Redox-Responsive Molecular Switches Based on Azoterpyridine-Bridged Ru/Os Complexes

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Dedicated to Professor Manabu Seno on the occasion of his 70th birthday

Abstract: Three new terpyridine-based dinuclear complexes, [(tpy)Ru(azotpy)-Ru(tpy)]$^{4+}$ (tpy = 2,2′:6′,2″-terpyridine, azotpy = bis[2,6-bis(2-pyridyl)-4-pyridyl]-diazene), [(tpy)Os(azotpy)Os(tpy)]$^{4+}$, and [(tpy)Ru(azotpy)Os(tpy)]$^{4+}$ were prepared and their electrochemical and photophysical properties investigated. The bridging ligand, azotpy, in these complexes is reduced at less negative potentials than the unsubstituted tpy ligand. These complexes exhibit absorption bands due to the metal-to-ligand charge-transfer transitions both to the unsubstituted tpy ligand and the bridging azotpy ligand, the latter absorption being observed at the lower energy side of the former. These observations are consistent with the lower lying π* level of the azotpy ligand than that of the tpy ligand. These complexes are nonluminescent, since the excited electron is trapped in this lower lying π* level of the azotpy ligand in the excited state. Reduction of this bridging ligand by constant potential electrolysis renders the shape of absorption spectra for these complexes nearly identical to those of the parent complexes, $[M(tpy)_2]^{2+}$ (M = Ru, Os). In this reduced state, the homodinuclear Os complex becomes luminescent at room temperature, whereas the homodinuclear Ru complex becomes luminescent at 77 K, thus establishing their photoswitching behavior. The reduced heterodinuclear complex exhibits luminescence from the Os center, which is sensitized by the Ru center in the same molecule as evidenced by the excitation spectra. Thus, the intramolecular energy transfer can be switched on and off by the redox reaction of the bridging component.

Keywords: bridging ligands · energy transfer · molecular devices · molecular switches · redox chemistry

Introduction

Processing photons and electrons at the molecular or supramolecular level has received considerable attention in recent years, since studies on these processes may lay the foundation for the development of molecule-based electronic/photonic devices.[1] Electron-transfer and energy-transfer processes provide a means for electronic communication in molecular devices. Switching of these processes in response to a given signal is required to process information at the molecular level. Several molecular switches for intramolecular photo/electronic processes, including energy transfer[2] and electron transfer,[3] have been realized so far. Zahavy and Fox reported an Os^{II}–Ni^{II}–Pd^{II} trimetallic complex, in which the intervening Ni complex is redox-responsive to switch photo-induced *electron-transfer* paths.[3g]

We have previously shown that Ru/Os-bipyridine (bpy)-type homodinuclear and heterodinuclear complexes bridged by bis[2,6-bis(2-pyridyl)-4-pyridyl]diazene (azobpy), $[(bpy)_2M(azobpy)M(bpy)_2]^{4+}$, play the role of a switch for luminescence and intramolecular *energy transfer*, respectively.[4] When the bridging ligand is neutral, the metal-to-ligand charge-transfer (MLCT) excited state is rapidly thermally deactivated. On the other hand, when the bridging ligand is electrochemically reduced, the photo-excited state behaves more or less like the parent complexes, $[M(bpy)_2]^{2+}$, leading to luminescence (homonuclear) or intramolecular energy transfer (heteronuclear). When one wishes to incorporate these switching units in larger multi-metal complexes, bpy-based complexes would pose a geometrical problem, since they inevitably consist of a mixture of optical and stereo-isomers. This problem is cleverly circumvented by using 2,2′:6′,2″-terpyridine (tpy)-based complexes.[5] The introduction of a single substituent in the 4′-position of the tpy ligand makes geometrically well-defined, that is, linear, extended multi-metal complexes.

