Ruthenium Complexes Containing an Azobipyridine Ligand as Redox-Responsive Molecular Switches

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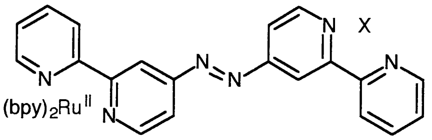
Mononuclear and dinuclear ruthenium complexes containing an azobipyridine ligand serve as reversible redox-responsive molecular switches modulating electron localization in the excited-state that can be read out through the emission intensity.

Molecular switches are important components of tantalizing future molecular electronic/photonic devices.[1] Switching is effected by functional units reversibly responsive to external input such as photons,[2,3] electrons,[4,5] and pH.[6] The azo group is one of the most versatile functional units, which may be photochromic,[7] pH-responsive,[8] and redox-active, depending on the substituents. The azo linkage is also used as molecular wire that mediates electronic communications between photo/redox-active groups.[9] Here we wish to report on mononuclear (**1**) and dinuclear (**2**) ruthenium complexes containing a new bridging ligand, 4-azo-(2,2'-bipyridine) (**3**), which have been revealed to be reversibly responsive to redox input,[10] switching electron localization in the excited-state that can be read out through the emission.



X = none **1**
$Ru^{II}(bpy)_2$ **2**

4-Nitro-2,2'-bipyridyl 1-oxide[11] was reductively coupled by $NaBH_4$ with Pd-C from 0 °C to 80 °C in methanol. After column separation ($CHCl_3$/EtAc), it was crystallized from EtOH to afford **3** (37%, mp 235 °C). The ligand **3** was complexed with *cis*-$Ru(bpy)_2Cl_2$[12] (bpy = 2,2'-bipyridine) in refluxing methoxyethanol/CH_2Cl_2. A large excess of **3** and the metal were used to prepare **1** and **2**, respectively. After column separation through alumina (CH_3CN/EtOH), the complexes were crystallized from EtOH as PF_6^- salts (**1**: 66 %, mp 198-199 °C; **2**: 63 %, mp >375 °C).[13]

Table 1 summarizes the electrochemical properties. The ligand **3** is reduced at -0.75 V for **1** and -0.59 and -1.02 for **2**. The reduction of bpy starts at more negative potential than -1.6 V. Hence it is possible to selectively reduce **3** without affecting bpys. Another point to note is that only one two-electron oxidation couple corresponding to $Ru^{III/II}$ appears at 0.89 V (the peak separation is 70 mV) for **2** without splitting, which indicates that the two metal centers behave independently to oxidation.

The electronic absorption spectra of **1** and **2** in CH_3CN have two absorption maxima in the visible region at 440 nm and 490 nm for **1** and 450 nm and 550 nm for **2** (Figure 1). The absorption at the shorter wavelengths can be assigned to the metal-to-ligand charge-transfer (MLCT) d → π*(bpy) transitions (path a in Figure 2),[14] while the longer wavelength absorptions to MLCT d → π*(**3**) transition (path b).[15] Oxidation of Ru^{II} to Ru^{III} results in the disappearance of both of the two absorption bands with isosbectic points, as a natural consequence of the depletion of the d-electron relevant to the MLCT transition. An interesting feature appears when the ligand **3** is reduced with the electrode potential in the range of -0.6 and -1 V. The shorter wavelength absorption is slightly perturbed, while the longer wavelength absorption disappears with isosbectic points as shown in Figure 1 for **2**. The mononuclear **1** exhibits a similar behavior. This electrochromism can be explained based on the scheme in Figure 2. The reduction will fill the π* orbital relevant to the MLCT transition to **3** to suppress the electron transfer through path b and only path a becomes available. Reduction of **2** at -1 V and at -0.6 V gives the same electrochromic behavior, which indicates one-electron reduction of **3** is enough to inhibit path b. The spectral change is fully reversible; the original spectrum is recovered by the reoxidation. Thus the redox input switches on/off of the CT path b in the Franck-Condon process for **1** and **2**.

