Tetranuclear Ru Complex Linked via Redox-Active Azobis(bipyridine) Ligands as a Redox-Responsive Photoswitch

Joe Otsuki,* Dong-Mei Li, Katsuhiko Sato, Asako Nakagome, Toshio Takido, Isao Yoshikawa,† Tetsuo Akasaka,† and Koji Araki†

College of Science and Technology, Nihon University, 1-8-14 Kanda Surugadai, Chiyoda-ku, Tokyo 101-8308

†Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505

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A tetranuclear Ru complex linked by 4,4″-azobis(2,2′-bipyridine) (azobpy), $[Ru\{(azobpy)Ru(bpy)_2\}_3][PF_6]_8$ (bpy = 2,2′-bipyridine) has been prepared and fully characterized. Cyclic and differential pulse voltammetries show that two kinds of oxidation occur, the one at the less positive potential being assigned to the oxidation of the three peripheral Ru ions, while the other to that of the central Ru ion. On a cathodic scan, a pair of three-electron (one electron on each azobpy) reductions of azobpy ligands appear at less negative potentials than terminal bpy ligands. A low-energy metal-to-ligand charge transfer (MLCT) absorption band involving the π^*-orbitals of azobpy ligands is observed in addition to the usual MLCT band involving terminal bpy ligands. These results indicate the presence of a low-lying π^* level of azobpy. A selective reduction of azobpy ligands renders the non-luminescent complex into a moderately luminescent species. This light switch is reversible, implying the utility of this branched structure in energy delivering molecular systems.

We are developing molecular switches using dinuclear Ru and Os complexes involving 4,4″-azobis(2,2′-bipyridine) (azobpy)[1,2] or 4′,4″″-azobis(2,2′:6′,2″-terpyridine) (azotpy)[3] as a bridging ligand.[4] When the azo ligand is neutral in these complexes, the metal-to-ligand charge transfer (MLCT) excited state[5,6] is rapidly thermally deactivated, and no luminescence is observed. On the other hand, when the azo ligand is electrochemically reduced, the complexes behave more or less like the respective parent complexes, $[M(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) and $[M(tpy)_2]^{2+}$ (tpy = 2,2′:6′,2″-terpyridine), resulting in luminescence or energy transfer upon photo-excitation.

Thus, directional energy transfer can be controlled by using a metal-azobpy-metal or metal-azotpy-metal scaffold. Branching of the scaffold into a Y-shaped structure may be of interest as a way to provide a means to control the course of energy transfer. One may envisage, for example, to make the excited state of one of the peripheral complexes to be an input site and to usher this energy into one of the other two output sites, as shown in Fig. 1a. Alternatively, all three peripheral complexes may be used as an antenna to funnel energy into the central position, as shown in Fig. 1b. Although several antenna systems have been reported,[7] this system is unique in that it has a switching function, enabling energy transfer only when desired. Herein, as a first step toward these possible developments, we report on the synthesis and properties of a tetranuclear Ru complex bridged by azobpy, namely, $[Ru\{(azobpy)Ru(bpy)_2\}_3][PF_6]_8$ (Ru_4).[8]

Results and Discussion

There are two possible routes to prepare Ru_4. One is to first prepare $[Ru(azobpy)_3]^{2+}$, followed by coupling with three equivalents of a $[RuCl_2(bpy)_2]$ fragment. Our attempt to prepare $[Ru(azobpy)_3]^{2+}$ was unsuccessful, however, probably due to the formation of polymeric complexes. The other is a reaction of $RuCl_3$ and mononuclear $[(bpy)_2Ru(azobpy)]^{2+}$, which is a known complex (Scheme 1).[1,2] This method was found to give the desired Ru_4, although the yield (14%) was relatively low. The crude reaction mixture may contain partially reacted less-than-four metallic species, as judged from their larger R_f values in TLC, as well as some polymeric materials which could be produced by ligand exchange under the reaction conditions, although a precise analysis of these materials has not been attempted. The desired four-metallic complex was purified by silica-gel chromatography with a mixture of CH_3CN and aqueous KNO_3 as an eluent.