We have therefore prepared bis[2,6-bis(2-pyridyl)-4-pyridyl]diazene (azotpy) to be used in extended multi-metal

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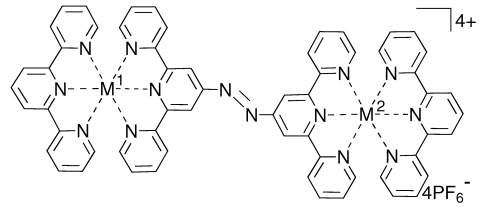
complexes. Before starting to make extended multi-metal complexes, however, we had to confirm the switching performance for the tpy-based complex. Here we show that the tpy-based complexes that contain azotpy as a bridging ligand, that is, $[(tpy)Ru(azotpy)Ru(tpy)]^{4+}$ (Ru-azotpy-Ru),



Ru-azotpy-Ru $M^1 = M^2 = Ru$
Os-azotpy-Os $M^1 = M^2 = Os$
Ru-azotpy-Os $M^1 = Ru$, $M^2 = Os$

$[(tpy)Os(azotpy)Os(tpy)]^{4+}$ (Os-azotpy-Os) and $[(tpy)Ru(azotpy)Os(tpy)]^{4+}$ (Ru-azotpy-Os), indeed play the role of switches. The heteronuclear Ru-azotpy-Os, in particular, constitutes a switch for intramolecular energy transfer responding to redox stimuli as schematically shown in Figure 1.

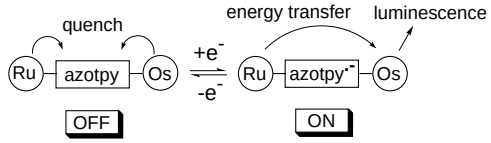


Figure 1. The energy-transfer switch based on Ru-azotpy-Os.

Abstract in Japanese:

3 種類の新しいテルピリジン系複核錯体—$[(tpy)Ru(azotpy)Ru(tpy)]^{4+}$ (tpy = 2,2':6',2"-terpyridine, azotpy = bis[2,6-bis(2-pyridyl)-4-pyridyl]diazene), $[(tpy)Os(azotpy)Os(tpy)]^{4+}$ および $[(tpy)Ru(azotpy)Os(tpy)]^{4+}$—を合成し、その電気化学的、光物理的性質を調べた。これらの錯体中の架橋配位子 azotpy は無置換 tpy 配位子よりも、より正側の負電位で還元される。これらの錯体は、無置換 tpy 配位子と架橋 azotpy 配位子の両方への金属—配位子電荷移動遷移による吸収帯を示す。後者の吸収は、前者の吸収の低エネルギー側にあらわれる。これらの結果は、tpy 配位子に比べて azotpy 配位子の π^* レベルが低いということを示している。励起状態で、この低エネルギー π^* レベルに励起電子がトラップされるために、これらの錯体は無発光性である。この架橋配位子を定電位電解によって還元すると、これらの錯体の吸収スペクトルの形は親錯体($[M(tpy)_2]^{2+}$ (M = Ru, Os)) のものとほぼ同じになる。この還元状態では、ホモ複核 Os 錯体は室温で、ホモ複核 Ru 錯体は 77K で発光性となり、フォトスイッチとしての挙動を示す。還元型ヘテロ複核錯体は Os 中心からの発光を示すが、同一分子内の Ru 中心によって増感されていることが、励起スペクトルによって明らかになった。つまり、分子内エネルギー移動が架橋部分の酸化還元反応によってスイッチオン／オフできる。

Results and Discussion

Synthesis: The ditopic ligand, azotpy, was synthesized by a reductive condensation reaction of 4′-nitro-2,2′:6′,2″-terpyridine[6] (NO_2–tpy) by using Zn powder as a reductant in a refluxing mixture of concentrated aqueous NaOH solution and benzene for 3 h. These reaction conditions have been found to be crucial. As the reduction of NO_2–tpy proceeded, corresponding azoxyterpyridine (azoxytpy), azotpy, and aminoterpyridine (NH_2–tpy) were produced following this sequence of oxidation states. The complete consumption of azoxytpy was necessary, since it was impossible to separate azotpy from azoxytpy by chromatography or recrystallization. On the other hand, a prolonged reaction time tended to result in over-reduction of the intermediates into NH_2–tpy, leading to a low yield of the desired azotpy. Thus, the key to the successful preparation of azotpy was to find the right reducing agent and the right time window for the reaction. Several attempts using other reducing agents such as $NaBH_4$/Pd–C or $LiAlH_4$ failed, since an appreciable amount of NH_2–tpy started to form before azoxytpy was consumed.

