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Excited state isomerization in a new ruthenium chelating sulfoxide complex

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ABSTRACT

Electrochemical and photochemical studies of a photochromic complex with a chelating sulfoxide are reported. Electrochemical data do not support evidence for isomerization following electrochemical oxidation. However, irradiation of solutions containing $[Ru(bpy)_2(PhNSO)](PF_6)_2$ (bpy is 2,2′-bipyridine, PhNSO is *N*-benzylidine-2-(ethylsulfinyl)ethanamine) demonstrate excited state S → O isomerization. The S-bonded absorption maximum is 382 nm, while the O-bonded isomer features absorption maxima at 360 and 486 nm. The quantum yield of isomerization is 0.033 and the S-bonded isomer is emissive at low temperature (77 K). These data and an electronic structural model explaining this reactivity are introduced.

1. Introduction

Molecules capable of storing photonic energy as potential energy have clear applications as molecular information storage devices [1–3]. Photochromic compounds are excellent candidates for these types of applications. Photochromic compounds are molecular devices which employ photonic energy for bond breaking and bond formation processes. While organic molecules that display photochromic behavior have been well documented [4], transition metal complexes have only recently garnered similar attention [5,6].

One group of photochemical complexes that have been studied are d^6 transition metal–sulfoxide complexes [7–13]. These molecules exhibit intramolecular excited state S → O and ground state O → S isomerization. This work focuses on a new complex within this family of complexes $[Ru(bpy)_2(PhNSO)](PF_6)_2$ (bpy is 2,2′-bipyridine, PhNSO is *N*-benzylidine-2-(ethylsulfinyl) ethanamine). This complex features an inner coordination sphere markedly similar to $[Ru(tpy)(bpy)(dmso)]^{2+}$ (tpy is 2,2′,6′-terpyridine, dmso is dimethylsulfoxide) [13]. The lability of O-bonded dmso with respect to solvolysis has been shown to inhibit investigation of these molecules. By incorporating the sulfoxide ligand into a chelating ligand, it is hoped that the stability of the photoproduct will be increased while the electronic structure and photochromic capabilities will be maintained [10,14–16]. Herein, we report our findings of a photochromic complex with a new chelating sulfoxide ligand.

2. Experimental

2.1. Materials and methods

The compound *cis*-$Ru(bpy)_2Cl_2{\cdot}xH_2O$ was either synthesized using published methods [17], or purchased from Strem and used as is. The reagents 2,2′-bipyridine (bpy), benzaldehyde, 1-(ethylthio)ethylamine hydrochloric acid, 3-chloroperbenzoic acid (*m*-CPBA) and all solvents were purchased from Aldrich and were used as is. Tetra *n*-butyl ammonium hexafluorophosphate ($TBAPF_6$), for use in electrochemical measurements, was purchased from Fluka and recrystallized from hot ethanol three times. Acetonitrile and methanol for electrochemical experiments were of spectroscopic grade and purchased from Burdick and Jackson. All other reagents and solvents were used without further purification.

2.2. Instrumentation and spectral measurements

Electronic absorption spectra were collected on an Agilent 8453 spectrophotometer. Bulk photolysis experiments were conducted using a 75 W Xenon-arc lamp (Oriel) fitted with a Canon standard camera UV filter. Proton nuclear magnetic resonance (^1H NMR) spectra were collected on both a 300 MHz Bruker AG spectrometer and a 500 MHz Varian spectrometer. All deuterated solvents used for ^1H NMR measurements were purchased from Cambridge isotopes and used as is. Emission spectra were collected at 77 K in 4:1 ethanol:methanol solution on a PTI C-60 Fluorimeter equipped with a Hamamatsu R928 PMT (185–900 nm). Emission quantum yields were obtained by comparison of the integrated intensity of the emission spectra with that obtained for $Ru(bpy)_3{}^{2+}$ using previously published quantum yield values [18].

