

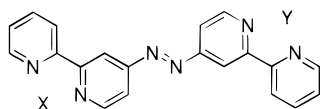
Redox-Responsive Molecular Switch for Intramolecular Energy Transfer

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Molecular electronic/photonic devices refer to systems in which spatially directed electron or energy-transfer processes take place at the (supra)molecular level.^{1–4} Required in such systems are molecular components that work as switches for electron^{5–7} or energy transfer.⁸ We recently synthesized mono-



	X	Y
1	Ru(bpy) ₂	-
2	Ru(bpy) ₂	Ru(bpy) ₂
3	Ru(bpy) ₂	Os(bpy) ₂
4	Os(bpy) ₂	Os(bpy) ₂

4,4'-azo-(2,2'-bipyridine) (L) as redox-responsive switches for electron localization in the excited state.⁹ These complexes are almost nonemissive when L is neutral, since the electron is trapped by L in the metal-to-ligand charge-transfer (MLCT) excited state. Selective reduction of L by electrode renders the complexes highly emissive, since the access of the excited electron to L is prevented, and consequently, it is localized in the terminal bipyridines (bpy). The emissive state can be utilized for subsequent photophysical processes such as electron/energy transfer.^{10–12}

For heterodinuclear Ru and Os polypyridyl complexes, it is well established that intramolecular energy transfer occurs from the MLCT state of the Ru center to the Os center.^{10,13–15} To

Table 1. Redox Properties (V vs Fc/Fc⁺)^a

	bpy ^{0/-1}	L ^{-1/-2}	L ^{0/-1}	Ru ^{III/II}	Os ^{III/II}
2	-1.84	-1.12	-0.69	0.79	
3	-1.65	-0.97	-0.57	1.11	0.68
4	-1.79	-1.11	-0.72		0.52

^a The cyclic voltammetry was conducted with glassy C, Pt, and Ag/Ag⁺ as working, counter, and reference electrodes, respectively, under a N₂ atmosphere. Millimolar amount of samples were used in CH₃CN containing 0.1 M tetrabutylammonium perchlorate. All redox waves are reversible.

take a step further and develop a switch for energy transfer, we prepared a heterodinuclear Ru and Os complex connected by L (**3**) to see if the redox reaction switches on/off the intramolecular energy-transfer process, which was indeed the case as described in the following.

The heteronuclear complex, **3**, was synthesized via [Os(bpy)₂L]Cl₂ which was prepared from [Os(bpy)₂]Cl₂¹⁶ and L.¹⁷ Metal complexes were formed in refluxing 2-methoxyethanol and purified as PF₆⁻ salts by column chromatography (Al₂O₃, CH₃CN/EtOH) and reprecipitation (CH₃CN/Et₂O).¹⁸

Table 1 summarizes the electrochemical properties for the dinuclear complexes. The redox potentials for the two consecutive one-electron reduction of L are at ca. -0.6 to -1.1 V. These potentials are more positive than those required for the reduction of bpy which are at ca. -1.7 to -1.8 V, making it possible to selectively reduce L without affecting bpy.

Red-shifted absorption bands are exhibited at 550 nm for **2**, whereas they are at ca. 590 and 800 nm for **3** and **4**, in addition to the typical spin-allowed MLCT band at 450 nm and related spin-forbidden transitions for Os complexes.^{11,12} The spectrum for **3** is nearly superimposed with the averaged spectrum for **2** and **4**. The red-shifted absorption bands are assigned to the MLCT transitions to L.⁹ The LUMO of L is lower in energy than that of bpy, which is reflected in the more positive redox potentials for L (Table 1). The assignment is further supported by spectroelectrochemical measurements.¹⁹ When L is subjected to exhaustive reduction, the longer wavelength absorption bands disappear with isosbestic points and the spectra become more similar to those of typical polypyridyl complexes (Figure 1 for **3**). This means that the charge injection into L is suppressed for the reduced species.²⁰

The emission intensity of these complexes is largely diminished from those of usual tris(bipyridine) complexes. For example, the emission intensity of **2** is only 1.7% that of [Ru(bpy)₃]²⁺. This is because the MLCT excited state is trapped

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(17) Preparation of **3** via **1** was of less yield.