Due to the strong coordination of three Cl atoms, the reaction of azotpy and the precursor complexes, $[M(tpy)Cl_3]$ (M = Ru, Os), required harsh conditions that induced some decomposition of azotpy; $[M(tpy)(NH_2–tpy)]^{2+}$ was found in the product mixture. Thus we transformed the trichlorides into more substitution-active complexes, $[Ru(tpy)(acetone)_3]^{2+}$[7] and $[Os(tpy)(H_2O)_3]^{3+}$,[8] before complexation with azotpy. The dinuclear complexes obtained were purified either by chromatography on silica gel followed by crystallization from methanol, or preparative TLC on silica. All new compounds were characterized by ^1H and ^{13}C NMR spectroscopy and FAB, ES, or MALDI-TOF mass spectrometry. All complexes apart from Ru-azotpy-Os, the purity of which was carefully confirmed by TLC, were also characterized by elemental analyses.

Electrochemical properties: The dinuclear complexes studied here exhibit reversible redox waves, the potentials of which are summarized in Table 1, together with those of reference complexes. The metal centers in the dinuclear complexes are slightly easier to oxidize than those in the model complexes, despite the additional positive charge present at the other terminal of the bridging ligand, suggestive of a weaker ligand field in these complexes due to the electron-withdrawing propensity of the complex-as-ligand $[M(azotpy)(tpy)]^{2+}$. Only one oxidation wave in either Ru-azotpy-Ru or Os-azotpy-Os was observed, indicating that the internal metal–metal

Table 1. Redox potentials ([V] vs Fc/Fc^+).[a]

	$tpy^{-1/-2}$	$tpy^{0/-1}$	$azotpy^{-1/-2}$	$azotpy^{0/-1}$	$Os^{+3/+2}$	$Ru^{+3/+2}$
Ru-azotpy-Ru		–1.87[b]	–1.15	–0.77		0.86[c]
Os-azotpy-Os		–1.87[b]	–1.18	–0.82	0.57[c]	
Ru-azotpy-Os		–1.86[b]	–1.15	–0.79	0.56	0.90
Ru-azotpy		–1.86		–0.92		0.88
$[Ru(tpy)_2]^{2+}$[d]	–1.92	–1.67				0.92
$[Os(tpy)_2]^{2+}$[d]	–1.95	–1.63			0.58	

[a] All redox waves are reversible. [b] Two-electron reduction. [c] Two-electron oxidation. [d] Ref. [26].

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interaction for the dinuclear complexes is not strong. As for the ligand-centered processes, the reference complexes are reduced at two distinct potentials more negative than -1.6 V (vs Fc/Fc^+) for the two respective tpy ligands. For the dinuclear complexes, reduction steps involving the bridging azotpy ligand occur at less negative potentials, for example, -0.77 V (one-electron) and -1.15 V (one-electron) for Ru-azotpy-Ru, than that of the two-electron reduction of terminal tpy ligands.[9] This provides evidence that the π^* level of azotpy is lower in energy than that of tpy. The important point here for application to the switching device is that it is possible to effect redox reactions of the bridging ligand without affecting the terminal ligands. It is reported that the reduction of related azopyridines occurs in two one-electron steps.[10] While the product of the first reduction is a stable anion radical, the second reduction is often followed by chemical reactions, such as abstraction of hydrogen from solvent molecules.

Photophysical properties: The electronic spectra for $[Ru(tpy)_2]^{2+}$ type complexes are characterized by a relatively intense, broad absorption band around 470 nm due to a spin-allowed $d \rightarrow \pi^*$ MLCT transition.[5] The absorption spectrum for Ru-azotpy-Ru is shown in Figure 2a (ox). This dinuclear

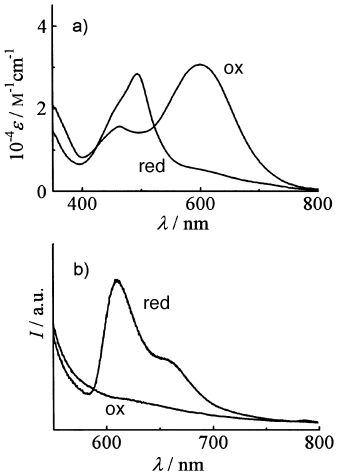

Figure 2. a) Absorption spectra for Ru-azotpy-Ru (ox) and Ru-azotpy$^{\bullet-}$-Ru (red) in DMF at 25 °C. b) Luminescence spectra for Ru-azotpy-Ru (ox) and Ru-azotpy$^{\bullet-}$-Ru (red) in DMF at 77 K. $\lambda_{ex} = 523$ nm (isosbestic).

