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Femtosecond Isomerization in a Photochromic Molecular Switch**

*Nicholas V. Mockus, Daniel Rabinovich, Jeffrey L. Petersen, and Jeffrey J. Rack**

The concept of molecular information storage has long served as inspiration for chemists.[1–3] Light is often conceived as the trigger to switch between two (or more) molecular ground states. Light energy performs work on the molecule, thus storing photonic energy as potential energy. Maximizing the work performed on a molecule represents a new strategy in the design of molecular-based information systems. The development of bistable molecules with efficient switching mechanisms is tantamount to success in this field. Photochromic compounds are excellent candidates in this regard. These molecular devices convert light energy to potential energy for excited-state bond rupture and bond construction. Phototriggered molecular motions in stilbenes, azobenzenes, dithienylethenes, overcrowded alkenes, and spiro compounds demonstrate the versatility of organic-based structures that feature this reactivity.[4] An important aspect of this approach is that the switching reactions between states must be rapid to maximize the work performed on the molecule.

Photochromic complexes based on ruthenium or osmium polypyridyl complexes have further appeal, as their electrochemical signatures provide an independent means of monitoring the color changes associated with these photoactive complexes. Our efforts in this field have focused on ruthenium and osmium sulfoxide complexes that feature intramolecular excited-state S→O and ground-state O→S isomerization reactions. The change in ligation shifts the redox potential $E^{\circ\prime}$ ($M^{3+/2+}$) between 0.3 V and 0.8 V for these two states, depending upon the compound.[5,6] The time constant for excited-state isomerization has been measured to be as rapid as 475 ps, with isomerization quantum yields as great as 0.80.[7,8] Recently, we incorporated the sulfoxide moiety within a chelate, while retaining the photochromic action associated with the sulfoxide.[9,10] We reasoned that limiting the degrees of freedom of the bound sulfoxide would provide an excited-state O→S isomerization pathway, thus maximizing work and limiting heat loss after excitation. Herein, we report a photochromic ruthenium disulfoxide complex that exhibits excited-state S→O and excited-state O→S isomerization on a femtosecond timescale by two different colors of light.

The photochromic disulfoxide complex $[Ru(bpy)_2(OSSO)]^{2+}$ (bpy = 2,2′-bipyridine, OSSO = dimethylbis(methylsulfinylmethyl)silane) is prepared through oxidation of the dithioether parent with a peroxide oxidant, chloroperoxybenzoic acid (*m*-CPBA). The molecular structures of both ruthenium complexes were confirmed by single crystal X-ray diffractometry, and that of the disulfoxide complex is shown in Figure 1. The chelating disulfoxide ligand orients the two sulfoxide functional groups in a *cis* S-bonded arrangement on the ruthenium atom. The ground-state complex ([S,S]) features a low-energy absorption maximum in the electronic spectrum at 350 nm ($\varepsilon = 4560\,cm^{-1}M^{-1}$), as shown in Figure 2 (black trace). Expectedly, the electronic spectrum is similar to that observed for the related bis(dimethylsulfoxide) (dmso) complexes *cis*-$[Ru(bpy)_2(dmso)_2]^{2+}$ and *cis*-$[Os(bpy)_2(dmso)_2]^{2+}$.[11–13] Similar to $[Ru(bpy)_3]^{2+}$, the prototypical molecule in this class, the lowest energy transition is assigned as a Ru dπ→bpy π* charge–transfer (CT) transition. Previous studies of $[Ru(bpy)_3]^{2+}$ have demonstrated femtosecond intersystem crossing following excitation to form a thermally

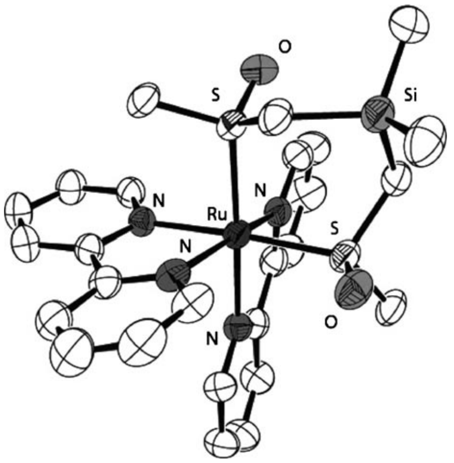

Figure 1. Thermal ellipsoid plot (30% probability) of $[Ru(bpy)_2(OSSO)]^{2+}$. Hydrogen atoms are omitted for clarity.

