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Turning Off Phototriggered Linkage Isomerizations in Ruthenium Dimethyl Sulfoxide Complexes

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We report on the spectroscopy, electrochemistry, and linkage isomerization in a family of [Ru(tpy)(L2)(dmso)]$^{z+}$ complexes (tpy is 2,2′:6′,2″-terpyridine, dmso is dimethyl sulfoxide, and L2 is a variable ligand: 2,2′-bipyridine (bpy), 2-picolinate (pic), *N,N,N′,N′*-tetramethylethylenediamine (tmen), acetylacetonate (acac), or malonate (mal)). The identity of this bidentate ligand serves to tune the absorption maxima (λ_{max} = 419–502 nm) and the reduction potential ($E_{1/2}$ = 1.67 to 0.82 V) of these complexes. Photochemical and electrochemical studies show that S→O and O→S linkage isomerization may be triggered through an electron transfer mechanism, resulting in dramatic shifts in both the absorption maxima and the reduction potential (for [Ru(tpy)(pic)-(dmso)]$^+$ S-bonded, 421 nm, 1.38 V vs Ag/AgCl; O-bonded, 527 nm, 1.38 V vs Ag/AgCl). Certain of these complexes [Ru(tpy)-(acac)(dmso)]$^+$ and [Ru(tpy)(mal)(dmso)] do not undergo isomerization. These results are discussed in the context of electron transfer triggered isomerization.

Intramolecular phototriggered excited-state linkage isomerizations occur for certain complexes containing NO, SO$_2$, or dimethyl sulfoxide (dmso) ligands.[1–6] These systems are of interest due to their potential application in molecular information storage and solar energy conversion.[7,8] A recent review showcases many of these examples.[9] However, a

Table 1. UV−Vis, Electrochemical, and Infrared Data for [Ru(tpy)(L2)(dmso)]$^{z+}$

compound	λ_{max} (nm)		$E_{1/2}$ (V)		ν(SO) (cm^{-1})^c	ΔE_{abs} (cm^{-1})	ΔE_{ec} (cm^{-1})
	S^a	O^a	S^b	O^b			
[Ru(tpy)(bpy)(dmso)]$^{2+}$	419	490	1.67	1.10	1102	3860	4040
[Ru(tpy)(pic)(dmso)]$^+$	421	527	1.38	0.65	1089	4780	5890
[Ru(tpy)(tmen)(dmso)]$^{2+}$	429	530	1.65	1.03	1066	4230	4840
[Ru(tpy)(acac)(dmso)]$^+$	468		0.95		1088		
[Ru(tpy)(mal)(dmso)]	502		0.82		1083		

^{a} In dimethyl sulfoxide solution. ^{b} In CH$_3$CN, 0.1 M TBAPF$_6$, glassy carbon working electrode, Pt wire counter electrode, vs Ag/AgCl. ^{c} KBr pellet.
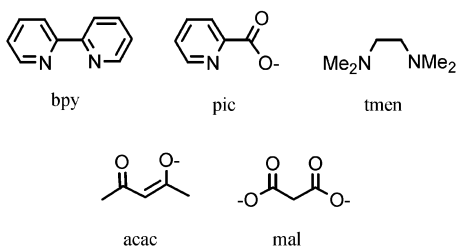
unifying hypothesis permitting insight into the mechanism of excited-state isomerization in transition metal complexes has not emerged. Examples of photochromism and electrochromism exist for ruthenium−polypyridine−dimethyl sulfoxide complexes in which S→O and O→S linkage isomerizations are triggered through electron transfer.[3,6,10] In pursuit of mechanistic information, our approach has been to design compounds that contain a metal capable of one-electron redox chemistry (Ru$^{3+/2+}$), an ambidentate ligand for linkage isomerization (dmso), and a ligand available for metal-to-ligand charge transfer (MLCT) photochemistry.[3,10] We have chosen [Ru(tpy)(L2)(dmso)]$^{z+}$ (tpy is 2,2′:6′,2″-terpyridine; L2 is a variable bidentate ligand) as our motif both for synthetic versatility and for tuning of the electronic properties. In the course of our studies, we have found that linkage isomerization may be disfavored or encouraged in response to the electronic nature of the bidentate ligand. Herein we report on the spectroscopy, electrochemistry, and linkage isomerization in this family of [Ru(tpy)(L2)(dmso)]$^{z+}$ complexes.