complex can be considered as a heteroleptic mixed-ligand complex with tpy and $[(azotpy)Ru(tpy)]^{2+}$ as ligands. The spectrum can be interpreted as a mixture of the higher energy $Ru \rightarrow tpy$ (463 nm) and the lower energy $Ru \rightarrow azotpy$ (ca. 600 nm) CT bands as summarized in Table 2. This shows that the π^* of azotpy is lower than that of the terminal tpy, in keeping with the above-described electrochemical results. The separate CT bands are consistent with the localized model of the CT excitation.[11]

The absorption maximum of the spin-allowed MLCT band in the visible region for $[Os(tpy)_2]^{2+}$ lies at the same wavelength as that of $[Ru(tpy)_2]^{2+}$. In addition to this band, the spin-forbidden MLCT band is apparent in the lower energy region due to the large spin-orbit coupling caused by the

Table 2. Absorption and luminescence properties at 25 °C.

	Absorption λ_{max} [nm] ($10^{-4}\varepsilon$ [$cm^{-1}M^{-1}$])			Luminescence λ_{max} [nm] (rel. int.)
	^{1}MLCT[a]	^{1}MLCT[b]/^{3}MLCT[c]	^{3}MLCT[d]	
Ru-azotpy-Ru	463 (1.53)	598 (3.02)		–
Ru-azotpy$^{\bullet-}$-Ru	493 (2.81)			610[f]
Os-azotpy-Os	475 (1.73[e])	630 (3.33)	783 (1.70)	–
Os-azotpy$^{\bullet-}$-Os	499 (2.97)	638 (1.01[e])		777 (0.04[g])
Ru-azotpy-Os	469 (1.56)	616 (3.09)	768 (0.85)	–
Ru-azotpy$^{\bullet-}$-Os	496 (2.79)	635 (0.59[e])		775 (0.04[g])
$[Ru(tpy)_2]^{2+}$	479 (1.64)			608[f]
$[Os(tpy)_2]^{2+}$	480 (1.48)	661 (0.41)		722 (1)[g]

[a] Ru → or Os → tpy. [b] Ru → or Os → azotpy. [c] Os → tpy. [d] Os → azotpy. [e] Shoulder. [f] 77 K. [g] $\lambda_{ex} = 650$ nm.

heavy atom effect of Os.[5] In the same way as applied to Ru-azotpy-Ru, the absorption spectrum of Os-azotpy-Os (Figure 3a, ox) is interpreted as a mixture of the higher energy $Os \rightarrow tpy$ (475 nm and 630 nm for the spin-allowed and spin-forbidden MLCT, respectively) and the lower energy $Os \rightarrow$ azotpy (630 nm and 783 nm for the spin-allowed and spin-forbidden MLCT, respectively) CT bands.

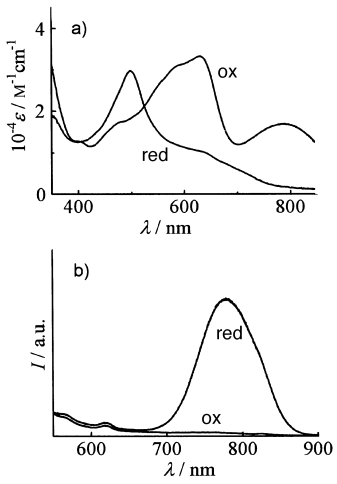

Figure 3. a) Absorption spectra for Os-azotpy-Os (ox) and Os-azotpy$^{\bullet-}$-Os (red) in DMF at 25 °C. b) Luminescence spectra for Os-azotpy-Os (ox) and Os-azotpy$^{\bullet-}$-Os (red) in DMF at 25 °C. $\lambda_{ex} = 524$ nm (isosbestic).

The shape of the absorption spectrum of Ru-azotpy-Os (Figure 4a, ox) is quite like the superposition of the spectra of Ru-azotpy-Ru and Os-azotpy-Os. This indicates that the transitions are due to the independent Ru and Os units. Hence, the assignment of the homodinuclear complexes applies naturally to this heterodinuclear complex, which is given in Table 2.

