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Room-Temperature Photochromism in *cis*- and *trans*-[Ru(bpy)$_2$(dmso)$_2$]$^{2+}$

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We report on phototriggered Ru–S → Ru–O and thermal Ru–O → Ru–S intramolecular linkage isomerizations in *cis*- and *trans*-[Ru(bpy)$_2$(dmso)$_2$]$^{2+}$. The cis complex features only S-bonded sulfoxides (*cis*-[S,S]), whereas the trans isomer is characterized by S- and O-bonded dmso ligands. Both *cis*-[S,S] and *trans*-[S,O] exhibit photochromism at room temperature in dmso solution and ionic liquid (IL). Rates of reaction in IL were monitored by UV–visible spectroscopy and are similar to those reported in dmso solution ($k_{\mathrm{O}\rightarrow\mathrm{S}}$ ranges from $\sim 10^{-3}$ to 10^{-4} s^{-1}). Cyclic voltammetric measurements of *cis*-[S,S] and *trans*-[S,O] are consistent with an electrochemically triggered linkage isomerism mechanism. While both *cis*-[S,S] and *trans*-[S,O] are photochromic at room temperature, neither complex is emissive. However, upon cooling to 77 K, *cis*-[S,S] exhibits LMCT (ligand-to-metal charge transfer) emission typical of many ruthenium polypyridine complexes. In contrast to *cis*-[S,S], *trans*-[S,O] does not show any detectable emission even at 77 K.

Excited-state linkage isomerizations of coordinated ligands are unusual transformations in coordination chemistry.[1,2] A recent report of *cis*-[Ru(bpy)$_2$(dmso)$_2$]$^{2+}$ (bpy = 2,2′-bipyridine; dmso = dimethyl sulfoxide) demonstrated S → O and O → S linkage isomerizations of dimethyl sulfoxide.[3] The yellow, ground-state complex features bis-S-bound sulfoxides, which upon irradiation in dmso solution yields a red, bis-O-bound species through a photosolvation pathway. This complex rearranges to a metastable S,O complex and then to the starting material in two successive bimolecular steps. However, the closely related [Ru(tpy)(bpy)(dmso)]$^{2+}$ (tpy = 2,2′:6′,2″-terpyridine) complex exhibits S → O and O → S intramolecular isomerizations in the solid state.[4] We questioned if these isomerizations in [Ru(bpy)$_2$(dmso)$_2$]$^{2+}$might also take place *intramolecularly and in the solid state*. Further, the luminescent behavior of [Ru(tpy)(bpy)(dmso)]$^{2+}$ is highly temperature dependent with O-bound emission observed at room temperature.[4] We anticipated that the emissive characteristics of [Ru(bpy)$_2$(dmso)$_2$]$^{2+}$ would be different and are curious about the factors that control exited-state isomerizations. Herein, we report on phototriggered Ru−S → Ru−O and thermal Ru−O → Ru−S intramolecular linkage isomerizations in *cis*- and *trans*-[Ru(bpy)$_2$(dmso)$_2$]$^{2+}$ as well as low-temperature emission of the cis isomer.

The ruthenium−dmso complexes may be prepared through halide abstraction from Ru(bpy)$_2$Cl$_2$ in refluxing neat dmso solution, or in alcohol or halocarbon solvents containing dmso (see Supporting Information). Each method produces a yellow solid identified as *cis*-[Ru(bpy)$_2$(dmso)$_2$]$^{2+}$ (*cis*-[S,S]) by its moderately intense Ru dπ → bpy π^* metal-to-ligand charge-transfer (MLCT) transition at 348 nm (Figure 1: $\epsilon_{348} = 6900$ M^{-1} cm^{-1}), which is identical to that found for the solid prepared by the literature procedure.[3] Crystallographic data reveal the bis-S-bound geometries of the two cis dmso ligands.[3] However, under *gentle* heating (40−50 °C, 20 min) in neat dmso or at room temperature in dmso−alcohol or dmso−halocarbon mixtures, the reaction mixture acquires a deep-orange color that features a drastically red-shifted MLCT transition (Figure 1: $\lambda_{\max} = 420$ nm; $\epsilon_{420} = 3800$ M^{-1} cm^{-1}). The red-shifted MLCT is inconsistent with a bis, *cis*-S-bound configuration: a shift from 348 to 420 nm is unexpected from a simple cis−trans rearrangement. For *cis*- and *trans*-[Ru(bpy)$_2$(H$_2$O)$_2$]$^{2+}$, the absorption maxima are similar (490 and 485 nm, respectively), suggesting that the substantial red-shift observed in the electronic spectrum is not due to a simple cis−trans isomerization.[5−7] In addition, the solubility of *trans*-[S,O] and insolubility of *cis*-[SS] in CH$_2$Cl$_2$ further demonstrates that these compounds are inequivalent. A complex containing trans S-bound and O-bound dmso ligands is the most