(18) Selected data for [Os(bpy)₂L](PF₆)₂: 61%; mp 198–199 °C; ¹H NMR ((CD₃)₂CO) δ 7.45–7.7 (6H), 7.84 (dd, 1H, J 6.0, 2.1 Hz), 7.95–8.2 (13H), 8.36 (d, 1H, J 6.4 Hz), 8.64 (d, 1H, J 8.1 Hz), 8.8–8.9 (4H), 8.94 (d, 1H, J 1.3 Hz), 9.02 (d, 1H, J 5.1 Hz), 9.15 (d, 1H, J 7.7 Hz), 9.35 (d, 1H, J 1.7 Hz); IR (KBr, cm⁻¹) 558, 764, 839, 1026, 1240, 1262, 1449, 1464, 1584; SIMS 1131 [M⁺]. Anal. Calcd for C₄₀H₃₀N₁₀Os·2(PF₆)·3(H₂O): C, 40.54; H, 3.06; N, 11.82. Found: C, 40.93; H, 2.59; N, 11.50%. Selected data for **3**: 28%; mp > 300 °C; ¹H NMR (CD₃CN) δ 7.3–7.5 (10H), 7.6–7.85 (12H), 7.9–8.15 (12H), 8.5–8.55 (8H), 8.66 (dd, 2H, J 6.4, 3.1 Hz), 8.93 (dd, 2H, J 7.0, 2.1 Hz); IR (KBr, cm⁻¹) 558, 764, 850, 1019, 1242, 1266, 1426, 1447, 1464, 1605, 1698, 3450; SIMS 1689 [M - PF₆]. Anal. Calcd for C₆₀H₄₆N₁₄OsRu·4(PF₆): C, 39.29; H, 2.53; N, 10.69. Found: C, 38.99; H, 2.56; N, 10.83%. Selected data for **4**: 41%; mp > 300 °C; ¹H NMR (CD₃CN) δ 7.3–7.4 (10H), 7.6–7.7 (12H), 7.85–8.0 (12H), 8.5–8.55 (8H), 8.66 (d, 2H, J 7.9 Hz), 8.91 (d, 2H, J 2.2 Hz); IR (KBr, cm⁻¹) 558, 762, 839, 1010, 1240, 1262, 1424, 1447, 1464, 1607; SIMS 1633 [M - 2(PF₆)]. Anal. Calcd for C₆₀H₄₆N₁₄Os₂·4(PF₆): C, 37.47; H, 2.41; N, 10.20. Found: C, 37.29; H, 2.53; N, 9.74%.

(19) Controlled-potential reduction was conducted in a 1 × 1 cm² glass cell until no more spectroscopic change was observed. All studies were made in Ar or N₂-saturated CH₃CN.

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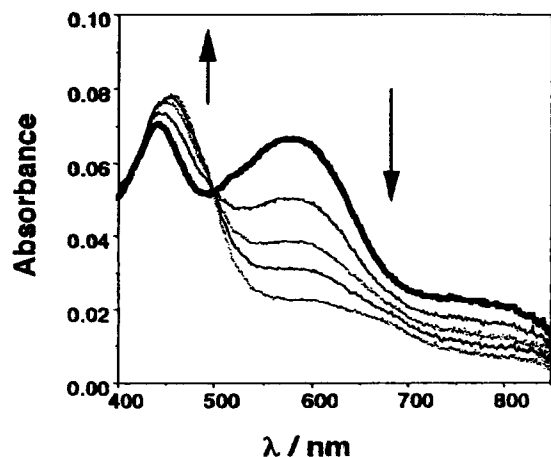


Figure 1. Changes in the visible absorption spectrum for **3** ($3 \mu\text{M}$) in CH_3CN containing 0.1 M tetrabutylammonium perchlorate under a constant potential at -1.1 V in the reduction process indicated by the arrows. The bold curve indicates the spectrum of the initial nonreduced species.

in the low-energy L-localized MLCT state and deactivated nonradiatively.⁹ The residual emission of these complexes could be due to the presence of a small amount of an emissive impurity, since their lifetimes are quite long: $0.5 \mu\text{s}$ for **2** and $0.4 \mu\text{s}$ for **3** at around 650 nm .²¹ No short-lived emission related to the quenching pathway by L is observed for either complex, which suggests that the quenching is very efficient and rapid.

