Inorganic Chemistry

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Ligand-Triplet-Fueled Long-Lived Charge Separation in Ruthenium(II) Complexes with Bithienyl-Functionalized Ligands

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Supporting Information

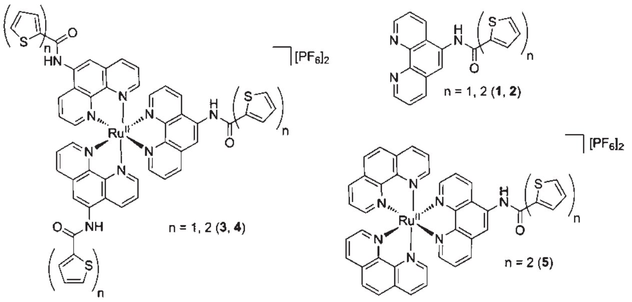
ABSTRACT: Ruthenium(II) polypyridyl complexes with pendant bithienyl ligands exhibiting unusually long-lived ($\tau \sim 3-7\ \mu s$) charge-separated excited states and a large amount of stored energy ($\Delta G^\circ \sim 2.0$ eV) are reported. A long-lived ligand-localized triplet acts as an energy reservoir to fuel population of an interligand charge-transfer state via an intermediate metal-to-ligand charge-transfer state in these complexes.

New methods for efficiently converting solar energy to useable chemical energy are urgently needed.[1] Approaches that mimic photosynthesis[2] rely on achieving long-lived charge-separated (CS) states via multistep, vectorial photoinduced electron transfer.[3] Metal complexes with polypyridyl ligands are ideal for applications in solar energy conversion[4] and artificial photosynthesis[5] owing to their long excited-state lifetimes, redox properties, chemical stability, and excited-state reactivity.[6] Metal-to-ligand charge-transfer (MLCT) states of ~2.1 eV are accessible in ruthenium polypyridyl complexes and may act as the gateway to interligand charge-transfer (ILCT) states that further separate the electron−hole pair.[7] Covalently linking donor and/or acceptor moieties to the ruthenium(II) polypyridyl chromophore to give diads or triads can generate ILCT states; however, in most cases, the energy stored (ΔG°) is appreciably less than the MLCT energy and is frequently below 1 eV.[8] Furthermore, most ILCTs have lifetimes limited to $\sim 1\ \mu s$.[8] Combined, these factors limit the utility of these systems in artificial photosynthesis.

The lifetimes of ^{3}MLCT states can be extended appreciably by excited-state equilibration involving ligands with energetically accessible and long-lived triplet states (^{3}LC).[9] Such long-lived MLCT states can, in principle, go on to generate CS (or ILCT) states. Here, we report a system in which a long-lived ligand-localized triplet acts as an energy reservoir to fuel population of an ILCT state with an unusually long lifetime ($\tau \sim 7\ \mu s$) and a large amount of stored energy (ΔG° ca. 2.0 eV) via an intermediate MLCT state.

Our approach is to introduce oligothiophenes as ligands into ruthenium polypyridyl complexes.[10] The role of the oligothiophene is to reductively quench the initially formed ruthenium(III) species upon photoexcitation, resulting in a CS state where a hole (h$^+$) is localized on the oligothiophene. In addition, reversible energy transfer from low-lying LC states on the conjugated ligand results in an extension of the excited-state lifetime.[9,11] Conjugated oligomers also provide a route to thin films of these complexes by electropolymerization,[12] allowing applications in photovoltaic devices.

Ruthenium(II) polypyridyl complexes **3**−**5** incorporate the thienyl- and bithienyl-functionalized diimines **1** and **2** as ligands. Increasing the number of thienyl moieties in the ligand (cf. **3** and **4**) and varying the number of conjugated ligands (cf. **4** and **5**) shed light on the photophysical behavior of these complexes.



