign the first oxidation for **4** as primarily oligothienyl-based rather than Ru-based as originally concluded in the absence of the EPR data.[11]

Spectroelectrochemical (SEC) experiments revealed that one-electron oxidations of **1**−**3** resulted in bleaching of the lowest energy (MLCT) bands that also occurs for [Ru(bpy)$_3$]$^{3+}$,[15] with simultaneous formation of three main absorption bands (Table S2). As an example, the cation $\mathbf{3}^+$ displays an intense transition at 577 nm, a lower energy band at 663 nm, and a broad band at 1329 nm (Figure 3a), and similar bands are observed for $\mathbf{1}^+$ and $\mathbf{2}^+$. One-electron oxidation of **4** also results in bleaching of the band at 497 nm and the growth of three new bands (Figure 3b), red-shifted from those observed for $\mathbf{1}^+$−$\mathbf{3}^+$. These observations are best explained by considering the frontier molecular orbitals in these complexes (Figure 4), where mixing of the metal and oligothienyl π orbitals results in a HOMO of mixed character, with a diminishing metal contribution as the conjugation length is extended. Singly oxidized oligo-

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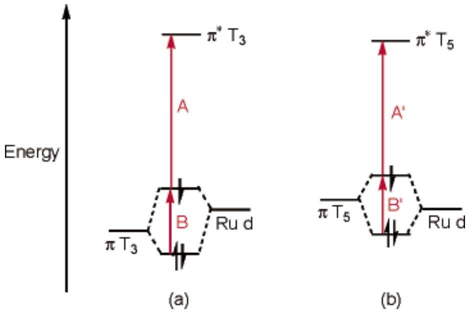

Figure 4. Qualitative molecular orbital diagram for (a) $\mathbf{1}^+$ and (b) $\mathbf{4}^+$. T_3 and T_5 are the terthienyl and pentathienyl fragments, respectively.

thiophenes show two electronic transitions,[16,17] including SOMO → LUMO $\pi-\pi^*$ transitions that are consistent with the energy and intensities of A and A′. The low-energy absorptions are attributed to transitions (B, B′) between mixed Ru/oligothienyl orbitals that are close in energy. The bands of intermediate energy are presumably due to transitions from lower-lying π orbitals to the SOMO.

The SEC spectra of $\mathbf{4}^+$ and the TA spectrum of **4** display identical bleaching of the 485 nm transition and growth of the 679 nm band. The similarity in these spectra gives rise to the possibility that excitation of **4** results in a transient species in which the same SOMO → $\pi^*(T_5)$ transition occurs as in $\mathbf{4}^+$. This is possible if the transient species is the product of an intramolecular electron transfer where an electron is transferred from a mixed metal−π oligothienyl orbital. In this case, the probable destination of the electron transfer is the bipyridine ligand, consistent with the reductive cyclic voltammetry of this compound.[11] Significantly, **1**−**3** do not show a long-lived transient. If the transient species in **4** is a CT state, then the absence of a comparable long-lived transient in **1**−**3** may be attributed to the change in the nature of the HOMO with the extension of conjugation length. The stabilization provided by delocalization of the positive charge in the longer pentathienyl group could result in a longer-lived CT state for **4**.

Schanze has observed $\pi-\pi^*$ triplet transitions in metal-organic conjugated systems,[8,18] and the possibility that the observed transient in **4** is due to triplet−triplet absorption from an intraligand $\pi-\pi^*$ triplet state should be considered. Emission and transient features due to triplet states are observed by Schanze when the triplet energy falls below the energy of the MLCT state in systems in which a $[\mathrm{Ru(bpy)_3}]^{2+}$ group is embedded in a conjugated backbone. The triplet energies of the oligothienyl ligands may be estimated from data for unsubstituted oligothiophenes,[19] since the absorption and emission spectra for the ligands shift only slightly relative to the unsubstituted analogues. This suggests the triplet energies for the terthienyl ligands are ∼1.9 eV while the energy for the triplet state of the pentathienyl ligand would lie at ∼1.7 eV. In complexes **1**−**3**, the MLCT energies can be calculated from the difference in oxidation and reduction potentials,[20] giving MLCT energies of ∼1.6 eV, consistent with the energies of the emission bands observed from these complexes. In complex **4**, the nature of the HOMO has shifted to pentathienyl-based (vide supra), and no emission is observed[11] so it is more difficult to estimate the energy of the CT state. The lowest energy band in the absorption spectrum of **4**, however, is lower in energy than the MLCT band for **1**−**3**,[11] so it is safe to assume that the CT state lies below 1.6 eV and thus below the triplet state for the pentathienyl ligand. This supports the assignment of the transient in **4** as the CT state rather than a triplet−triplet absorption; however, it should be noted that this conclusion relies on the accuracy of the estimates of state energies.

The results described herein are significant since they demonstrate that the conjugation length of the ligand results in changes both to the HOMO and the excited state in hybrid metal−organic conjugated oligomers. The proposed CT state could be used to introduce long-lived positive charges into extended conjugated chains, permitting application in photovoltaic or photoelectrochemical cells.

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Supporting Information Available: Experimental procedures and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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