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[*] N. V. Mockus, Dr. J. J. Rack
Department of Chemistry and Biochemistry
Ohio University
Clippinger Laboratories, Athens, OH 45701 (USA)
Fax: (+1) 740-593-0148
E-mail: rack@helios.phy.ohiou.edu

Dr. D. Rabinovich
Department of Chemistry
University of North Carolina at Charlotte
Charlotte, NC 28223 (USA)

Dr. J. L. Petersen
C. Eugene Bennett Department of Chemistry
West Virginia University
Morgantown, WV, 26506-6045 (USA)

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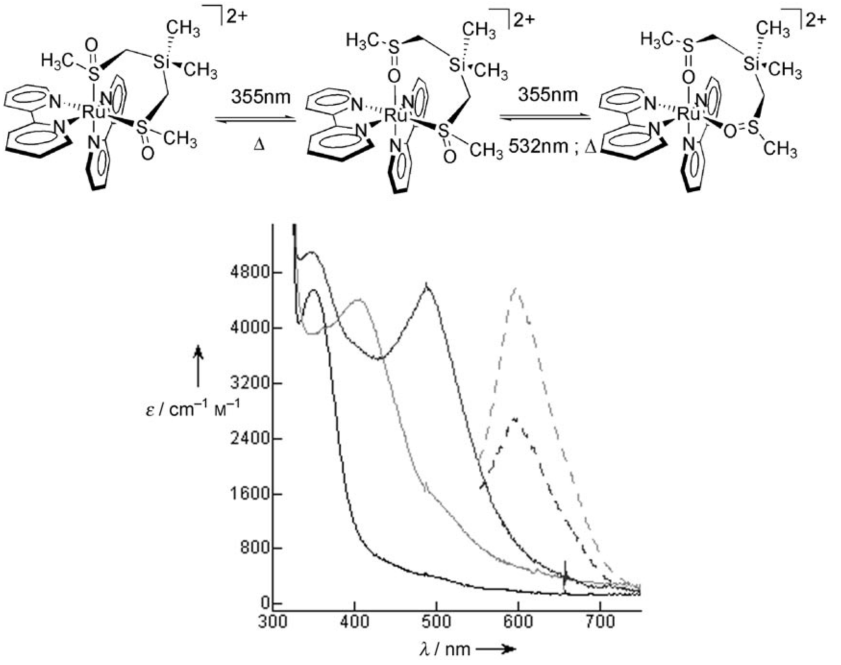

Figure 2. Top: Schematic depiction of structural rearrangement owing to isomerization. Bottom: Absorption (solid lines) and emission spectra (dashed lines) of [S,S] (black), [S,O] (light gray), and [O,O] (dark gray) complexes.

equilibrated metal-to-ligand charge-transfer (MLCT) state in approximately 300 fs.[14–17]

Irradiation of [S,S] by sunlight, fluorescent room lighting, or monochromatic laser light in alcoholic, halocarbon, or weakly basic solvents shows evidence of intramolecular S→O isomerization of both sulfoxide moieties. Changes in the color of the microcrystalline solid are also observed during irradiation, indicating that similar molecular changes occur in the solid state. These absorption changes for [S,S] in propylene carbonate solution are shown in Figure 2. During irradiation, the intensity of the absorption at 350 nm corresponding to [S,S] diminishes, while a single new peak at 400 nm appears. Continued irradiation results in loss of intensity at 400 nm with concomitant growth at 348 and 489 nm ($\varepsilon_{348}=5110$, $\varepsilon_{489}=4570\,\mathrm{cm^{-1}M^{-1}}$). The absorption maxima are associated with isomers of the bound, chelating sulfoxide ligands. The ground-state complex [S,S] yields the metastable S,O-bound complex [S,O], which then produces the metastable O,O-bound complex [O,O] through two successive photoisomerization reactions. Isomerization quantum yields ($\Phi_{S\to O}$) for each sulfoxide moiety are large, suggestive of rapid isomerization. In propylene carbonate, $\Phi_{SS\to SO}=0.55(\pm0.06)$ and $\Phi_{SO\to OO}=0.035(\pm0.005)$ with 327-nm excitation. Importantly, these absorption changes are reversible at room temperature in the absence of light. The [O,O] complex spontaneously yields the [S,O] complex, which then produces the [S,S] complex. A specific rate constant of $2.5(\pm0.2)\times10^{-4}\,\mathrm{s^{-1}}$ was determined for the [O,O]→[S,O] transformation. Reversion to [S,S] from [S,O] is much slower, and the latter complex appears over a period of 3–4 days. These data demonstrate excited-state S→O and ground-state O→S reactions for the three isomers of $[\mathrm{Ru(bpy)_2(OSSO)}]^{2+}$.