Homoleptic metal complexes **3** and **4** were prepared by reacting **1** or **2** with Ru(DMSO)$_4$Cl$_2$, and **5** was prepared by the reaction of **2** with Ru(phen)$_2$Cl$_2$ (phen = 1,10-phenanthroline). The absorption spectrum of **3** (Figure 1a) exhibits moderately intense d → π* MLCT bands ($\lambda_{max} = 450$ nm with a shoulder at $\lambda_{max} = 420$ nm) and LC bands in the UV region. These spectral features are comparable to those observed for [Ru(phen)$_3$][PF$_6$]$_2$ (**6**; Figure S1 in the Supporting Information, SI).[13] Similar spectra are found for **4** and **5** with an additional intense band at $\lambda_{max} = 355$ nm, attributed to a bithienyl $\pi \rightarrow \pi^*$ transition. Furthermore, no significant ground-state electronic interaction between the Ru^{II} core and the thienyl moieties is evident from these spectra.

Excitation into the lowest-energy absorption band of **3**−**5** results in identical emission spectra with $\lambda_{max} = 596$ nm (Figure 1a), similar to that observed for **6**. Quantum yields for **3**−**5** (Table 1) are comparable to that of *rac*/Δ/Λ-Ru(phen)$_3^{2+}$ ($\Phi_{em} = 0.052$).[14] Interestingly, emission lifetimes, τ_{em} ($\lambda_{ex} = 453$ nm), vary significantly for the three complexes. By comparison, **6** has an emission lifetime of 523 ns under identical conditions.

The time-resolved transient absorption (TA) differential spectrum of **3** shows spectral features that closely resemble those observed for **6** (Figure 1b).[15] The similarity in emission and TA

Received: August 30, 2011
Published: September 21, 2011

dx.doi.org/10.1021/ic201895y | *Inorg. Chem.* 2011, 50, 9939–9941

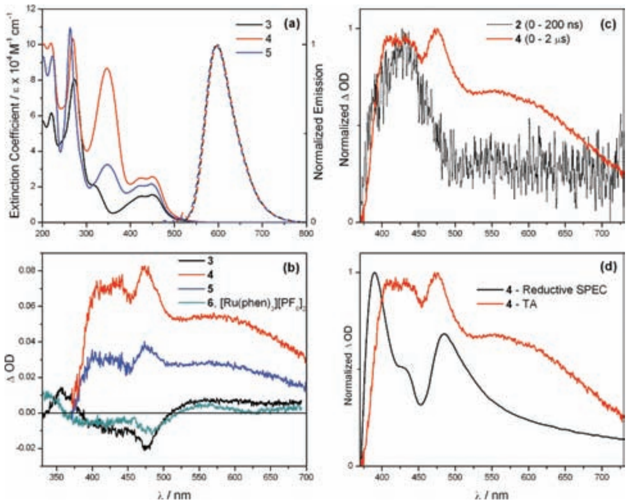


Figure 1. (a) Absorption (solid) and uncorrected normalized emission spectra (dashed, λ_{ex} = 450 nm) of **3**−**5**. (b) Differential excited-state TA spectra of **3** (black), **4** (red), **5** (blue), and **6** [Ru(phen)$_3$][PF$_6$]$_2$ (teal) collected 200 ns after excitation. (c) Differential excited-state TA spectra of ligand **2** (black) and **4** collected at longer time regimes (10 μM solutions in CH$_3$CN purged with argon; λ_{ex} = 355 nm; fwhm = 35 ps). (d) Reductive spectroelectrochemistry of **4** (−0.85 V, 50 μM solution in CH$_3$CN, black) and differential excited-state spectrum of **4** (red).

