

A Trimetallic Mixed Ru(II)/Fe(II) Terpyridyl Complex with A Long-Lived Excited State in Solution at Room Temperature

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The development of chromophores for light harvesting and visible light sensitization of photochemical processes has evolved considerably. Complex and effective systems have been developed consisting of multiporphyrin arrays,^{1,2} metal diimine and triimine complexes,^{3–12} and a variety of other related chromophores.^{13–17} Among the most widely studied transition metal complexes have been low-spin d^6 transition metal complex derivatives of bipyridyl and terpyridyl ligands. These complexes are of interest because they absorb a significant portion of the visible spectrum, have relatively long-lived excited states ($>1 \mu\text{s}$), are often stable following one-electron oxidation and reduction, and exhibit good photochemical stability.¹⁸ The equilibrated excited state of these complexes has been assigned as a metal-to-ligand charge transfer (MLCT) state. First-row transition metal complexes in this series (e.g., Fe(II)) have not proved to be effective sensitizers because low-energy ligand field excited states on the metal provide non-radiative decay pathways that significantly decrease excited-state lifetimes and lead to facile complex decomposition.^{19–22} Recently, we have prepared a variety of phenylene–vinylene-substituted terpyridyl ligands that, when coordinated to Ru(II), have long-lived excited states that are localized on the phenylene–vinylene-containing ligand (^3IL).²³ In these complexes the lowest-energy absorption transition is MLCT; intersystem crossing leads to a long-lived triplet excited-state localized on the ligand (^3IL) that serves as the reactive excited state for energy- and electron-transfer reactions.²⁴ In this report we describe the photophysical behavior of two trimetallic terpyridyl complex light-harvesting ensembles containing two Ru(II) centers and an Fe(II) center. Through control of the phenylene–vinylene moiety an Fe(II)-containing complex having a long-lived excited state can be prepared. To our knowledge this is the first example of an Fe(II) diimine- or triimine-containing complex with an excited-state lifetime long enough for bimolecular reactions.

The complexes reported here are shown in Chart 1. The monometallic Ru(II) complexes were prepared from the respective bridging ligands and $[(\text{mpt})\text{RuCl}_3]$ ($\text{mpt} = 4'-(p\text{-methylphenyl})\text{-}2,2',6',2''\text{-terpyridine}$) using literature methods.²⁵ The trimetallic Fe(II) complexes, **RutvtFetvtRu** and **RutvpvtFetvpvtRu**, were prepared in CH_3CN solution at room temperature by adding an acetonitrile solution of $\text{Fe}(\text{ClO}_4)_2$ to solutions containing the monometallic Ru(II) complex. The trimetallic Ru(II) complexes, **RutvtRutvtRu** and **RutvpvtRutvpvtRu**, were prepared by reaction of the monometallic complex in ethanol with RuCl_3 at reflux under an Ar blanket. The complexes were characterized by ^1H NMR spectroscopy, electrospray mass spectrometry, cyclic voltammetry, and spectrophotometry.

Figure 1 shows changes in the visible absorption spectrum following addition of Fe(II) to a solution of **Rutvt** in CH_3CN at room temperature. The long wavelength absorption band that develops is the Fe(II) to terpyridine MLCT transition. The inset to Figure 1, showing absorption changes at 575 nm, indicates that

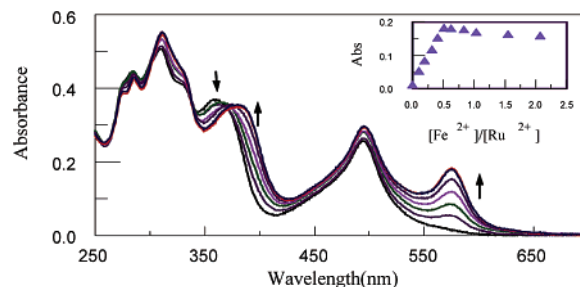
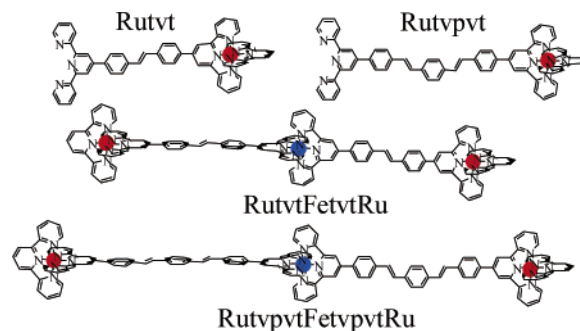


Figure 1. Absorption spectra of an CH_3CN solution containing **Rutvt** following addition of varying amounts of $\text{Fe}(\text{ClO}_4)_2$. The inset shows the absorbance change at 575 nm as a function of the equivalents of $\text{Fe}(\text{ClO}_4)_2$ added.

Chart 1. Monometallic and Trimetallic Complexes



the reaction is complete following addition of a stoichiometric amount (0.5 equiv) of Fe(II) yielding **RutvtFetvtRu**; the decrease in absorption following further addition of Fe(II) is associated with gradual formation of monoterpyridyl Fe(II) complexes. The composition of the trimetallic complex was verified by electrospray mass spectroscopy.

