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Photochromic Complexes

Two-Color Reversible Switching in a Photochromic Ruthenium Sulfoxide Complex**

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Reversible, external triggering of molecules between two ground states is central to the operation of modern molecular machines.[1–3] A desirable trigger is light, as it provides an ample amount of energy in a short burst of time. Although light is commonly employed for the formation of many different types of metastable states,[4–8] in practice it is difficult to employ light to regenerate the initial ground state. The enthalpic and entropic factors that favor the photochemical generation of the metastable state from the ground state must necessarily be disfavored for the opposing photochemical reaction. Moreover, the photoproduct often reverts to the ground state thermally. Irradiation of photochromic compounds yields metastable states that exhibit distinct electronic structures compared to their ground states.[9] Whilst a number of organic photochromic compounds feature reversible or two-color photoswitching between metastable and ground states, such reactivity is rare in transition metal complexes.[10] Herein, we report our findings on a ruthenium sulfoxide complex that features two-color photochromism.

The complex $[Ru(bpy)_2(pySO)](PF_6)_2$ (bpy = 2,2′-bipyridine, pySO = 2-(isopropylsulfinylmethyl)pyridine) was prepared from reaction of *cis*-$[Ru(bpy)_2Cl_2]$ with pySO. The structure and formulation of the complex was verified by one-and-two-dimensional ^1H NMR, IR spectroscopy, and elemental analysis. The ^1H NMR spectrum is consistent with the presence of two isomers, which are most likely diastereomers, as both the ruthenium and sulfur centers are chiral. Elemental analysis of the isomeric mixture supports this assignment. The lowest-energy transition in the electronic spectrum occurs at 370 nm ($\varepsilon = 7250\ \mathrm{cm^{-1}M^{-1}}$) and is assigned to a Ru $d\pi \rightarrow$ bpy π^* charge-transfer transition based on its energy and intensity (Figure 1). This transition is similar to that observed for other chelating S-bonded sulfoxides.[11] Furthermore, the structurally characterized complex $[Ru(bpy)_2(py)(dmso)]^{2+}$ (dmso = dimethylsulfoxide), which has no chelation, features a maximum absorbance at 400 nm for the S-bonded isomer.[12] Therefore, the chelate complex exhibits an additional 2000 $\mathrm{cm^{-1}}$ of stabilization relative to the non-chelate form.

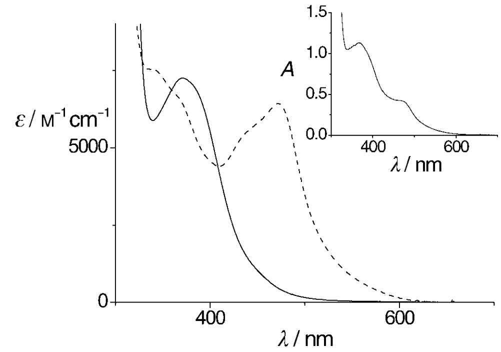

Figure 1. Absorption of S-bonded (——) and O-bonded (– – –) isomers. The spectrum of the O-bonded isomer was extrapolated from the photostationary state spectrum. Inset: Spectrum depicting the photostationary state obtained following white-light irradiation of the S-bonded isomer.

White light irradiation of $[Ru(bpy)_2(pySO)]^{2+}$ in propylene carbonate solution results in a decrease in the absorbance at 370 nm concomitant with an increase at 472 nm (Figure 1, inset). In accord with other ruthenium sulfoxide complexes,[13] the spectral changes indicate an intramolecular $S \rightarrow O$ isomerization, with an isosbestic point at 408 nm. However, the observed spectral changes are muted in comparison to these other complexes. We questioned whether or not this spectrum represented a photostationary state. Accordingly, irradiation of this solution with 355 nm light resulted in a more pronounced absorbance at 472 nm (quantum efficiency $\Phi_{S\rightarrow O} = 0.11(2)$). This value is similar to that of the O-bonded isomer of $[Ru(bpy)_2(py)(dmso)]^{2+}$ (476 nm)[12] and $[Ru(bpy)_2(pic)]^{+}$ (483 nm; pic = 2-pyridinecarboxylate),[14] which feature N and O donors in the $Ru^{II}(bpy)_2$ coordination sphere. The S-bonded and extracted O-bonded spectra ($\varepsilon_{472nm} = 6400\ \mathrm{cm^{-1}M^{-1}}$) are shown in Figure 1. The IR spectrum provides structural evidence for isomerization; the ground-state S-bonded isomer has a band at $\tilde{\nu}(S{=}O) = 1090\ \mathrm{cm^{-1}}$ which is replaced by a band at $\tilde{\nu}(S{=}O) = 1060\ \mathrm{cm^{-1}}$ upon irradiation. This new feature is ascribed to the O-bonded isomer.[15,16]