Table 1. Photophysical Data

compound	λ_{em} (nm)[a]	Φ_{em}[b,c]	τ_{em} (μs)[c,d]	τ_{ex} (μs)[c,e]
1	308			
2	405			>10
3	596[f]	0.047 ± 0.005	0.89	0.97
4	596[f]	0.071 ± 0.001	7.4	6.3
5	596[f]	0.058 ± 0.001	2.9	2.6
6	600[f]		0.52	0.53

[a] Uncorrected, room temperature, CH$_3$CN solution. [b] Absolute quantum yield at room temperature. [c] Samples prepared in air and purged with argon for 30 min. [d] λ_{ex} = 453 nm. [e] λ_{ex} = 355 nm (fwhm = 35 ps). [f] λ_{ex} = 450 nm.

lifetimes (Figure S2 in the SI) for **3** (891 ns vs 973 ns), and similarities to the TA and emission spectra for related species, strongly supports the assignment of the major excited-state species in **3** as a ^{3}MLCT state. In contrast, TA spectra of **4** and **5** exhibit a broad, multifeatured absorption between 390 and 450 nm, a lower-energy feature at ∼450−500 nm, and a broad, low-energy absorbance at ∼550 nm (Figure 1b). A ground-state bleach is also observed at 340 nm (t < 100 ns), corresponding to the ground-state bithienyl $\pi \rightarrow \pi^*$ absorption (Figure S3 in the SI). Evidently, the states observed in the TA spectra of **4** and **5** are quite different from the ^{3}MLCT state observed for **3** and **6**.

It is well established that ^{3}LC states can equilibrate with ^{3}MLCT states of comparable energies.[9] The triplet energy of unsubstituted bithiophene is 2.2 eV,[16] close to the ^{3}MLCT energy (596 nm, 2.08 eV) of **4** and **5**, suggesting that equilibration of the ^{3}LC and ^{3}MLCT states is possible. The excited-state absorption of **2** at 400 nm (Figure 1c) is coincident with the high-energy band in the TA spectrum of **4** and **5**; thus, it is likely that a nonemissive ^{3}LC state is present in the complexes and is responsible, in part, for the long lifetime of the excited state. This is further evidenced by the approximately 3-fold decrease in lifetime between **5** and **4**, where **5** has only a third of the bithienyl substituents of **4** and thus a smaller "triplet reservoir", an effect previously observed in ruthenium(II) pyrenyl complexes.[17]

It is possible that a CS ^{3}ILCT state can also equilibrate with the ^{3}MLCT state, in addition to the ^{3}LC state, as evidenced by additional bands in the spectra of **4** and **5** that are absent in **2**. This ^{3}ILCT state would form by the reductive quenching of ruthenium(III) by the bithienyl group, giving a ^{3}ILCT state consisting of a bithienyl cation and an anion either localized on the phen group or possibly delocalized to the amide.

Differential pulse voltammetry (DPV) of **4** shows two waves corresponding to oxidation of the Ru^{II} center and bithienyl moieties (first positive-going scan; Figure S7 in the SI). Oxidative polymerization of the bithienyl groups occurs as sequential scans show increasing currents and formation of a yellow film on the electrode (Figure S8 in the SI). In contrast to **6** (first reduction ∼ −1.35 V; Figure S9 in the SI), reductive DPV of **4** shows a broad cathodic process with a pronounced anodic peak at −0.9 V assigned to reduction of the substituted phen ligand.[18] Despite the less negative reduction potential in **4**, no red shift is observed in the emission spectrum or the MLCT absorption of **4** compared to **6**, attributed to the bichromophoric nature of **4**.[19] Gibbs free-energy changes for intramolecular electron transfer are ∼−14 kJ mol^{-1} (−0.14 eV),[20] indicating that the formation of an intramolecular ILCT state is energetically feasible.