The long lifetimes of metastable [S,O] and [O,O] enable facile investigation of these individual complexes. Steady-state and time-resolved emission spectra of the [S,O] and [O,O] complexes reveal a rich photochemistry. In addition to isomerization to form [O,O], excitation of [S,O] at 355 or 400 nm, but not 532 nm, produces an emission spectrum with a maximum at 600 nm and a lifetime of 2 ns (Figure 2, light gray dashed line). The emission quantum yield (Φ_{EM}) is 0.009. This relatively small emission quantum yield is not unexpected given the large isomerization quantum yield. The emission is attributed to the [S,O] triplet excited state (${}^3\mathrm{Ru}_{SO}{}^*$), based on the Stokes shift and on similar observations for S,O-bound $[\mathrm{Os(bpy)_2(dmso)_2}]^{2+}$. Remarkably, excitation of [O,O] at 500 or 532 nm (or 400 nm) shows a less intense emission at 600 nm (Figure 2, dark gray dashed line), thus indicating formation of the [S,O] emitting state through excited-state O→S isomerization. Naturally, the [S,O] emission quantum yield obtained from excitation of ground-state [O,O] is reduced relative to that obtained from excitation of ground-state [S,O]. The emission quantum yield is 1.7×10^{-4}. No other emission feature is observed at longer wavelengths. Excitation of either [S,O] or [O,O] individually produces the same emissive species at 600 nm. These data illustrate [S,O]→[O,O] isomerization with 355-nm light and [O,O]→[S,O] isomerization with 532-nm light.

The picosecond transient absorption spectra of [S,O] are shown in Figure 3. While complicated, the gross features demonstrate that formation of ground-state [O,O], produced

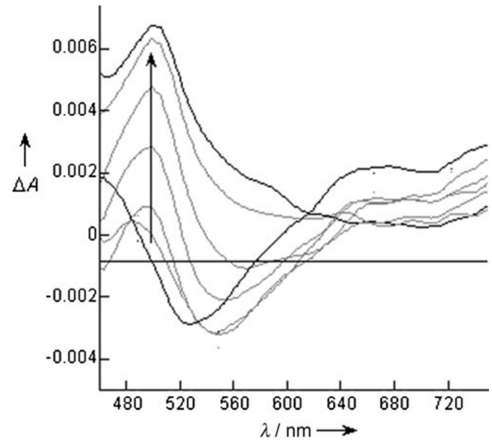

Figure 3. Transient absorption spectra (400-nm excitation) of [S,O]. Time traces are at 1.59, 7.50, 15.00, 32.53, 149.78, 549.66, and 1089.66 ps. The arrow denotes evolution of traces over time.

from 400-nm excitation of ground-state [S,O], is complete within approximately 1100 ps. Indeed, the spectral trace at approximately 1100 ps matches well with the steady-state absorption maximum at approximately 490 nm exhibited by ground-state [O,O] (Figure 2, solid dark gray line). Isomerization of [S,O] to form excited-state [O,O] and its decay must be rapid. The 490-nm absorption maximum indicative of ground-state [O,O] is first discernable in the 15-picosecond transient absorption spectrum. Not only does this finding suggest an excited-state [O,O] decay lifetime of hundreds of picoseconds, but it requires that isomerization must have been completed prior to this time. The traces at earlier times indicate the presence of at least two species in solution, namely excited-state [S,O] and excited-state [O,O]. The bleach feature with shifting maximum and intensity between approximately 525 and 565 nm does not correspond to an absorption feature of either [S,O] or [O,O] ground states and, as such, must represent a short-lived emissive state. This excited state is termed $^3\mathrm{Ru_{SO}}^{*\prime}$.