The presence of a photostationary state with white light irradiation indicates an excited-state photochemical pathway for $O \rightarrow S$ isomerization from longer wavelengths. Accordingly, 470 nm irradiation of a solution that contains predominately the O-isomer resulted in a decrease of the absorbance at 472 nm concomitant with an increase at 370 nm ($\Phi_{O\rightarrow S} =$

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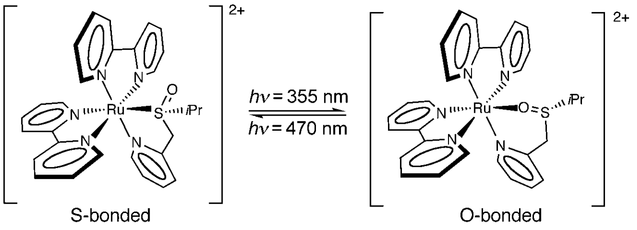
0.027(6)). The forward and reverse reactions are depicted in Scheme 1 (see also Movie in the Supporting Information). Studies to determine the long-term photostability of this cycle are underway. Such two-color reactivity is exceptionally rare in transition-metal photochromic complexes at room temperature.[10] For example, sodium nitroprusside and many of its derivatives feature isomerization of the bound nitrosyl ligand, but only in the solid state at low temperature.[17,18] Heilweil, Webster, Burkey and co-workers have reported one such example in their studies of ultrafast photochromic organometallic compounds.[19]



Scheme 1. Isomerization between S-bonded and O-bonded $[Ru(bpy)_2(pySO)]^{2+}$ isomers upon excitation with UV light.

Picosecond transient absorption data for the S-bonded isomer are shown in Figure 2. Initial traces from $t = 0$ to 10 ps yield the formation of a bleach feature centered at 372 nm, which coincides closely with the ground-state absorbance maximum. This feature is attributed to the depletion of the ground-state metal–ligand charge-transfer (MLCT) absorption, and is accompanied by a broad positive peak from about 450 nm to the limit of detection. This long-wavelength feature is qualitatively similar to those observed in the transient spectra of $[Ru(bpy)_3]^{2+}$ and related complexes. It is thus interpreted as arising from the ligand–metal charge-transfer (LMCT) transition from a neutral bpy ligand to the oxidized ruthenium(III) center and a $\pi^* \rightarrow \pi^*$ transition from the reduced bpy ligand. From 10 ps to about 1500 ps, a bleach, or negative peak, at 372 nm and the broad low-energy absorption decrease in intensity, yielding a bleach centered at about 380 nm and positive absorption at circa 465 nm. This spectrum agrees closely with the difference spectrum between the S-bonded and O-bonded spectra, indicating relaxation to the O-bonded ground state within 1500 ps. In accord with $[Ru(bpy)_2(OSO)]^+$,[20] there is no evidence for the formation of an O-bonded excited state in the transient spectra, indicating that S→O isomerization occurs from a CT excited state of S-bonded character to the O-bonded ground state. Transient spectra were fitted to a bi-exponential rate law, yielding rate constants of $4.5 \times 10^{11}\,s^{-1}$ and $6.1 \times 10^9\,s^{-1}$ (Figure 2, inset). The fast rate constant is interpreted as localization from the Franck–Condon state to the thermalized S-bonded excited state, with a time constant of 2.2 ps. The slow rate constant therefore corresponds to the relaxation from the S-bonded excited state to both the S-bonded and O-bonded ground states. The time constant for photochromic S→O isomerization was thus found to be 1.5 ns.

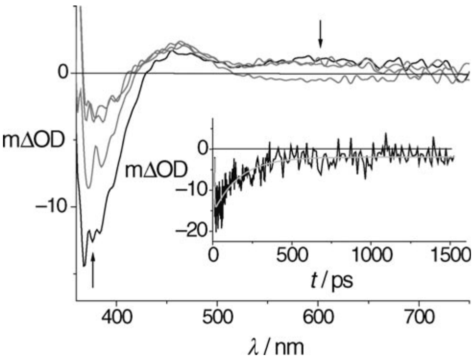


Figure 2. Transient absorption spectra of $S\text{-}[Ru(bpy)_2(pySO)]^{2+}$ with 350 nm excitation in propylene carbonate solution. mΔOD represents $10^{-3} \times \Delta OD$, where ΔOD is the change in optical density. The arrows indicate evolution of traces over time. Traces at 10, 100, 500, and 1500 ps after the laser pulse.