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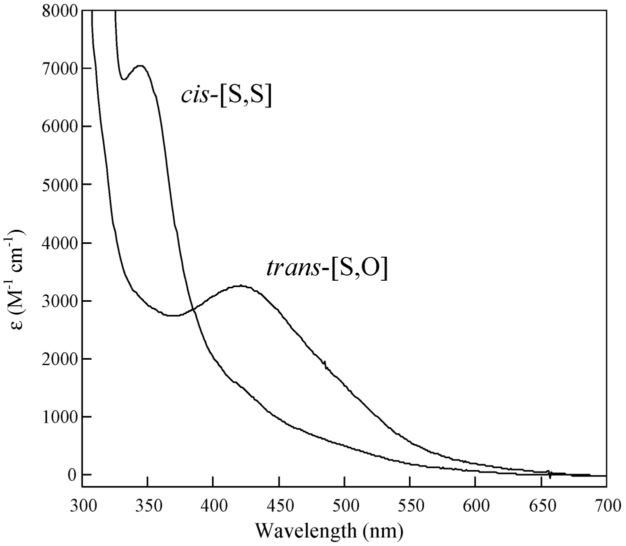

Figure 1. Absorption spectra of *cis*-[S,S] and *trans*-[S,O]-$[Ru(bpy)_2(dmso)_2]^{2+}$ in dmso: λ_{max}(*cis*-S,S) = 348 nm, λ_{max}(*trans*-S,O) = 420 nm.

Table 1. Rates of O → S Isomerization in *cis*- and *trans*-$[Ru(bpy)_2(dmso)_2]^{2+}$

rates (s^{-1})	*cis*-$[Ru(bpy)_2(dmso)_2]^{2+}$	*trans*-$[Ru(bpy)_2(dmso)_2]^{2+}$
O,O → S,O (IL)	$3.1(3) \times 10^{-3}$	$4.0(3) \times 10^{-3}$
S,O → S,S (IL)	$1.1(1) \times 10^{-4}$	
O,O → S,O (dmso)	$3.2(2) \times 10^{-3}$	$2.1(2) \times 10^{-3}$
S,O → S,S (dmso)	$1.3(1) \times 10^{-4}$	

probable (*trans*-[S,O]). Although the isomer was never identified, the spectrum of the isolated orange solid is remarkably similar to that obtained from reaction of dmso and *trans*-$[Ru(bpy)_2(H_2O)_2]^{2+}$.[8]

Both *cis*-[S,S] and *trans*-[S,O] are photochromic at room temperature in dmso solution and ionic liquids as well as in polystyrene films and crystals. Following irradiation of the MLCT band, light yellow-orange solutions, films, or microcrystalline solids containing either *cis*-[S,S] or *trans*-[S,O] yield solutions, films, or solids that appear deep-red or purple. Absorption spectra in dmso or ionic liquids reveal maxima at 347 and 496 nm for the cis isomer and 351 and 497 nm for the trans isomer. In accord with previous reports,[3,9,10] these new species are consistent with O-bound linkage isomers of the starting materials. Expectedly, both complexes thermally revert to their respective starting materials in all media.