The tri-Ru(II) complexes, **RutvtRutvtRu** and **RutvpvtRutvpvtRu**, are both weakly luminescent in degassed CH_3CN at room temperature with maxima at 670 and 700 nm, respectively. The excited-state lifetime of the **tvvt** complex is less than 10 ns in CH_3CN at room temperature, while that of the **tvpvt** complex is 320 ± 10 ns. In addition, the luminescence of the **tvpvt** complex is nearly completely quenched by oxygen, behavior not characteristic of MLCT excited states of most Ru diimine and triimine complexes.²⁶ These observations, combined with transient absorption data, suggest that the emitting excited state differs in the two complexes.²³ We believe **RutvtRutvtRu** has a lowest-energy excited state that is $\text{Ru}(d\pi)\text{-tv}(\pi^*)$ $^3\text{MLCT}$ while **RutvpvtRutvpvtRu** has a ^3IL state with a significant degree of charge-transfer character.²⁷

The photophysical behavior of the two Fe(II)-containing complexes differ dramatically, and the differences are most readily seen in transient absorption spectra. Figure 2 shows steady-state and transient absorption spectra following 495 nm excitation of **Rutvt**

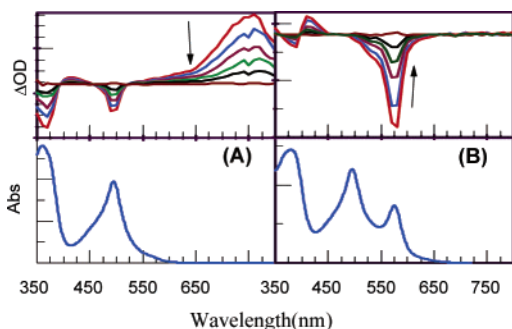


Figure 2. Ground-state and transient absorption spectra following 495 nm excitation of (A) **Rutvt** and (B) **RutvtFetvptRu**. The transient spectra shown were obtained at times between 15 and 50 ns following excitation.

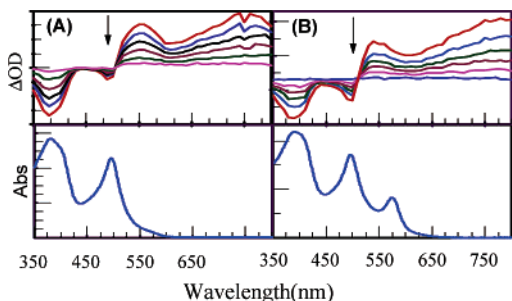


Figure 3. Ground-state and transient absorption spectra following 495 nm excitation of (A) **Rutvpvt** and (B) **RutvpvtFetvptRu**. The transient spectra shown are for times between 100 and 1000 ns following excitation.

and **RutvtFetvptRu** in deaerated CH_3CN . The spectrum of **Rutvt** shows bleaching of the ground-state absorption (Ru to tpy MLCT) at 500 nm and an absorption in the red associated with the ligand localized state. In **RutvtFetvptRu** the transient absorption spectrum following excitation into the Ru to tpy MLCT (495 nm) shows only features associated with an excited state localized on the Fe(II) center: bleaching of the Fe to tpy MLCT absorption at 575 nm and a weak excited state absorption around 400 nm. The excited state decay is too fast to measure using nanosecond time resolution, and all we can say at this time is that the lifetime is shorter than 10 ns. This behavior is what is expected if excitation energy drains from the Ru to tpy MLCT state (the state principally excited with 495 nm excitation) into the much lower-energy Fe to tpy MLCT state and lower-energy ligand field states of the Fe(II) terpyridine chromophore.

The transient behavior of **RutvpvtFetvptRu** differs significantly from that of the corresponding **vtv** complex. Figure 3 shows spectra of **Rutvpvt** and **RutvpvtFetvptRu** obtained at various delays following excitation at 495 nm. Both complexes have transients that decay over several hundred nanoseconds. The transient spectrum of **RutvpvtFetvptRu** is much longer lived ($\tau = 275 \pm 10$ ns) than that of the monophenylene–vinylene complex and shows no evidence of bleaching of the iron to terpyridine MLCT absorption beyond the first few nanoseconds. The remarkable feature is that the bis-terpyridyl Fe(II) central metal center of the complex, which has low-energy triplet and quintet ligand field states, does not result in rapid nonradiative relaxation of the excited state.

The transient behavior on the 10–30 ns time scale (not shown in Figure 3) clearly shows bleaching of the Fe to tpy MLCT state at 575 nm. The bleaching gives way to the net transient absorbance shown in Figure 3; however, it is not clear that decay of the Fe to tpy MLCT state results in sensitization of the long-lived state of

the complex. Excitation directly into the Fe to tpy MLCT absorption at 575 nm also yields the long-lived triplet in significant yield; thus, decay of the initially formed Fe to tpy MLCT state also leads to population of the long-lived ^3IL state. **RutvpvtFetvptRu** is also weakly luminescent, with a maximum of 700 nm, nearly identical to that of **RutvpvtRutvpvtRu**.

Very recently we have demonstrated that the same behavior is observed with bis-terpyridyl ligands bridged by bis- and tetraphenylene–vinylene moieties having two alkoxy substituents. The Ru/Fe/Ru tetraphenylene–vinylene derivative also has a long-lived transient with a lifetime in excess of 10 μs . We are in the process of examining the ultrafast photophysics of a series of mixed iron/ruthenium complexes to better understand the factors influencing excited-state decay and to develop a better understanding of the electronic structure of the long-lived excited state.

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Supporting Information Available: Synthesis and characterization of the mono- and trimetallic complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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