The O-bonded transient absorption spectra with excitation at 473 nm are shown in Figure 3. Within 1 ps of the laser pulse, a bleach centered at 472 nm is formed. There are also positive absorption features in the near UV (350–400 nm) and a broad, weak absorbance feature from about 600 nm to the NIR. As with the S-bonded complex, these features are indicative of the depletion of the ground state MLCT of the O-bonded complex and the rise of absorption from the LMCT and $\pi^* \rightarrow \pi^*$ transitions. These features then decay to a spectrum with positive absorption from 350–400 nm and weakly negative absorption at 472 nm. Although obscured by a consistently strong negative absorption owing to the laser excitation source at 473 nm, the spectrum at 500 ps resembles the difference spectrum between the O-bonded and S-bonded spectra. The transient spectra were fitted as for the S-bonded complex, and yielded bi-exponential rate constants of $1.4 \times 10^{11}\,s^{-1}$ and $5.9 \times 10^9\,s^{-1}$. The fast rate is assigned to relaxation of the Franck–Condon state to the thermalized O-bonded state, with a time constant of 7.4 ps. The slow rate constant is tentatively ascribed to relaxation of the thermally-relaxed

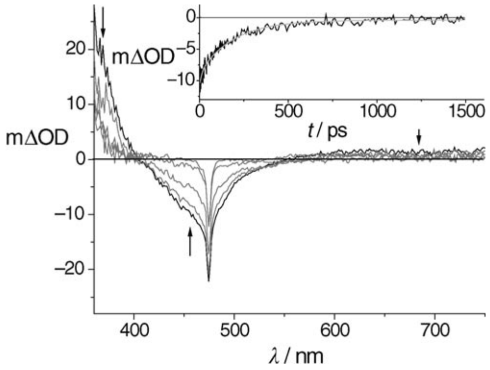


Figure 3. Transient absorption spectra of the O-bonded isomer in a propylene carbonate solution with excitation at 473 nm. The arrow indicates evolution of traces over time. Traces at 1, 10, 100, 500, and 1490 ps after laser pulse.

O-bonded excited state to the S-bonded and O-bonded ground states, and yields a time constant for the O→S photochromic isomerization of 6.3 ns.

Both S- and O-bonded isomers of $[Ru(bpy)_2(pySO)]^{2+}$ emit at 77 K in a 2-methyltetrahydrofuran/propylene carbonate (4:1) glass. Excitation at 400 nm yields an intense emission band at 518 nm ($\Phi_{EM} = 0.90$) and a weak emission feature at 618 nm ($\Phi_{EM} = 0.27$). Excitation spectra ascribe the 618 nm emission to the 472 nm absorption (O-bonded) and the 518 nm emission to the 370 nm absorption (S-bonded). Electrochemical studies reveal a single S-bonded and O-bonded $Ru^{3+/2+}$ reduction potential at 1.35 V and 0.75 V, respectively, which is consistent with electron-transfer-triggered isomerization of the sulfoxide. An energy level diagram (Figure 4) was then constructed by employing these values. Whilst additional studies are needed, a feature that may explain the unusual photoreversible behavior exhibited by this compound is that the O-bonded ^{3}MLCT excited state is higher than the S-bonded ^{3}MLCT. Future studies will involve improving our understanding of this rare photoreactivity and fabricating other compounds that feature this behavior.

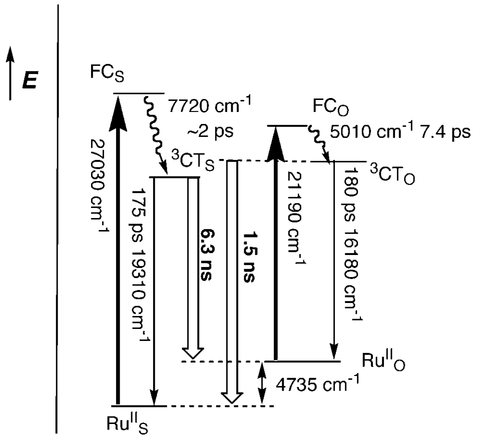


Figure 4. Energy level diagram of $[Ru(bpy)_2(pySO)]^{2+}$. Ru^{II}_S, Ru^{II}_O: ground-state energy levels of S-bonded and O-bonded isomers; FC_S, FC_O: Franck–Condon states. Isomerization between ^3CT_S and Ru^{II}_O and between ^3CT_O and Ru^{II}_S occurs along a multi-dimensional reaction coordinate involving spin and nuclear coordinates.

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