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Cyclic voltammetry was performed on a CH Instruments CH1730A Electrochemical Analyzer. This workstation contains a digital simulation package as part of the software package to operate the workstation (CHI version 2.06). The working electrode was a glassy-carbon electrode (BAS) or Pt disk electrode where the electrode surface area is 2.0 mm^2. The counter and reference electrodes were Pt wire and Ag/AgCl, respectively. Electrochemical measurements were typically performed in dichloromethane, methanol, acetonitrile or propylene carbonate solutions containing 0.1 M $\mathrm{TBAPF_6}$ or *N*,*N*-butylmethylpyrrolidinium sulfonamide electrolyte in a one compartment cell.

2.3. Synthesis of N-benzylidine-2-(ethylthio)ethanamine (PhNS)

Benzaldehyde (360 μL, 3.5 mmol) and 1-(ethylthio)ethylamine hydrochloric acid (501.7 mg, 3.5 mmol) were dissolved in a mixture of MeOH:1,2-dichloroethane (1:4). NaOH (157.8 mg, 3.9 mmol) was added to solution to neutralize the hydrochloric acid, and the solution was heated to reflux for 2 days. The reaction was allowed to cool to room temperature. Solid NaCl was removed by vacuum filtration and any unreacted (ethylthio)ethylamine was precipitated by addition of ethyl ether. This solid was removed by vacuum filtration, and the filtrate was reduced to an orange oil by rotary evaporation. Yield: 378.3 mg (~350 μL, 55%). ^{1}H NMR ($\mathrm{CDCl_3}$, 500 MHz) δ: 8.31 (s, CH=N, 1H), 7.74 (d, Ph, 1H), 7.73 (d, Ph, 1H), 7.42 (m, Ph, 3H), 3.83 (t, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2S}$, 2H), 2.88 (t, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{S}$, 2H), 2.60 (q, $\mathrm{SC}\mathit{H}_2\mathrm{CH_3}$, 2H), 1.27 (t, $\mathrm{SCH_2C}\mathit{H}_3$, 3H).

2.4. Synthesis of $[\mathrm{Ru(bpy)_2(PhNS)}](\mathrm{PF_6})_2$

Dark purple *cis*-$\mathrm{Ru(bpy)_2Cl_2}$ (120.4 mg, 0.25 mmol), PhNS ligand (52 μL, 0.25 mmol) and two equivalents of $\mathrm{AgPF_6}$ (129.5 mg, 5.0 mmol) are dissolved in 100 mL 1,2-dichloroethane. The reaction was heated to reflux for 24 h under argon in the absence of light. The solution changed from purple to red/orange as the reaction progressed, during which time solid AgCl precipitated. The solution was cooled to −30 °C to ensure precipitation of all AgCl and was then filtered to collect two equivalents of AgCl. The filtrate volume was reduced to dryness and reconstituted with acetone/EtOH. Acetone was removed by rotary evaporation causing the product to precipitate as an red–orange solid. The product was isolated via vacuum filtration, washed with ether (3× 15 mL), and air-dried. Yield: 139.5 mg (80%). UV–vis (MeOH) λ_{max} = 436 nm (6550 $\mathrm{M^{-1}\,cm^{-1}}$). $E^{0\prime}$ $\mathrm{Ru}^{3+/2+}$ vs. Ag/AgCl = 1.31 V. ^{1}H NMR ($\mathrm{CD_3CN}$, 500 MHz) δ: 9.28 (s, bpy, 1H), 9.10 (d, bpy 1H), 9.01 (d, bpy, 1H), 8.45 (d, bpy, 1H), 8.26 (d, bpy, 2H), 8.18 (d, bpy, 2H), 7.83 (m, bpy/PhNS, 4H), 7.58 (t, bpy, 1H), 7.31 (d, bpy, 1H), 7.12 (t, bpy, 1H), 7.00 (t, Ph, 1H), 6.91 (d, bpy, 1H), 6.87 (d, bpy, 1H), 6.76 (t, Ph, 2H), 6.45 (d, Ph, 2H), 4.31 (t, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2S}$, 1H), 4.08 (t, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2S}$, 1H), 3.20 (t, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{S}$, 1H), 2.86 (t, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{S}$, 1H), 1.79 (q, $\mathrm{SC}\mathit{H}_2\mathrm{CH_3}$, 1H), 1.37 (q, $\mathrm{SC}\mathit{H}_2\mathrm{CH_3}$, 1H), 0.97 (t, $\mathrm{SCH_2C}\mathit{H}_3$, 3H) Anal. Calcd. for $\mathrm{C_{31}H_{31}F_{12}N_5P_2RuS}$: C, 41.52; H, 3.48; N, 7.81; S, 3.58%. Found: C, 41.62; H, 3.55; N, 7.89; S, 3.67%.