Table 1. Redox properties (V vs. Ag/Ag^+)^a

	$bpy^{0/-1}$	$\mathbf{3}^{-1/-2}$	$\mathbf{3}^{0/-1}$	$Ru^{III/II}$
1	-1.69		-0.75	1.09
2	-1.74	-1.02	-0.59	0.89
3^b			-1.08	

^{a}The cyclic voltammetry was conducted with glassy C, Pt, and Ag/Ag^+ as working, counter and reference electrodes, respectively, under N_2 atmosphere. Millimolar amount of samples were used in CH_3CN containing 0.1 M tetrabutylammonium perchlorate. In our system, the ferrocenium/ferrocene couple was observed at +100 mV. ^{b}In CH_2Cl_2.

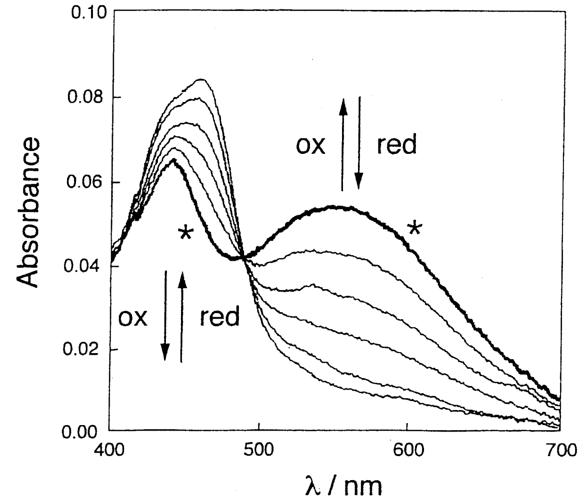


Figure 1. Changes in electronic absorption of **2** (3 μM) in CH_3CN containing 0.1 M tetrabutylammonium perchlorate under a constant potential at -0.6 V in the reduction process indicated by the arrow 'red.' The asterisked bold line indicates the spectrum of non-reduced species.

Another feature that is switched by the redox reaction is the emission properties. The emission of **1** and **2** is nearly completely quenched; its intensity (λ_{max} = 640 nm) is only 1.4% and 1.7%, respectively, of that of $Ru(bpy)_3^{2+}$ in CH_3CN. When the ligand **3** is neutral, the MLCT excited state will eventually be trapped in the low energy **3**-localized MLCT state during its lifetime (path c) and deactivated non-radiatively.[7] The reduction of **3** would raise the energy of the available $\pi^*(\mathbf{3})$ level and thus suppress this quenching process. It is indeed the case and the emission of **1** and **2** increases on reduction of **3** (Figure 3) as a result of the excited-state charge localization in bpys.[16] The degree of increase in the emission coincides with the degree of change in the absorption when the complexes are excited at the isosbectic wavelength (480 nm), which indicates that the reduction of **3** suppress path b in the absorption and path c during the excited state lifetime, simultaneously. More than 14- and 19-fold increase in the emission has been attained for **1** and **2**, respectively, which sets the lower limit of the emission intensity of the reduced species.[17] The emission behavior is also reversible.

Thus it has been demonstrated that **1** and **2** serve as redox-responsive molecular switches modulating electron localization in the excited-state, that can be read out through the emission intensity. The emitting state of the reduced species may be used in the subsequent electron or energy transfer processes by combining this switching component with appropriate redox active groups or molecular wires, leading to a redox controlled electron/energy transfer devices.

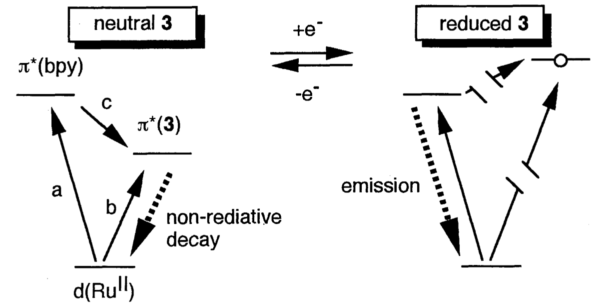


Figure 2. The functional mode of the molecular switches **1** and **2**.