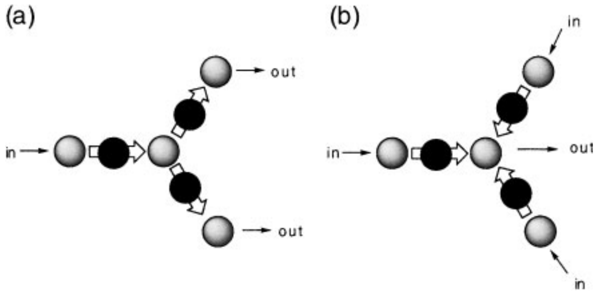
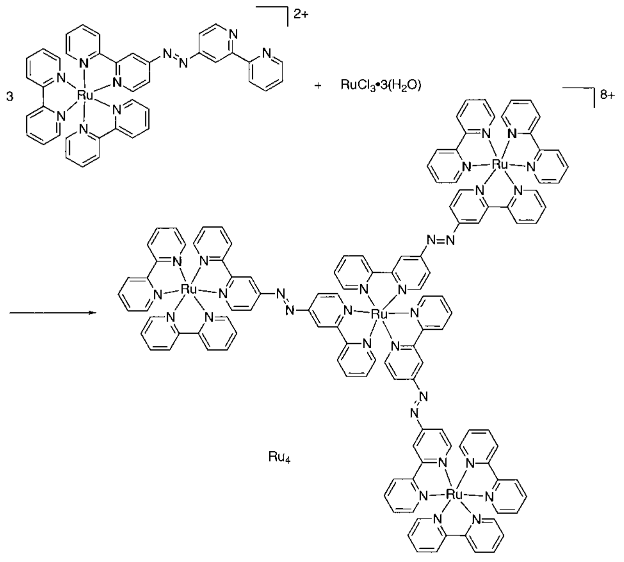


Fig. 1. The possible utility of tetranuclear metal complexes as a scaffold for directional energy transfer with switching function. Energy transfer may occur among metal centers (shaded circles), which is switched on and off depending on the redox state of the bridging ligands (black circles on arrows). Input energy may be directed along a desired course (a) or funneled into the center (b).



Scheme 1.

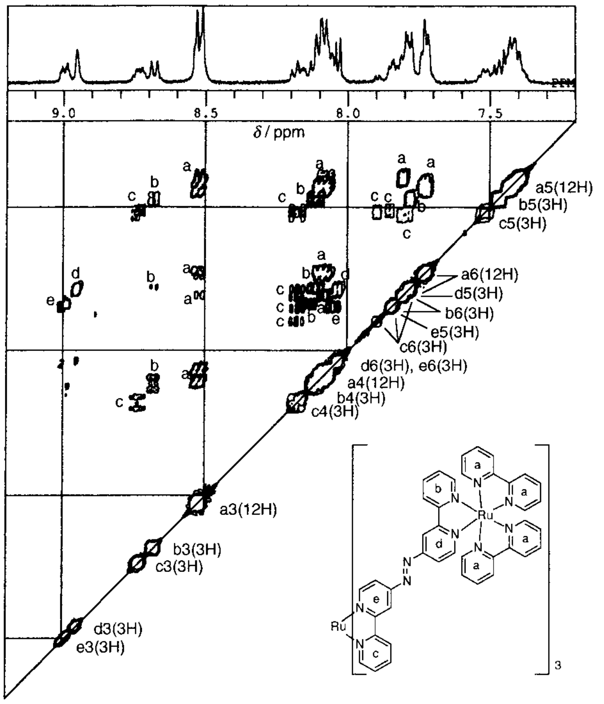


Fig. 2. ^{1}H–^{1}H NMR COSY spectrum of Ru_4 in CD_3CN and its assignment.

The formation of tetranuclear Ru_4 was evident from electrospray mass spectrometry. The spectrum shows two major broad peaks, reflecting the distribution of the isotopes of Ru, centered at 1613 and 1026, corresponding to the species $[M–2(PF_6)]^{2+}$ and $[M–3(PF_6)]^{3+}$, respectively, and a small peak centered at 734, corresponding to $[M–4(PF_6)]^{4+}$.