None of these dinuclear complexes exhibit luminescence at room temperature. It is known that $[Ru(tpy)_2]^{2+}$ is practically nonluminescent and its excited state lifetime is very short (250 ps) at room temperature.[5] This evidently makes $[Ru(tpy)_2]^{2+}$ less favorable relative to $[Ru(bpy)_3]^{2+}$ as a photosensitizer or a light input site in molecular devices. The low-lying metal-centered excited state due to a relatively weak ligand field in $[Ru(tpy)_2]^{2+}$ is available to quench the luminescent ^{3}MLCT state. Hence, several attempts have focused on a way to improve its photophysical properties. In

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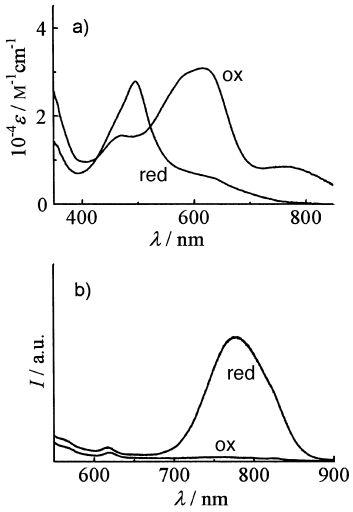

Figure 4. a) Absorption spectra for Ru-azotpy-Os (ox) and Ru-azotpy$^{\bullet-}$-Os (red) in DMF at 25 °C. b) Luminescence spectra for Ru-azotpy-Os (ox) and Ru-azotpy$^{\bullet-}$-Os (red) in DMF at 25 °C. $\lambda_{ex} = 522$ nm (isosbestic).

the course of these studies, it has been found that the use of electron-withdrawing substituents[12] or groups that effect electronic delocalization over the tpy fragment[13] prolongs the excited state lifetime of Ru–tpy complexes. However, despite the fact that the relevant substituent in Ru-azotpy-Ru, that is, −N=N−tpy, is both electron withdrawing and has a formally extended conjugation, the complex remains nonemissive at room temperature. Furthermore, this complex is nonemissive even at 77 K, at which $[Ru(tpy)_2]^{2+}$ exhibits a long-lived luminescence.[5] Even the osmium complex, Os-azotpy-Os, the parent complex of which, $[Os(tpy)_2]^{2+}$, is moderately luminescent at room temperature, is nonluminescent. There was no indication of emission up to 900 nm, excluding the possibility of low-energy luminescence corresponding to the low energy absorption of this complex. Finally, Ru-azotpy-Os is also nonluminescent.

The ^{3}MLCT excited state produced by light absorption for these complexes can be described as $[(tpy)M^{3+}(azotpy^{\bullet-})M^{2+}(tpy)]$, in which the excited electron is localized in the lower lying π* level of the bridging azotpy ligand. Several possibilities may be invoked as the reasons for the nonluminescent nature of this state, although which predominates is unclear at present. Firstly, the lower energy gap relative to the parent complex should result in a larger overlap of vibronic states between the excited and ground states; this leads to an increased rate of nonradiative deactivation of the excited state into the ground state, in accord with the energy-gap law.[14] Secondly, isomerization or twisting about the N=N bond at the excited state may be possible. In the excited state, the bridging ligand is reduced to the radical anion, azotpy$^{\bullet-}$, which may undergo facile *cis-trans* isomerization as is known for compounds such as stilbene and azobenzene.[15] Thirdly, the internal conversion from the ^{3}MLCT excited state to the ligand-localized triplet state, $[(tpy)M^{2+}(^3azotpy^*)M^{2+}(tpy)]$, might give an efficient route for the quenching of luminescence.[16] Finally, an increased basicity of azo nitrogens in the reduced bridging ligand might induce interactions of this site with solvent molecules, providing a means of quenching.[17]