All of the complexes in this study feature S-bonded dmso in their ground-state structures as evidenced by the electronic absorption, electrochemical, and infrared (ν(SO)) data (Table 1). Ligand metathesis of the chloro or aqua starting materials to yield the corresponding dmso complexes reveals absorption and electrochemical shifts in accord with dπ stabilization and S-bonding. The choice of bidentate ligand (Chart 1) provides variational control of the reduction potential. For

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Chart 1. Bidentate Ligands Used in This Study

bpy   pic   tmen

acac   mal

A

B

$$trans\text{-}[Ru(tpy)(pic)(dmSo)]^+ \xrightleftharpoons[298\ K]{h\nu} trans\text{-}[Ru(tpy)(pic)(dmsO)]^+$$

Figure 1. (a) Cyclic voltammogram (50 mV/s) of [Ru(tpy)(pic)(dmso)]$^+$ revealing both S-bonded and O-bonded isomers. (b) Electronic absorption specta of S- and O-bonded isomers of [Ru(tpy)(pic)(dmso)]$^+$ in ionic liquid.

example, the Ru$^{3+/2+}$ reduction potential spans a range of ~350 mV in the corresponding [Ru(tpy)(L2)(OH$_2$)]$^{z+}$ complexes.[11] We anticipated a similar range for the dmso complexes.

Expectedly, the lowest energy Ru d$\pi \rightarrow$ tpy π^* MLCT transition shifts to lower energy as the bidentate ligand is substituted from bipyridine (419 nm) to tmen (429 nm) to malonate (502 nm). Concomitant with these absorption changes, a range of nearly 800 mV in $E_{1/2}$(Ru$^{3+/2+}$) is observed upon substitution of bpy (1.67 V) with malonate (0.82 V) in the cyclic voltammetry of these complexes. These trends are consistent with destabilization of the t$_{2g}$ dπ orbital set upon substitution of the strong-field π-acidic ligand (bpy) with a weak-field π-basic ligand (mal) within the complex. It is clear from the data that this set of bidentate ligands modulates the electronic structure of these complexes.

Infrared spectra reveal ν(SO) stretching frequencies within the expected range (1102−1066 cm^{-1}) for S-bonded dmso ligands.[12] Stretching frequencies for O-bonded dmso typically appear at lower frequencies (900−950 cm^{-1}). A correlation between the ν(SO) stretching frequency and the absorbance or electrochemical data is not evident.

Cyclic voltammograms of [Ru(tpy)(L2)(dmso)]$^{z+}$ (L2 = acac, $z = 1$; mal, $z = 0$) are simple, reversible one-electron couples. The ratio of the peak currents is unity, and a plot of peak current vs (scan rate)$^{1/2}$ yields a straight line. In contrast, voltammograms of [Ru(tpy)(L2)(dmso)]$^{z+}$ (L2 = bpy, tmen, $z = 2$; pic, $z = 1$;) are irreversible. A representative example is shown in Figure 1A for *trans*-[Ru(tpy)(pic)-(dmso)]$^+$.[13] Following oxidation of S-bonded Ru^{II} (Ru^{II}−S) at 1.38 V (vs Ag/AgCl) and reversing the scan polarity, the corresponding cathodic wave is not observed. Instead, a new couple appears at 0.65 V ($i_{pa}/i_{pc} \neq 1$). The absence of current at 0.65 V on the first anodic scan indicates that this chemical species is only formed following oxidation of Ru^{II}−S at ~1.4 V. This new species is indicative of an O-bonded dmso isomer. Similar shifts have been observed in other Ru^{II}−dmso studies.[3,14−18] The lower energy couples featured in the voltammograms of [Ru(tpy)(bpy)(dmso)]$^{2+}$ (S, 1.67 V;
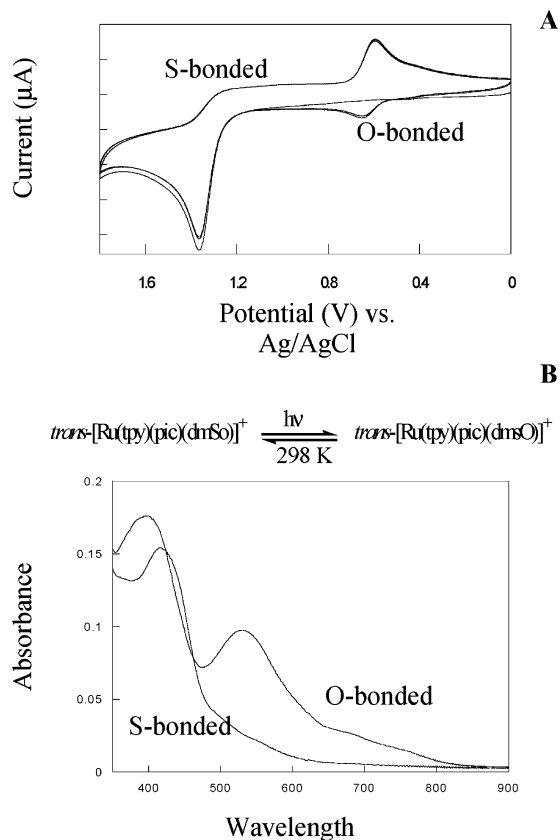
O, 1.1 V) and [Ru(tpy)(tmen)(dmso)]$^{2+}$ (S, 1.65 V; O, 1.03 V) are accordingly ascribed to O-bonded dmso isomers (Table 1).