All ^{1}H-NMR resonances were assigned as summarized in Experimental with the help of knowledge concerning changes in the chemical shifts induced by Ru complex formation[9] and ^{1}H–^{1}H COSY spectroscopy, as shown in Fig. 2. As indicated in the figure, all of the diagonal and cross peaks have been identified. The relatively simple spectrum was pleasantly surprising, since the obtained complex must be a mixture of many stereo (*fac* and *mer*) and optical (Δ and Λ) isomers. Apparently, the chemical shifts are not very different among these isomers, except for the protons at the 6-position of the pyridine rings, whose chemical shifts are scattered in the range of 7.7–7.9 ppm. This is because these protons are most proximal to another ligand in the complex and thus their chemical shifts are most sensitive to the differences among isomers.

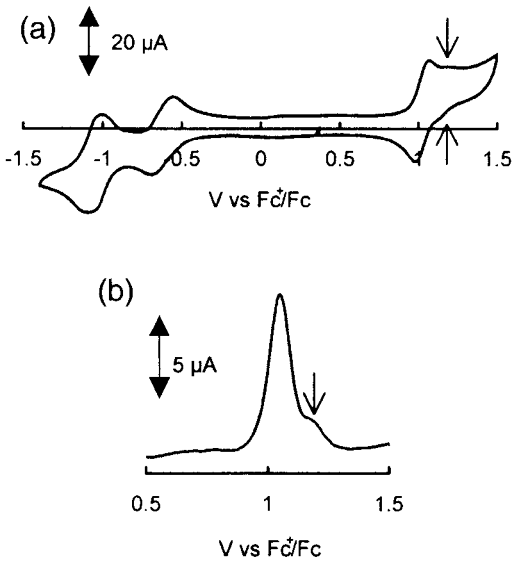


Fig. 3. Electrochemical measurements of Ru_4 in CH_3CN. (a) Cyclic voltammogram (100 mV s^{-1}). (b) Differential pulse voltammogram for the anodic region (50-mV pulse, 50-ms pulse width, 300-ms period, 25 mV s^{-1} scan rate). The redox couple indicated by the pair of arrows in (a) corresponds to the shoulder also pointed by the arrow in (b).

Table 1. Redox Potentials of Complexes vs Fc^+/Fc[a)]

Complexes	$bpy^{0/-1}$ [b)]	$azobpy^{-1/-2}$	$azobpy^{0/-1}$	$Ru^{3+/2+}$
$[Ru(bpy)_3]^{2+}$	−1.73			0.89
Ru_2	≈ −1.8	−1.14	−0.69	0.95
Ru_4	≈ −1.8	−1.18	−0.73	0.96 ≈ 1.1
Ru_4[c)]	−1.86	−1.21	−0.78	≈ 0.9[d)]

a) In CH_3CN unless otherwise noted. b) Only the least negative potentials are shown. c) In DMF. d) The second oxidation is obscured due to the potential window of DMF.

A cyclic voltammogram for a CH_3CN solution of Ru_4 is given in Fig. 3a, and the redox potentials obtained therefrom are listed in Table 1 along with the data for $[Ru(bpy)_3]^{2+}$ and $[(bpy)_2Ru(azobpy)Ru(bpy)_2][PF_6]_4$ (Ru_2)[1] for a comparison. It is noted that, at the positive side of the major $Ru^{3+/2+}$ couple, there is another small redox couple, as indicated by the pair of arrows. The redox couple is also evident from the differential pulse voltammogram taken for the anodic region, as shown in Fig. 3b. We attribute this small redox couple to a $Ru^{3+/2+}$ reaction at the central Ru ion based on the following considerations.