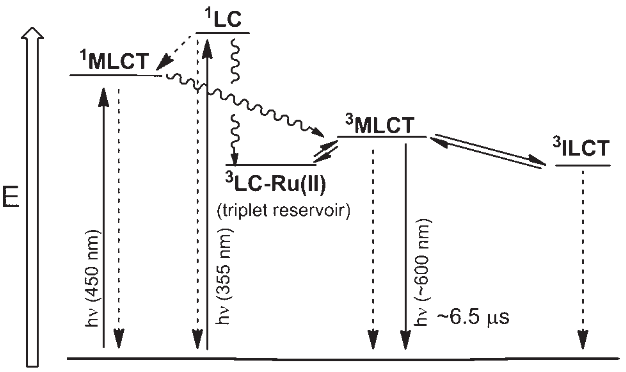
The broadness and poor reversibility of the DPV peaks in **4** makes a definitive assignment of the stored energy, $\Delta G°$, of the ILCT state impossible. However, its value may be estimated as ≥1.9 eV. This compares to a calculated value of 2.0 eV in **3** and reveals that it is energetically accessible.

Reductive spectroelectrochemistry of **4** shows three spectral features (Figure 1d), differing substantially from the spectra obtained upon electroreduction of **6** (Figure S11 in the SI). As a result, the spectral features of **4**$^-$ are assigned to a substituted phen anion bound to a Ru^{II} center. Comparison of the spectrum of **4**$^-$ with the TA spectrum of **4** shows significant overlap, suggesting that the excited state is similar to the Ru^{II}phen$^-$ state observed in the spectroelectrochemistry.

Oxidation of **2** with NOPF$_6$ showed growth of a band between ∼375 and 440 nm (Figure S12 in the SI) due to **2**$^+$. In the TA spectra of **4**, some of the high-energy features between 390 and 450 nm may correspond to an oxidized bithienyl moiety, previously shown to absorb at 420 nm.[21] Furthermore, the addition of a sacrificial electron donor (tetrathiafulvalene; Figure S13 in the SI) or acceptor (methyl viologen; Figures S14 and S15 in the SI) during TA experiments results in bimolecular electron-transfer reactions that support the formation of a charge-separated species in **4**.

Three interacting excited states in **4** and **5** (Scheme 1) are proposed. A long-lived bithienyl-localized ^{3}LC state acts as a reservoir to populate both the ^{3}MLCT state, which is the only species to decay radiatively, and a ^{3}ILCT state, in which the electron and hole are localized on the phenanthroline and bithienyl portions of the complex, respectively. The emission at 596 nm for **4** and **5** along with the absence of any ^{3}MLCT bands in the TA spectra suggests that both the ^{3}LC and ^{3}ILCT states are close to, but slightly lower, in energy than the ^{3}MLCT state. In this case, the triplet reservoir extends the lifetimes of both the ^{3}MLCT and ^{3}ILCT states. In most ruthenium-based triads, the lifetime of the second CS state (typically an ILCT state) is on the order of 100−300 ns because back electron transfer is largely unimpeded.[22] Here, two factors extend this

Scheme 1. Jablonski Diagram of 4 in CH_3CN



lifetime into the microsecond regime. First, recombination occurs mainly via the higher-energy, less-populated ^{3}MLCT state. Second, back electron transfer from the ^{3}ILCT state to the ground state is nonradiative and a high-energy process ($-\Delta G^\circ \geq$ 1.9 eV) that could easily exceed the total back-electron-transfer reorganization energy and put this process in the inverted Marcus region.[8c,d]

These results suggest that further efforts to direct charge separation in ruthenium(II) complexes containing the bithienyl ligand **2** with other acceptor ligands could lead to long-lived excited states in which charge separation is vectorial and readily accessible to follow-on reactions. Charge separation in electropolymerized films may be of significant interest for energy-harvesting applications. Experiments are underway to probe the photophysics of these films and the application of these complexes in photoactive devices.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthetic methods and TA and DPV data. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

We acknowledge the NSERC (M.O.W.), NSF Grant CHE09-11720 (F.M.M. and N.R.T.), Robert A. Welch Foundation Grant Y-1301 (F.M.M.), and the Mountain Equipment Co-op (M.B.M.) for support. We thank Dr. Saeid Kamal (LASIR) for assistance with TA.

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