Picosecond transient absorption spectra of [O,O] produced from 400-nm excitation are shown in Figure 4. The traces at different time delays clearly show two bleach or negative peaks that decay at two distinct rates. The bleach feature at 490 nm matches well with the absorption maximum of ground-state [O,O] and is attributed to its recovery from the excited state. This process was also evident in Figure 3, occurring between 15 and 1100 ps. Furthermore, the same 525-nm emission feature from $^3\mathrm{Ru_{SO}}^{*\prime}$ is present in these time traces. Note that both excited-state [O,O] and emissive $^3\mathrm{Ru_{SO}}^{*\prime}$ are observed in the 1.5-ps spectrum. This finding indicates that isomerization has occurred prior to this time, within the approximately 750-fs instrument response time. In accord with the steady-state spectra, excitation of either [S,O] or [O,O] individually forms both excited states on an ultrafast timescale, thus indicating femtosecond excited-state S→O or O→S isomerization.

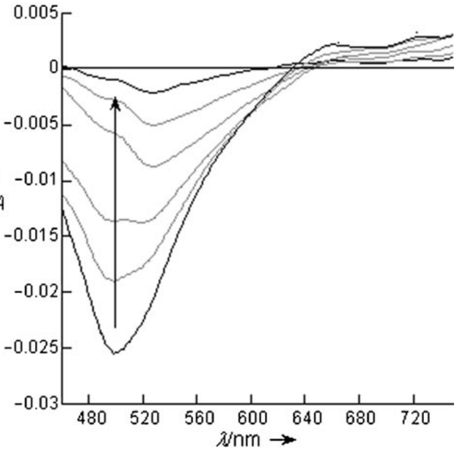

Figure 4. Transient absorption spectra (400-nm excitation) of [O,O] showing two distinct features, one at 490 nm, corresponding to ground-state recovery of [O,O], and one at approximately 520 nm, corresponding to excited-state emission of [S,O]. Note that both states are evident in the earliest time trace (1.49 ps). Time traces are at 1.49, 4.96, 10.26, 100.37, 402.34, and 1202.34 ps. The arrow denotes evolution of traces over time.

The data are summarized in Figure 5. Excitation of either [S,O] by 355-nm excitation or [O,O] by 532-nm excitation produces their respective initial singlet excited states, $^1\mathrm{Ru_{SO}}^*$ and $^1\mathrm{Ru_{OO}}^*$. Intersystem crossing and isomerization occurs on a femtosecond timescale to yield the high-energy emissive state $^3\mathrm{Ru_{SO}}^{*\prime}$ at 525 nm as well as the thermally relaxed ^{3}MLCT states $^3\mathrm{Ru_{SO}}^*$ or $^3\mathrm{Ru_{OO}}^*$. Both $^3\mathrm{Ru_{SO}}^*$ and $^3\mathrm{Ru_{OO}}^*$ spontaneously give their respective ground states (in 2 ns and approximately 100 ps, respectively) by standard mechanisms. Decay of $^3\mathrm{Ru_{SO}}^{*\prime}$ yields $^3\mathrm{Ru_{SO}}^*$ and $\mathrm{Ru_{SO}}$ in approximately 400 ps. Thus, the [O,O] ground state is produced 1 ns after 400-nm excitation of the [S,O] ground state, while the [S,O] state is produced 2 ns after 532-nm excitation of the [O,O] state. Further studies will discriminate the relative rates of isomerization and spin crossover on the excited-state surfaces.

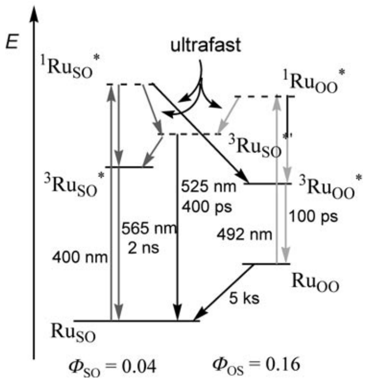

Figure 5. State diagram and reactivity for [S,O] and [O,O] isomers.