Upon going from $[Ru(bpy)_3]^{2+}$ ($E_{1/2}$ ($Ru^{3+/2+}$) = 0.89 V vs Fc^+/Fc) to Ru_2 (0.95 V), where one bpy is replaced by azobpy in terms of the coordinating ligands, the oxidation potential for $Ru^{3+/2+}$ is shifted positively by 60 mV. This is consistent with the fact that azobpy is a weaker σ-donor and a better π acceptor than bpy, due to the electron-withdrawing nature of the azo group. The coordination environment of the peripheral Ru ions in Ru_4 is nearly the same as that for Ru_2. Thus, the larger redox peak at 0.96 V may be assigned to the peripheral $Ru^{3+/2+}$. On the other hand, all three bpy's are replaced by azobpy's for the central Ru ion in Ru_4. Therefore, the redox potential for the central metal ion would be expected to be shifted positively even further. Thus, the smaller wave at ca. 1.1 V may be attributed to the central $Ru^{3+/2+}$.

Upon a cathodic scan, two consecutive reduction couples were observed before reaching potentials where the terminal bpy's were reduced. Azopyridines are known to experience two consecutive one-electron reductions.[10] Hence, we attribute the observed pair of waves to a reduction of the azobpy ligands in the complex. Thus, the first reduction is a three-electron reduction of azobpy's (one-electron on each azobpy) to make radical anions. A large part of the LUMO of azobpy lies at the –N=N– moiety in the π-conjugated system,[11] and thus the electron is injected into this part of the ligands by the first reduction. The second wave is attributed to an additional three-electron reduction of azobpy's (a second electron on each azobpy) to produce dianions of azobpy ligands. Indeed, ESR measurements for Ru_2 and related complexes support this assignment, since the reduced species prepared at potentials between the first and the second waves is ESR active, which becomes ESR inactive at more negative potentials than the second wave.[11] All of these redox reactions are reversible in the sense that the peak separations in the cyclic voltammogram are independent of the scan rate in the range of 50–200 mV s^{-1}. Upon a further cathodic scan, redox waves due to the reduction of peripheral bpy ligands are observed at around −1.8 V. Thus, the redox reactions for Ru_4 are summarized as follows:

terminal bpy ligands reduced

$$\overset{+xe^-}{\leftrightarrows} Ru^{2+}\{(azobpy)^{2-}Ru^{2+}(bpy)_2\}_3$$

$$\overset{+3e^-}{\leftrightarrows} Ru^{2+}\{(azobpy)^{\bullet -}Ru^{2+}(bpy)_2\}_3$$

$$\overset{+3e^-}{\leftrightarrows} Ru^{2+}\{(azobpy)Ru^{2+}(bpy)_2\}_3 \text{ (as-prepared)}$$

$$\overset{-3e^-}{\leftrightarrows} Ru^{2+}\{(azobpy)Ru^{3+}(bpy)_2\}_3$$

$$\overset{-e^-}{\leftrightarrows} Ru^{3+}\{(azobpy)Ru^{3+}(bpy)_2\}_3$$

The electronic spectral data for Ru_4 in CH_3CN are tabulated in Table 2. The overall shape of the spectrum is quite similar to that of Ru_2.[1] Two major broad peaks are observed in the visible region (cf. see Fig. 4). The higher energy absorption (444 nm) corresponds to the MLCT transition involving bpy ligands, which is also observed for the parent complex, $[Ru(bpy)_3]^{2+}$. The lower energy absorption band (555 nm) is characteristic for this family of complexes bearing azobpy. This is also the MLCT transition, but the relevant ligand orbital is the π* of azobpy. The difference in the excitation energy between the transitions, d (central Ru) → π* (azobpy) and d (peripheral Ru) → π* (azobpy), which should arise from the difference in the HOMO levels indicated by the electrochemical results, is not apparent, since the absorption band is rather broad.[12]

Table 2. Absorption Properties of Complexes[a)]

Complexes	λ_{max}/nm ($\varepsilon \times 10^{-3}$/cm^{-1} M^{-1})		
	LC[b)]	MLCT (d → bpy π*)	MLCT (d → azobpy π*)
$[Ru(bpy)_3]^{2+}$	286 (86)	450 (12)	—
Ru_2	286 (140)	439 (22)	558 (22)
Ru_4	285 (281)	444 (41)	555 (45)
Ru_4[c)]	288 (227)	445 (29)	569 (39)

a) In CH_3CN unless otherwise noted. b) Ligand centered ππ*. c) In DMF containing 0.1 M Bu_4NPF_6.