2.5. Synthesis of $[\mathrm{Ru(bpy)_2(PhNSO)}](\mathrm{PF_6})_2$ (PhNSO is N-benzylidine-2-(ethylsulfinyl)ethanamine)

Red–orange $[\mathrm{Ru(bpy)_2(PhNS)}](\mathrm{PF_6})_2$ (31.4 mg, 0.035 mmol) and 3-chloroperbenzoic acid (*m*-CPBA) (52.3 mg, 0.30 mmol) were dissolved in 25 mL methanol. The reaction was stirred at room temperature in the dark for 24 h. The solution volume was reduced to <5 mL and the product was precipitated by the addition of ether. The yellow–orange product was isolated via vacuum filtration, washed with ether (3× 15 mL), and air-dried. Yield: 28.9 mg (90%). UV–vis (MeOH) λ_{max} = 382 nm (S-bonded) (6670 $\mathrm{M^{-1}\,cm^{-1}}$). $E^{0\prime}$ $\mathrm{Ru}^{3+/2+}$ vs. Ag/AgCl = 1.10 V (O-bonded). ν(SO) = 1100 $\mathrm{cm^{-1}}$. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 300 MHz) δ: 9.83 (s, bpy, 1H), 9.48 (s, bpy, 1H), 9.00 (s, bpy, 1H), 8.73 (d, bpy, 1H), 8.49 (m, bpy/PhNSO, 4H), 8.31 (t, bpy, 1H), 8.18 (d, bpy, 1H), 8.02 (d, bpy, 2H), 7.89 (t, bpy, 1H), 7.78 (t, bpy, 1H), 7.39 (s, bpy, 1H), 7.31 (d, Ph, 1H), 7.04 (s, bpy, 2H), 6.83 (t, Ph, 2H), 6.72 (d, bpy, 1H), 6.58 (d, Ph, 2H), 4.42 (d, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2S(O)}$, 2H), 3.87 (s, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{S(O)}$, 2H), 2.41 (q, $\mathrm{S(O)C}\mathit{H}_2\mathrm{CH_3}$, 2H), 1.11 (t, $\mathrm{S(O)CH_2C}\mathit{H}_3$, 3H). Anal. Calcd. for $\mathrm{C_{31}H_{31}F_{12}N_5OP_2RuS}$: C, 40.80; H, 3.42; N, 7.67; S, 3.51%. Found: C, 41.04; H, 3.51; N, 7.74; S, 3.62%.

3. Results and discussion

3.1. Electronic absorption measurements

The lowest energy absorption in the electronic spectrum of the thioether complex $[\mathrm{Ru(bpy)_2(PhNS)}]^{2+}$, appears at 436 nm (6550 $\mathrm{M^{-1}\,cm^{-1}}$) and is assigned as a Ru d$\pi \rightarrow$ bpyπ^* metal-to-ligand charge transfer (MLCT) transition. Consistent with previous reports, this band blue shifts to 382 nm (6670 $\mathrm{M^{-1}\,cm^{-1}}$) upon oxidation of the thioether ligand to the sulfoxide, S-bonded $[\mathrm{Ru(bpy)_2(PhNSO)}]^{2+}$ (denoted S-$[\mathrm{Ru(bpy)_2(PhNSO)}]^{2+}$ hereafter). The absorption spectra are shown in Fig. 1. Both spectra feature low energy tails with significant absorbance well into the visible region, out to approximately 600 nm. Such characteristics are expected in the absorption spectra when compared to other ruthenium–thioether and ruthenium–sulfoxide complexes; the O-bonded isomers would absorb at lower energy than either the S-bonded isomers or their sulfide precursors [15,19–23]. Interestingly, the absorption maximum for $[\mathrm{Ru(tpy)(bpy)(dmso)}]^{2+}$ is 419 nm, indicating an increased stabilization of the dπ orbital set in $[\mathrm{Ru(bpy)_2(PhNSO)}]^{2+}$.