Reduction of L causes an increase in the emission intensities for **2** (rate constant $1.1 \times 10^6 \text{ s}^{-1}$) and **4** ($5.2 \times 10^7 \text{ s}^{-1}$) (Figure 2, top and middle),¹⁹ since the LUMO of L is not available for the excited electron which, then, is localized in the terminal bps. Upon reduction of L in the heteronuclear **3**, the emission from the Os center increases by an amount nearly parallel to that for **4** (93%),¹⁹ despite that the amount of Os center in **3** is one-half that in **4**, while the emission from the Ru center is intensified only a little (Figure 2, bottom). Comparing the emission of the reduced species of **3** with that of the reduced **2**, it is apparent that the emission from the Ru center is largely quenched (94%) by the presence of the Os center. Excitation spectrum²² for the reduced **4** detected at 760 nm shows two peaks at 660 and 505 nm with relative intensities of 1:0.18. On the other hand, the spectrum for the reduced **3** shows one peak at 660 nm and the other blue-shifted and more pronounced peak at 480 nm with relative intensities of 1:0.29. Finally, upon reduction of **3**, a new short-lived emission from the Ru center ($t = 1.6 \text{ ns}$; $6.3 \times 10^8 \text{ s}^{-1}$) appears and a comparable rise time is observed for the Os emission. These observations indicate that the intramolecular energy transfer from the Ru center to the Os center takes place in the reduced species of **3**. Applying more positive potentials to reoxidize the reduced **3** reverses the course of the reaction, which is shown by the absorption and emission spectra. Thus, the redox process is reversible.

(20) The same spectroscopic behavior was observed when the electrolysis was conducted at potentials more negative than the first and second wave (e.g., -0.7 and -1.1 V for **3**). Thus, one-electron reduction is enough to switch the excited-state pathways as described in the text. For the bulk electrolysis, the singly reduced species may be generated first by equilibration even when the more negative potential than the second reduction potential is applied. Properties of reduced species of related azopyridines were reported: Sadler, J. L.; Bard, A. J. *J. Am. Chem. Soc.* **1968**, *90*, 1979–1989. Bellamy, A. J.; MacKirdy, I. S.; Niven, C. E. *J. Chem. Soc., Perkin Trans. 2* **1983**, 183–185.

(21) Time-resolved luminescence studies were carried out with N_2 laser (337 nm) as the excitation source and a photomultiplier tube ($>100 \text{ ns}$) or a streak camera ($<100 \text{ ns}$) as the detector.

(22) See the Supporting Information.

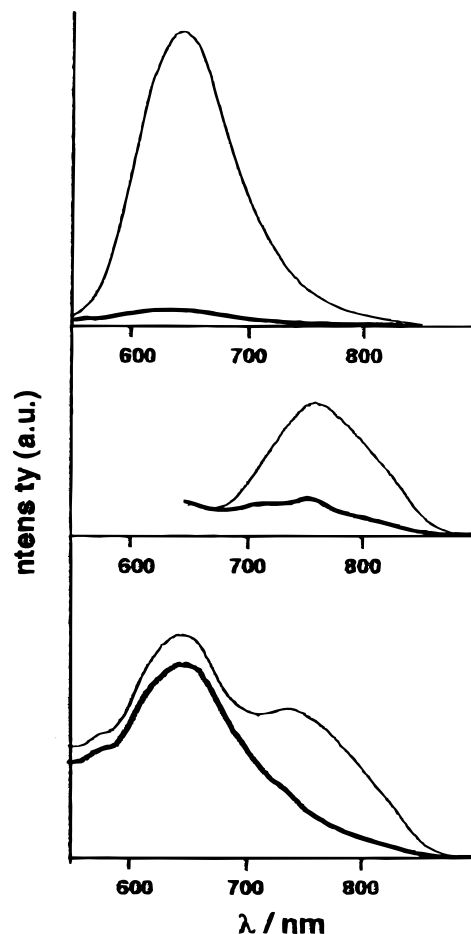


Figure 2. Luminescence spectra before (bold line) and after (thinner line) the reduction of L. Conditions are the same as in Figure 1. Excitations are at the isosbestic wavelengths at 480 , 505 , and 490 nm for **2** (top), **4** (middle), and **3** (bottom), respectively. The spectra for **2** are reduced to $1/20$ in scale with respect to the other spectra.

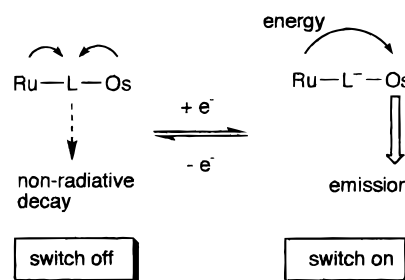


Figure 3. Schematic diagram of photophysical processes in response to the redox input for **3**.

Figure 3 illustrates what takes place in response to the redox input for **3**. When L is neutral, the excited electron is trapped by L. No energy transfer occurs, and so the switch is in the state of “off”. By the reduction of L, the trap is “clogged” by the electron and the energy at the Ru center can pass over to the Os center, which is detected by the emission therefrom. Thus, the reduced species is at the state of switch “on”. Such a switching component may find use in future (supra)molecular electronic/photonic devices.

Supporting Information Available: The excitation spectra for **3** and **4** (1 page). See any current masthead page for ordering and Internet access instructions.