To investigate ground-state Ru−O → Ru−S linkage isomerizations, samples were irradiated in *N*,*N*-butylmethylpyrrolidinium trifluoromethanesulfonimide ionic liquid (IL).[11] Rates of reaction were monitored by UV−visible spectroscopy and are similar to those reported in dmso solution (Table 1).[3] Following irradiation at room temperature of *cis*-[S,S]-$[Ru(bpy)_2(dmso)_2]^{2+}$ in IL to produce *cis*-[O,O], this isomer reverts to a metastable *cis*-[S,O] isomer with a rate constant of $3.1(3) \times 10^{-3}$ s^{-1}. The *cis*-[S,O] eventually yields *cis*-[S,S], but on a longer time scale ($k_{O\rightarrow S} = 1.1(1) \times 10^{-4}$ s^{-1}). The absorption spectrum of the *cis*-[S,O] intermediate is similar to that of *trans*-[S,O] isolated above, confirming the above assignment.

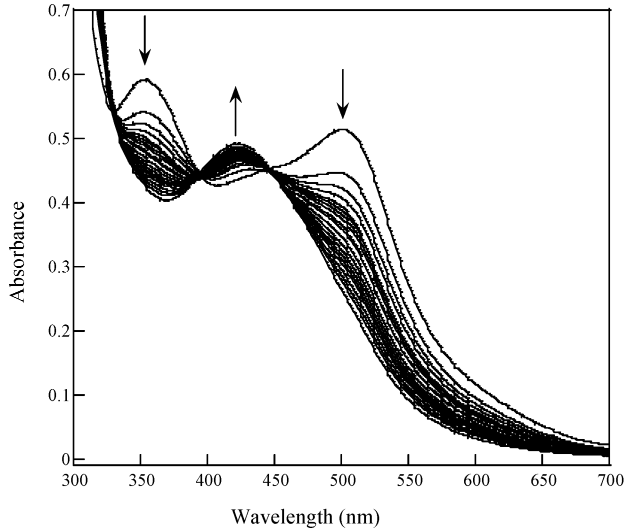

Figure 2. Thermal reversion of *trans*-[O,O] to the ground state, *trans*-[S,O], in ionic liquid.

Irradiation of *trans*-[S,O] in IL or dmso yields *trans*-[O,O] which rearranges to the *trans*-[S,O] starting material with a rate constant of $4.0(3) \times 10^{-3}$ s^{-1} (Table 1, Figure 2). Isomerization to *cis*-[S,S] from *trans*-[S,O] is not observed. The spectral features observed in these isomerizations are nearly identical to those observed in dmso solution and in polystyrene films. Due to the identical spectral changes in dmso and IL and the steady rate constant with varying $[Ru(bpy)_2(dmso)_2]^{2+}$ concentration, we propose that these S → O and O → S linkage isomerizations occur *intramolecularly*.

Cyclic voltammetric measurements of *cis*-[S,S] and *trans*-[S,O] are consistent with an electrochemically triggered linkage isomerism mechanism.[12−14] For *cis*-[S,S], only an oxidative wave near the solvent window (CH_3CN) at 2.2 V can be observed. Upon reversing the polarity, a quasi-reversible ($I_{pa}/I_{pc} \neq 1$) couple is revealed at 0.79 V vs Ag/AgCl). This couple is assigned to the *cis*-[O,O] isomer and is consistent with the lower energy MLCT bands observed in the electronic spectrum. The voltammogram of *trans*-[S,O] is more informative. For a scan rate of 0.1 V/s in CH_2Cl_2, a quasi-reversible couple at 1.26 V (vs Ag/AgCl) is observed. Upon reversing the polarity, a second quasi-reversible couple appears at 0.71 V (vs Ag/AgCl) and is assigned to *trans*-[O,O]. Increasing the scan rate to 1 V/s reveals a nearly reversible peak at 1.26 V ($I_{pa}/I_{pc} = 0.9$). In both examples, it is clear that the lower energy couple only appears following oxidation at the greater potential. Digital simulations of the voltammograms of *trans*-[S,O] suggest $k_{S\rightarrow O} = 0.5(1)$ s^{-1} and $k_{O\rightarrow S} = 3(1) \times 10^{-3}$ s^{-1}. This latter