Irradiation of the charge transfer band of S-$[\mathrm{Ru(bpy)_2(PhNSO)}]^{2+}$ yields the O-bonded photoproduct through excited state S → O isomerization. The change in ligation of the sulfoxide yields a dramatic red-shift in the MLCT transition. The maximum at 382 nm corresponding to the S-bonded sulfoxide diminishes while new maxima grow in at 360 and 486 nm. These maxima are similar to that observed for O-$[\mathrm{Ru(tpy)(bpy)(dmso)}]^{2+}$ and for $[\mathrm{Ru(tpy)(bpy)(OH_2)}]^{2+}$ [13,24]. Similar reactivity is observed in acetonitrile and methanol solvents, supporting the assignment of this being an intramolecular reorganization. The absorption spectra of

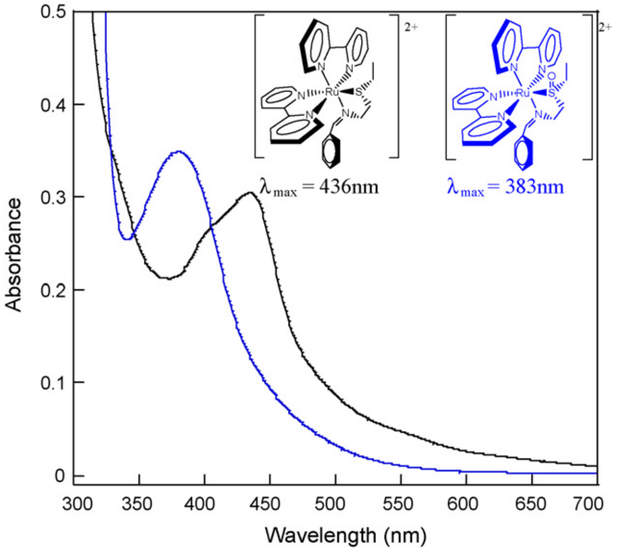

Fig. 1. Absorption spectra of $[\mathrm{Ru(bpy)_2(PhNS)}]^{2+}$ (black) and $[\mathrm{Ru(bpy)_2(PhNSO)}]^{2+}$ (blue) in methanol.

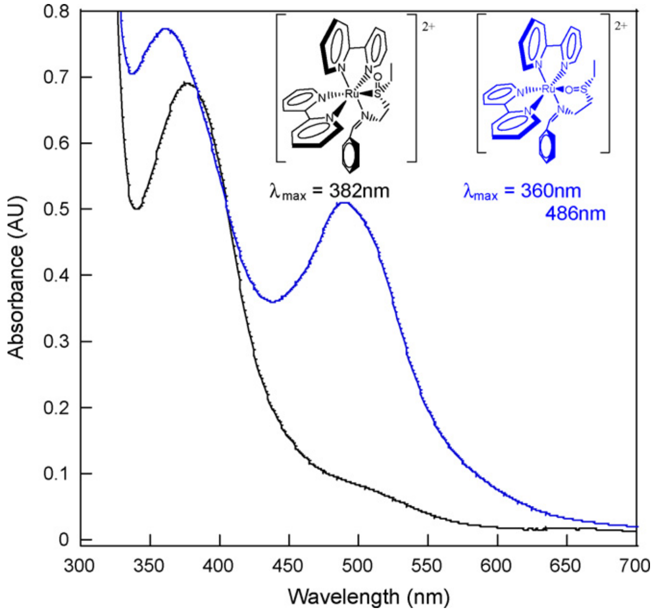

Fig. 2. Absorption spectra of S-$[Ru(bpy)_2(PhNSO)]^{2+}$ (black) and O-$[Ru(bpy)_2(PhNSO)]^{2+}$ (blue) in methanol.

the S- and O-bonded isomers of the sulfoxide complex are shown in Fig. 2.