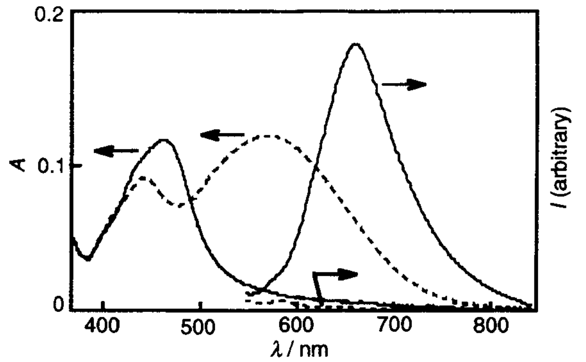


Fig. 4. Absorption and luminescence (λ_{ex} = 492 nm) spectra of as-prepared (- - -) and 3-electron reduced (—) Ru_4 in DMF (3 μM) containing 0.1 M Bu_4NPF_6.

The less-negative redox potentials for the reduction and the lower energy absorption band observed for Ru_4, and other Ru complexes bearing azobpy for that matter, as described above, are the manifestation of a low-lying π* level of azobpy. Hence, the excited electron is trapped in this orbital, resulting in a nearly complete quenching of the luminescence. No significant luminescence has been detected up to 900 nm at room temperature.

Spectroelectrochemical studies were conducted on Ru_4 to evaluate the possibility of switching its luminescence, as observed for Ru_2.[1] The stability of the reduced species was found to be solvent-dependent. Several cycles of reduction/re-oxidation were possible in DMF, while the reduced species degraded in CH_3CN on the time scale of electrolysis experiments. Hence, we describe the results obtained in DMF (containing 0.1 M Bu_4NPF_6). The electrochemical and spectroscopic properties of Ru_4 are quite similar in both solvents, although some differences, e.g. in spectral shape, are observed (see Tables 1 and 2). Upon a constant-potential electrolysis of Ru_4 around −0.9 V, a just sufficiently negative potential to produce the three-electron reduced species, the longer wavelength absorption band (569 nm) decreased with a concomitant slight increase in the shorter wavelength absorption band (465 nm), as shown in Fig. 4. This change is similar to that observed for Ru_2 reported previously.[1] This is explained by assuming that the reduction of the azobpy ligand hinders the MLCT path to this azobpy ligand. A luminescence centered at 662 nm appeared being concomitant with the absorption changes. The luminescence spectra for the reduced and the as-prepared complexes, when excited at 492 nm, where both species show the same absorbance, are also included in Fig. 4. The appearance of luminescence upon reduction is again a phenomenon also observed for Ru_2.[1] Now that the MLCT to the low-lying π^* orbital of azobpy is hindered, the excited state of the complex behaves more or less like the parent $^*[Ru(bpy)_3]^{2+}$. However, the relative luminescence intensity is still much smaller (0.08) and the λ_{max} (662 nm) is red-shifted as compared with those of $[Ru(bpy)_3]^{2+}$ (616 nm). The time-resolved luminescence measurement showed a single exponential decay with a lifetime of 186 ns, which is shorter than that of $[Ru(bpy)_3]^{2+}$ (555 ns) under the same conditions, being consistent with the steady-state result. The most likely reason for this quenching is electron transfer from the reduced azobpy$^{\bullet-}$ to the empty dπ orbital of the metal center in the MLCT state. The electrolysis was also conducted at -1.3 V, which should produce six-electron reduced species. The absorption and luminescence spectroscopic changes in this case were essentially the same as in the three-electron reduction, although the complex was more prone to degradation under this more negative potential.

These reversible changes in the luminescence, combined with the excellent on/off ratio (compare the two luminescence traces in Fig. 4) imply the utility of this branched tetranuclear complex as a molecular switching device. Combining Os centers with Ru centers would give rise to an energy level gradient in this scaffold, allowing the switching of directional energy transfer, which is being pursued in our laboratory.