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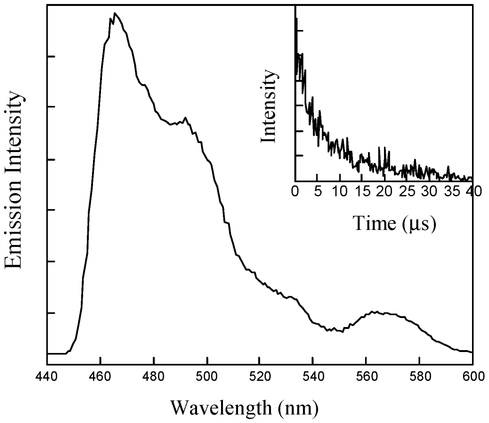

Figure 3. Emission spectrum of *cis*-[S,S]-$[\mathrm{Ru(bpy)_2(dmso)_2}]^{2+}$ at 77 K in 4:1 ethanol:methanol glass. $\lambda_{\mathrm{exc}} = 337.1$ nm. Inset: Emission decay trace recorded at 465 nm, $\tau = 6.2$ μs.

rate matches well with that previously determined from the irradiation experiments.

While both *cis*-[S,S] and *trans*-[S,O] are photochromic at room temperature, neither complex is emissive. However, upon cooling to 77 K in 4:1 ethanol:methanol glass, *cis*-[S,S] exhibits LMCT (ligand-to-metal charge-transfer) emission typical of many ruthenium polypyridine complexes (Figure 3). Interestingly, neither complex is photochromic at 77 K. Irradiation of *cis*-[S,S] at 77 K (Figure 3, inset) with $\lambda_{\mathrm{exc}} = 337.1$ nm produces an excited state that decays to ground state with $\tau = 6.2$ μs. This is consistent with that observed for $[\mathrm{Ru(bpy)_3}]^{2+*}$ at 77 K with $\tau = 4.9$ μs.[15] The peak spacings present in the *cis*-[S,S] spectrum are typical ($\sim$1200 cm^{-1}) for what is observed in many ruthenium polypyridine complexes ($\sim$1300 cm^{-1}).[16]

In contrast to *cis*-[S,S], *trans*-[S,O] does not show any detectable emission even at 77 K. A similar trend is seen in *cis*- and *trans*-$[\mathrm{Ru(bpy)(OH_2)_2}]^{2+}$, where the cis complex is strongly emissive but the trans isomer is only weakly emissive.[7] The origin of this effect may lie in a more efficient nonradiative decay pathway due to a weaker ligand field for the trans complex. A weaker ligand field is expected for trans complexes of the form $[\mathrm{Ru(bpy)_2(L)_2}]^{2+}$ because of the repulsive steric interaction between the hydrogen atoms at the α position of the bipyridine rings.[7] It is well-known that a major nonradiative excited-state decay pathway for ruthenium–polypyridine complexes is an activated process in which population of the ligand field states occurs from the ^{3}CT manifold.[17–19] A weaker ligand field would enhance this process even at lower temperatures.

These data indicate that formation of the O-bound species occurs intramolecularly and that the resultant photochromic effect is highly temperature dependent. Absorption spectra of glasses (77 K) containing either *cis*-[S,S] or *trans*-[S,O] show no evidence for the formation of bis-O-bonded metastable states or decomposition following irradiation. However, at room temperature isomerization may be phototriggered in a variety of media. Single-crystal spectroscopic studies of $[\mathrm{Ru(tpy)(bpy)(dmso)}]^{2+}$ show both S-bound and O-bound emission at intermediate temperatures (170 K).[4] Clearly, the ligand environment is an important parameter in determining the photochemistry of ruthenium(polypyridyl)–dmso complexes. A more thorough spectroscopic study of these complexes is currently underway to further our understanding of this chemistry.

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Supporting Information Available: Synthetic procedures, original kinetic data, cyclic voltammograms, and first-order plots of O → S thermal rates.

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