This excited state behavior may be rationalized through Hard-Soft Acid–base theory [25]. Upon excitation of the metal-to-ligand charge transfer band the ruthenium metal center is formally oxidized from Ru^{II} to Ru^{III}. This transformation acts as a trigger for linkage isomerization within the PhNSO ligand. The formally S-bonded ligand rearranges intramolecularly to an O-bonded geometry, resulting in a shift in the electronic properties of the complex. The newly formed O-bonded complex does not appear to thermally revert back to the S-bonded ground state at room temperature. This result is in stark contrast to previously investigated chelating sulfoxides, suggesting that the barrier to ground state reversion is greater in energy than in related chelating sulfoxide complexes [14,15].

The quantum yield for S → O isomerization ($\Phi_{S\rightarrow O}$) for S-$[Ru(bpy)_2(PhNSO)]^{2+}$ is similar to that observed for $[Ru(tpy)(bpy)(dmso)]^{2+}$ [13]. In methanol, $\Phi_{S\rightarrow O} = 0.033(\pm 0.003)$ with 417 nm irradiation. This value is approximately 10^2 times greater than photosubstitution of CH_3CN in pyridine for $[Ru(tpy)(bpy)(CH3CN)]^{2+}$, a process known to proceed through the LF states [26–28]. This larger quantum yield is suggestive of a separate mechanistic pathway for isomerization not involving the LF states. In contrast, other chelating sulfoxide complexes previously investigated have shown isomerization quantum yields approximately one order of magnitude greater. For example, the chelating sulfoxide complexes $[Ru(bpy)_2(OSO)]^{+}$ (OSO is 2-methylsulfinylbenzoate) exhibits $\Phi_{S\rightarrow O} = 0.45$ in methanol and $[Ru(bpy)_2(OSSO)]^{2+}$ (OSSO is dimethylbis(methylsulfinylmethyl)silane) features $\Phi_{SS\rightarrow SO} = 0.55$ in propylene carbonate [14,15]. One interpretation of these data is that the flexibility of the chelating sulfoxide ligand has significant influence on the dynamics of linkage isomerization. The quantum yield of isomerization represents the efficient use of excited state energy for bond breaking and bond formation. Flexible molecules disperse the excited state energy as heat, minimizing the amount of energy employed for work. In comparison of the two above-mentioned compounds $[Ru(bpy)_2(PhNSO)]^{2+}$ can be assumed to have increased flexibility than the other two complexes perhaps due to the ethyl bridge (C_2H_4) connecting the sulfoxide to the imine nitrogen. While we do not know precisely the motions on the excited state ^{3}MLCT surface (or the role of the Ligand Field states), it stands to reason that the PhNSO ligand is more flexible. These data suggest that to maximize the efficiency of linkage isomerization, more rigid sulfoxide ligands should be employed.