Irradiation of [Ru(tpy)(L2)(dmso)]$^{z+}$ complexes (L2 = bpy, pic, or tmen) in dmso solution, ionic liquid (N,N-butylmethylpyrrolidinium trifluoromethylsulfonimide),[19] or polymer films results in dramatic shifts in the lowest energy visible (MLCT) transitions. As seen in Figure 1B for [Ru-(tpy)(pic)(dmso)]$^+$, the original yellow solution (S-bound: λ_{max} = 421 nm) appears purple (λ_{max} = 527 nm) after irradiation in ionic liquid. Identical changes in the absorption spectrum of [Ru(tpy)(pic)(dmso)]$^+$ during irradiation are seen in dmso solution and polymer films. Following generation of the O-bonded isomer in ionic liquid, the S-bonded isomer is re-formed, yielding the original spectrum after a period of minutes. Similar changes in the absorption spectrum of [Ru(tpy)(bpy)(dmso)]$^{2+}$ (S, 419 nm; O, 490 nm) and [Ru-(tpy)(tmen)(dmso)]$^{2+}$ (S, 429 nm; O, 530 nm) are observed in dmso solution and ionic liquid. In accord with the electrochemical results, irradiation for extended periods of time of [Ru(tpy)(acac)(dmso)]$^+$ or [Ru(tpy)(mal)(dmso)] in neat dmso solution, ionic liquid, or polymer films does not reveal a change in the absorption spectrum of these complexes. The electrochemical and photochemical data indicate that S → O isomerization is strongly disfavored in these two examples.

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That electron transfer triggers isomerization in these complexes is evident through the electrochemical and photochemical studies. Voltammetric measurements require the formal oxidation or reduction of the metal center to initiate isomerization. Photochemical measurements mimic this action via MLCT photochemistry to form metastable O-bonded isomers. Examination of the energy differences from the electrochemical (ΔE_{ec}) and absorption (ΔE_{abs}) data (Table 1) show that an electron transfer mechanism is operative in these complexes. However, the disagreement of these values for [Ru(tpy)(pic)(dmso)]$^+$ suggests that other factors are critical for isomerization.

Surprisingly, isomerization is inhibited in [Ru(tpy)(acac)-(dmso)]$^+$ and [Ru(tpy)(mal)(dmso)]. In a primitive sense, it may be interpreted that these ligands do not allow the Ru^{III} center to appear hard enough to favor the hard O-donor over the soft S-donor.[20] It is clear that the π-bonding characteristics of the bidentate ligand have an important role in isomerization. That the reaction does not occur through either pathway (excited-state or ground-state) indicates a more substantial change in the electronic structure in this family of complexes. While the data support a decrease in the energy gap of the Ru$^{II/III}$–S surfaces (Table 1: decreasing λ_{max};

cathodic $E_{1/2}$ shifts), it is difficult to identify a trend in the energy gap of the Ru$^{II/III}$–O surfaces. Thus we are uncertain if the isomerism is prohibited due to a kinetic (activated barrier crossing) or thermodynamic (S-to-O surface crossing is no longer exergonic) barrier.

These results highlight the importance of ancillary ligands in photochromic (polypyridyl)ruthenium–dmso complexes. This study provides a framework with which to begin to understand these transformations. Further studies will address the mechanism of isomerism as well as determine the isomerization kinetics for these complexes.

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

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