Femtosecond isomerization is important in the design of efficient molecular switches. The photochemistry and photophysics of rhodopsin serve as an example.[18–21] The work performed in light-driven molecular machines, such as rhodopsin, is signal transduction. Light energy is transduced to electrochemical potential through isomerization. Rapid reactions maximize the amount of work to be performed. Excited-state *cis–trans* photoisomerization ($\Phi_{c\rightarrow t} = 0.67$) of the retinal chromophore occurs in approximately 200 fs, which promotes cleavage of the Schiff-base chromophore and actuation of a transmembrane proton pump on a longer timescale. The isomerization stores about 60 % of the incident light energy needed for the longer reactions. If the isomerization were slow, then much of the kinetic and potential energy gained from light absorption would be lost as heat. The efficiency of synthetic light-driven molecular machines is dependent upon their ability to react on a femtosecond timescale to light excitation in order to maximize signal transduction and energy conversion.

In addition to femtosecond isomerization for maximum signal transduction, this ruthenium sulfoxide complex has advantages over rhodopsin or other small-molecule organic mimics. The ruthenium salt is readily produced and can be optimized by synthetic modulation. A number of strategies exist to attach ruthenium complexes to light-addressable electrodes. As the Grätzel cell demonstrates, the two states can be monitored electrochemically by means of the $Ru^{3+/2+}$ reduction potential.[22,23] This stands in stark contrast to many organic systems that rely on a fluorescent signal to report on the molecular state.[24,25] Thus, we can envision an electrode patterned with ruthenium sulfoxide complexes capable of storing information delivered by light of different colors. We believe this molecule and others like it hold great promise in realizing molecular information storage devices.

Experimental Section

$[Ru(bpy)_2(OSSO)](PF_6)_2$: Red $[Ru(bpy)_2(SS)](PF_6)_2$ (51.0 mg, 0.0577 mmol, SS = dimethylbis(methylthiomethyl)silane) and 3-chloroperbenzoic acid (*m*-CPBA, 80.6 mg, 0.467 mmol) were dissolved in acetonitrile (25 mL). The reaction was stirred at room temperature in the dark for 3 h. The progress of the reaction was monitored by observing the blue shift of the ^{3}MLCT transition in the UV/Vis spectrum. The solution volume was reduced to less than 5 mL, and the product was precipitated by the addition of diethyl ether. The yellow-orange product was isolated by vacuum filtration. Excess *m*-CPBA and the reduced product, 3-chlorobenzoic acid, were removed by washing the solid ruthenium product with diethyl ether (3 × 15 mL); the complex was air-dried. Yield: 46.4 mg (90 %). UV/Vis (MeOH) $\lambda_{max} = 347$ nm (S,S-bonded, 6020 $cm^{-1}M^{-1}$). $E^{\circ\prime}$ $Ru^{3+/2+}$ vs. Ag/AgCl = 2.1 V (S,S-bonded), 1.4 V (S,O-bonded), 0.75 V (O,O-bonded). ^{1}H NMR ($(CD_3)_2CO$, 300 MHz): $\delta = 10.26$ (d, bpy, 2 H), 8.95 (d, bpy, 2 H), 8.84 (d, bpy, 2 H), 8.56 (t, bpy, 2 H), 8.33 (t, bpy, 2 H), 8.15 (t, bpy, 2 H), 7.66 (t, bpy, 2 H), 7.61 (t, bpy, 2 H), 3.75 (d, CH_2, 2 H), 3.04 (d, CH_2, 2 H), 2.40 (s, SCH_3, 6 H), 0.59 ppm (s, $SiCH_3$, 6 H). Elemental analysis calcd (%) for $C_{26}H_{32}F_{12}N_4O_2P_2RuS_2Si$: C 34.10, H 3.52, N 6.12, S 7.00; found: C 34.58, H 3.60, N 6.40, S 6.64.

Crystals suitable for structural determination were obtained by slow vapor diffusion of diethyl ether into acetonitrile solution. Single crystals were washed with the perfluoropolyether PFO-XR75 (Lancaster) and sealed under nitrogen in a glass capillary. Samples were optically aligned on the four-circle of a Siemens P4 diffractometer equipped with a graphite monochromatic crystal, a $Mo_{K\alpha}$ radiation source ($\lambda = 0.71073$ Å), and a SMART CCD detector. The structure was drawn using ORTEP.

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