3.2. *Electrochemical measurements*

Electrochemical experiments help confirm the assignment of photochemically triggered S → O linkage isomerization. Cyclic voltammograms of $[Ru(bpy)_2(PhNS)]^{2+}$ shows a reversible couple at 1.31 V vs. Ag/AgCl, and are otherwise unremarkable. The cyclic voltammogram of S-$[Ru(bpy)_2(PhNSO)]^{2+}$ prior to irradiation do not show evidence of isomerization within the electrochemical window. The reduction potential of the metal complex is expected to shift to a more positive potential upon chemical oxidation of the thioether ligand, and has apparently shifted to a potential greater than what can be accessed by the acetonitrile electrolyte solution (>1.8 V vs. Ag/AgCl). Irradiation of the electrolyte solution containing the sulfoxide complex produces a couple at 1.1 V vs. Ag/AgCl. This couple is assigned to the O-bonded complex. These potentials are consistent with $[Ru(tpy)(bpy)(dmso)]^{2+}$, which features reduction potentials of 1.6 and 1.1 V for the S-bonded and O-bonded conformations, respectively [13]. Moreover, the O-bonded complex features a reduction potential ~100 mV lower than that reported for the bis-acetonitrile complex $[Ru(bpy)_2(CH_3CN)_2]^{2+}$ ($E^{0\prime} = 1.2$ V vs. Ag/AgCl in CH_3CN), indicating that the new reduction potential is not due to ligand substitution by solvent [18]. Lastly, the absorption spectrum of the irradiated electrolyte solution is identical to that obtained from photolysis. Cyclic voltammograms of $[Ru(bpy)_2(PhNSO)]^{2+}$ before and after irradiation are shown in Fig. 3.

3.3. *Low-temperature emission studies*

The PhNS ligand and its analogous ruthenium complexes exhibit interesting emissive characteristics. The uncoordinated PhNS ligand is emissive at room temperature in methanol solution. Upon 355 nm excitation, ligand emission is observed with a maximum of 470 nm. The quantum yield of emission (Φ_{EM}) has been measured to be 0.044. The emission spectrum is shown in Fig. 4. While neither

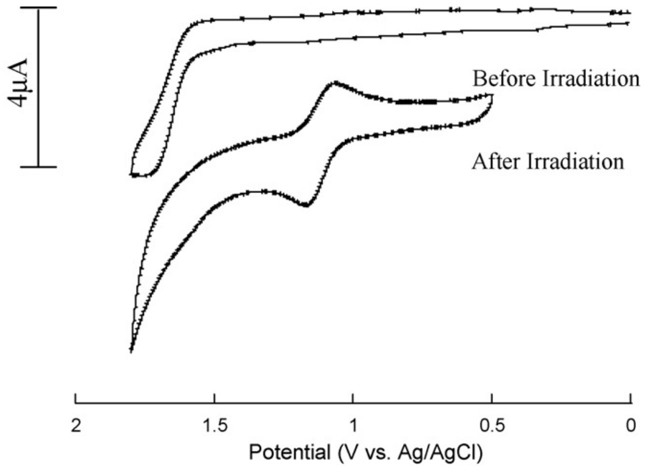

Fig. 3. Cyclic voltammogram of $[Ru(bpy)_2(PhNSO)]^{2+}$ before and after irradiation in 0.1 M $TBAPF_6$ in CH_3CN solution. Scan rate is 50 mV/s. The working electrode was a glassy-carbon electrode (BAS) with a surface of 2.0 mm^2. The counter and reference electrodes were a Pt wire and Ag/AgCl, respectively.

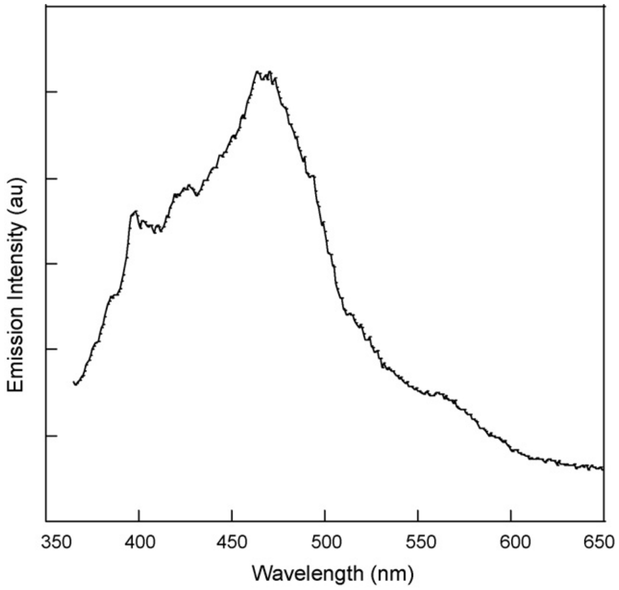

Fig. 4. Emission spectrum of PhNS at room temperature in methanol. Excitation is 355 nm.