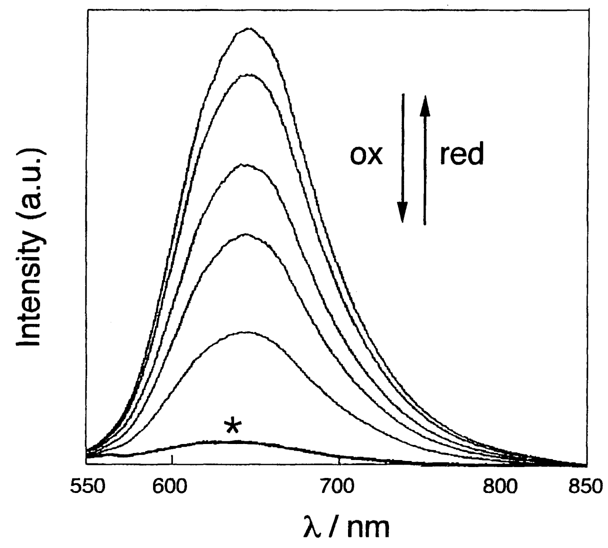


Figure 3. Changes in emission of **2**. The asterisked bold line indicates the spectrum of non-reduced species. Each iteration corresponds to that of Figure 1. The excitation wavelength is the isosbectic point at 480 nm.

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13 Selected data for **1**: ^1H NMR ($CDCl_3$, ppm) δ = 7.53 (m, 1H), 7.55-7.7 (5H), 7.93 (dd, 1H, J = 5 Hz, 2 Hz), 8.0-8.1 (5H), 8.13 (d, 1H, J = 5 Hz), 8.2-8.35 (6H), 8.39 (d, 1H, J = 6 Hz), 8.56 (d, 1H, J = 8 Hz), 8.77 (m, 1H), 8.85-8.95 (5H), 9.01 (d, 1H, J = 5 Hz), 9.14 (d, 1H, J = 8 Hz), 9.32 (d, 1H, J = 2 Hz); IR (KBr, cm^{-1}) 568, 731, 764, 839, 1271, 1391, 1447, 1464, 1560, 1584, 1605; SIMS m/z = 899 $[MH_2\text{-}PF_6]^+$; anal. calcd for $C_{40}H_{30}F_{12}N_{10}P_2Ru$: C, 46.12; H, 2.90; N, 13.45; found C, 46.73; H, 2.62, N, 13.23. For **2**: ^1H NMR (dmso, ppm) δ = 7.5-7.65 (10H), 7.7-7.8 (6H), 7.81 (d, 2H, J = 6 Hz), 7.86 (d, 2H, J = 6 Hz), 7.90 (d, 2H, J = 6 Hz), 8.09 (d, 2H, J = 6 Hz), 8.15-8.25 (10H), 8.75-8.85 (8H), 8.97 (d, 2H, J = 6 Hz), 9.20 (s, 2H); IR (KBr, cm^{-1}) 558, 731, 762, 839, 1240, 1447, 1466, 1605; SIMS 1456 $[M\text{-}2PF_6]^+$; Anal. Calcd for $C_{60}H_{48}F_{24}N_{14}OP_4Ru_2$ (monohydrate): C, 40.87; H, 2.74; N, 11.12%; Found C, 40.58; H, 2.66, N, 11.24%. For **3**: ^1H NMR ($CDCl_3$, ppm) δ = 7.38 (dd, 2H, J = 4.9, 6.8 Hz), 7.81 (dd, 2H, J = 1.7, 5.3 Hz), 7.88 (dt, 2H, J = 1.5, 7.9 Hz), 8.48 (d, 2H, J = 7.8 Hz), 8.76 (d, 2H, J = 4.6 Hz), 8.90 (d, 2H, J = 2.0 Hz), 8.92 (d, 2H, J = 5.1 Hz); IR (KBr, cm^{-1}) 652, 739, 790, 856, 1393, 1454, 1582, 2996, 3073; EI-MS calcd for $C_{20}H_{14}N_6$ 338.1280, found 338.1283; Anal. Calcd C, 71.00; H, 4.14; N, 24.85%; Found C, 71.30; H, 3.85; N, 24.77%.

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16 Although the emission and absorption spectra overlap around 600 nm, the self-absorption effect is less than 5% in emission intensity with absorption being as small as 0.05.

17 Completion of the reduction is difficult due to the limit in our electrolysis cell design.