Experimental

Materials and Instruments. The mononuclear complex $[Ru(bpy)_2(azobpy)](PF_6)_2$ was prepared as previously reported.[1] ^{1}H-NMR spectra were recorded on a JEOL JNM-GX400 spectrometer. Electrospray mass spectra were obtained with a JEOL JMS600H mass spectrometer. An elemental analysis was performed by the Chemical Analysis Center of the College of Science and Technology, Nihon University. UV-vis and luminescence data were obtained using Shimadzu UV-2400PC and RF-5300PC spectrophotometers, respectively. Electrochemical measurements were carried out with a Hokuto Denko HZ-3000 voltammetric analyzer. The electrochemical cell, maintained under N_2, was equipped with a Pt disk working electrode, a Pt-wire counter electrode, and an Ag/Ag$^+$ reference electrode. The supporting electrolyte solution was 0.1 M Bu_4NPF_6 in CH_3CN or DMF (both distilled from P_2O_5). Potentials are reported with respect to the internal Fc^+/Fc couple. Spectroelectrochemical experiments were performed on 3 μM samples in N_2-purged DMF containing 0.1 M $TBAPF_6$ in a spectrofluorimetric cell (optical path 1 cm), equipped with a Pt-mesh working electrode, an Ag/Ag$^+$ reference electrode, and a Pt-wire counter electrode separated with absorbent cotton. The time-resolved emission decay was measured by the irradiation of a reduced Ru_4 solution after electrolysis with a nitrogen laser pulse (337 nm) through a coumarin chromophore (447 nm). The emission was then dispersed with a Hamamatsu Photonics C-2830 disperser and monitored on a Hamamatsu Photonics M-2548 streak camera.

Synthesis of Ru_4. A suspension of $RuCl_3\cdot3(H_2O)$ (0.01 g, 0.04 mmol) and $[Ru(bpy)_2(azobpy)](PF_6)_2$ (0.12 g, 0.12 mmol) in 2:1 ethanol/water mixture (15 mL) was refluxed for 5 h under Ar. After the mixture was cooled to room temperature, water (10 mL) and NH_4PF_6 (0.15 g) were added. The resulting black precipitate was chromatographed on a silica-gel column with 3:1 CH_3CN/aqueous 0.4 M KNO_3. The desired band was concentrated on a rotary evaporator, to which NH_4PF_6 was added. The resulting solid was dissolved in a mixture of CH_3CN and H_2O, to which NH_4PF_6 was added. Only CH_3CN was evaporated with a rotary evaporator, resulting in precipitation again. This metathesis procedure was repeated three times to exchange the anion from NO_3^- to PF_6^- completely. Finally, the thus-obtained blue solid was washed with H_2O and ether, and dried under a vacuum (20 mg, 14%). Mp > 440 °C. ^{1}H NMR (CD_3CN, ppm) δ 7.35–7.55 (18H, m, H-a5, H-b5, H-c5), 7.7–7.9 (24H, m, H-a6, H-b6, H-c6, H-d5, H-e5), 8–8.2 (24H, m, H-a4, H-b4, H-c4, H-d6, H-e6), 8.52 (12H, d, $J = 8$ Hz, H-a3), 8.68 (3H, d, $J = 9$ Hz, H-b3), 8.7–8.75 (3H, m, H-c3), 8.96 (3H, s, H-d3), 8.95–9.05 (3H, m, H-e3). ESMS (CH_3CN) m/z 1613 ($[M-2(PF_6)]^{2+}$), 1026 ($[M-3(PF_6)]^{3+}$), 734 ($[M-4(PF_6)]^{4+}$). Found: C, 39.83; H, 2.82; N, 10.84%. Calcd for $C_{120}H_{90}F_{48}N_{30}P_8Ru_4\cdot8(H_2O)$: C, 39.38; H, 2.92; N, 11.48%.

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12 The 0.14-eV difference in the electronic energy around 555 nm corresponds to a 35-nm difference in wavelength, which should be obscured by the broad absorption bands (cf. see Fig. 4).