[Ru(bpy)$_2$(PhNS)]$^{2+}$ nor S-[Ru(bpy)$_2$(PhNSO)]$^{2+}$ show emission at room temperature, both are emissive at 77 K in methanol:ethanol glass (4:1, v/v). The emission spectra are shown in Figs. 5 and 6, respectively. The thioether complex [Ru(bpy)$_2$(PhNS)]$^{2+}$ exhibits an emission spectrum with a maximum at 575 nm and $\Phi_{EM} = 0.221$ with a lifetime of $\tau = 4.3$ μs. The low-temperature emission spectrum of S-[Ru(bpy)$_2$(PhNSO)]$^{2+}$ displays an intense emission with a maximum of 520 nm ($\Phi_{EM} = 0.106$) exhibiting a vibrational progression of ∼1370 cm^{-1}, which is in accord with that reported for the archetypical complex [Ru(bpy)$_3$]$^{2+}$ [18]. The lifetime of this emissive state is 5.6 μs, consistent with a ligand-to-metal charge transfer (LMCT) emissive transition [18]. Also observed in the S-[Ru(bpy)$_2$(PhNSO)]$^{2+}$ emission spectrum is a weak, low-energy emission near 660 nm. It is unclear as to whether this weak emission is further vibrational structure of the S-bonded emission spectrum, or due to an impurity. Photoconversion experiments to form the O-bonded isomer followed by low-temperature emission studies do not indicate the weak emission near 660 nm is due to this isomer. Indeed, no emission for the O-bonded complex was observed. This is in contrast to the emissive behavior observed for O-bonded [Ru(tpy)(bpy)(dmso)]$^{2+}$, which features room temperature emission at 720 nm [13].

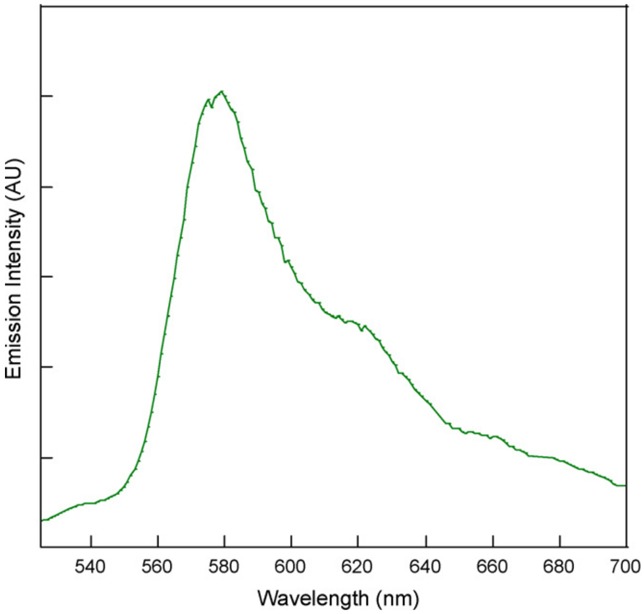

Fig. 5. Emission spectrum of [Ru(bpy)$_2$(PhNS)]$^{2+}$ at 77 K in methanol:ethanol glass. Excitation is 430 nm, $\Phi = 0.221$.

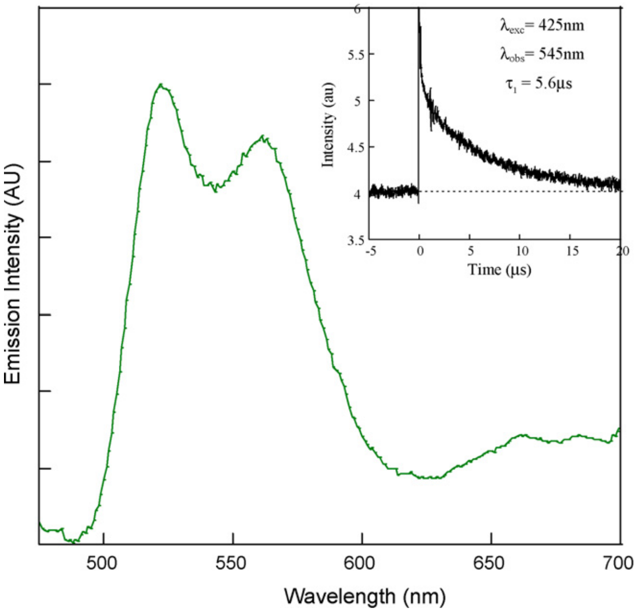

Fig. 6. Emission spectrum of S-[Ru(bpy)$_2$(PhNSO)]$^{2+}$ at 77 K in methanol:ethanol glass. Excitation is 380 nm, $\Phi = 0.106$.

The data are summarized in Fig. 7. Excitation of the ^{1}Ru$_S$ ground state initially populates the S-^{1}MLCT excited state, denoted as a solid line, ^{1}Ru$_S$*. Upon initial excitation, ^{1}MLCT → ^{3}MLCT relaxation is rapid, occurring on the order of a few hundred femtoseconds, as has been shown with similar ruthenium complexes [15,29–31]. Upon populating the ^{3}MLCT excited state, ^{3}Ru$^{II}{}_S$*, S-

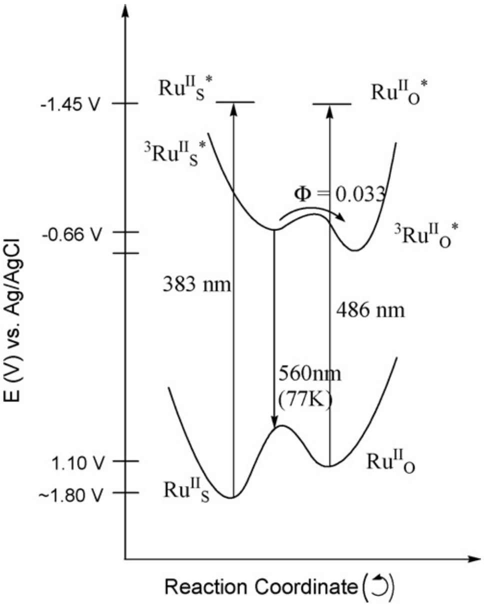

Fig. 7. Energy level diagram for [Ru(bpy)$_2$(PhNSO)]$^{2+}$.

$[Ru(bpy)_2(PhNSO)]^{2+}$ undergoes excited state S → O isomerization of the chelating sulfoxide ligand at room temperature, forming the ^{3}MLCT excited state O-bonded complex, $^3Ru^{II}{}_O{}^*$. This complex then nonradiatively relaxes to the ^1Ru_O metastable state. This complex displays no thermal reversion to the initial ^1Ru_S ground state at room temperature, indicating the energy barrier for reversion in high. Upon cooling to 77 K, S → O isomerization is no longer observed, while an emissive pathway for relaxation to the S-bonded ground state is revealed. These data suggests that isomerization is an activated process occurring on the charge transfer surface. Indeed, it is expected that the excited state surface should mirror that of the ground state, which also displays a high barrier between the S- and O-bonded states. In this mechanistic proposal, we indicate that the Ligand Field states do not play a prominent role as suggested by the relatively large $\Phi_{S\rightarrow O}$.

4. Conclusions

This work demonstrates that S → O isomerization may be observed in a new ruthenium chelating sulfoxide complex. Charge transfer excitation of S-$[Ru(bpy)_2(PhNSO)]^{2+}$ both in the solid state and in solution results in dramatic changes in both the electronic spectrum and in the cyclic voltammogram. This work expands upon the growing number of ruthenium complexes that exhibit phototriggered linkage isomerization. Future work will include direct observation of the isomerization as well as the synthesis of other complexes employing chelating sulfoxides.

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