Redox-responsive switching: We carried out spectroelectrochemical measurements in order to study the switching behavior of these complexes. A solution of each complex (10 μM) in DMF that contained 0.1 M tetrabutylammonium perchlorate (TBAP) was electrolyzed at a constant potential (−0.90 V for Ru-azotpy-Ru and Ru-azotpy-Os, −0.95 V for Os-azotpy-Os vs Fc/Fc^+) in a modified 1×1 cm^2 quartz cell until its spectrum no longer changed. At this potential, azotpy in the complex is reduced by one electron. On the other hand, applying −1.25 V for Ru-azotpy-Ru and Ru-azotpy-Os, and −1.30 V for Os-azotpy-Os should produce the dianion of the bridging ligand, $[(tpy)M^{2+}(azotpy^{2-})M^{2+}(tpy)]$. As far as absorption and luminescence spectra are concerned, however, the responses of the system were the same irrespective of which potential was used for the constant potential electrolysis. Hence, the electrolysis experiments were done under the milder condition of one-electron reduction. For Ru-azotpy-Ru, reduction of the azotpy in the complex caused a decrease in absorption of the longer wavelength band and an increase in the shorter wavelength one as shown in Figure 2a. The absorption spectrum of the reduced complex, Ru-azotpy$^{\bullet-}$-Ru, is similar to that of $[Ru(tpy)_2]^{2+}$. The change in the absorption spectrum can be explained by assuming that the reduction of azotpy in the complex makes the π* level of azotpy higher in energy, at least up to that of tpy. The spectrum of the reduced form of this complex reversibly returned to the original spectrum by reoxidation of azotpy$^{\bullet-}$ back to azotpy in the complex, and this redox cycle could be repeated several times without a significant deterioration. Even the reduced form shows no emission at 25 °C because of the nonemissive property of $[Ru(tpy)_2]^{2+}$. Photoswitching behavior was observed at 77 K; the reduced form emits at 610 nm (Figure 2b), whereas the neutral form shows no emission.

The change in the absorption spectrum for Os-azotpy-Os upon reduction was the same as that observed for Ru-azotpy-Ru in its nature; the longer wavelength absorbance decreased, while the shorter one increased, so that the spectrum of Os-azotpy$^{\bullet-}$-Os is similar to that of $[Os(tpy)_2]^{2+}$ (Figure 3a). The reduced form exhibits an emission at 775 nm at 25 °C, whereas the neutral form shows no emission (Figure 3b). Thus, this complex plays the role of a redox-responsive photoswitch. The luminescence from Os-azotpy$^{\bullet-}$-Os is red-shifted by as much as 55 nm and is lower in intensity in comparison with that from $[Os(tpy)_2]^{2+}$, suggesting that the electronic properties of these complexes are quite different despite the apparent similarities in their absorption spectra.

The heteronuclear complex Ru-azotpy-Os shows the same behavior as the above homonuclear complexes in terms of the change in absorption spectrum on the redox processes, as shown in Figure 4a; the spectrum for Ru-azotpy$^{\bullet-}$-Os nearly matches the averaged spectrum of Ru-azotpy$^{\bullet-}$-Ru and Os-azotpy$^{\bullet-}$-Os. The reduced form exhibits the Os-based luminescence at 775 nm, whereas the neutral form shows no emission (Figure 4b). In order to examine if intramolecular energy transfer from the Ru center to the Os center occurs in the reduced form, we compared the excitation spectra for Os-azotpy$^{\bullet-}$-Os and Ru-azotpy$^{\bullet-}$-Os (Figure 5). The luminescence was monitored at 775 nm, which is the λ_{max} of the Os-based luminescence. The spectra are normalized at the

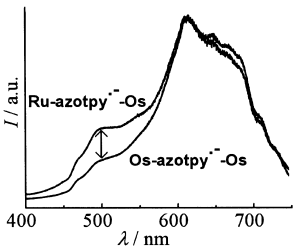

Figure 5. Excitation spectra monitored at 775 nm for Ru-azotpy•−-Os and Os-azotpy•−-Os in DMF at 25 °C, which are normalized at 610 nm. The arrow indicates the contribution by intramolecular energy transfer.

610 nm peak, at which only the Os-based component is excited. Therefore, the excess luminescence intensity at 500 nm, at which the Ru- and the Os-based units are excited in a 1:1 ratio, for Ru-azotpy•−-Os over that for Os-azotpy•−-Os, as indicated by the arrow in the graph, comes from the excitation of the Ru-based unit through intramolecular energy transfer. Thus the excitation spectra indicate that the energy transfer takes place with an approximately 70% efficiency. Upon the reoxidation, the absorption and luminescence spectra nearly returned to the original shapes, although repetition of this redox cycle resulted in some deterioration of response (e.g., the absorbance at 600 nm recovered up to ≈80% of the original value after three cycles for Ru-azotpy-Os). As such, the heterodinuclear complex Ru-azotpy-Os works as a molecular switch for intramolecular energy transfer.[18] Note from Figure 4b that the on/off ratio (≈30), critical in digital processing, is dramatically improved from the previously reported bpy-based system (≈2.5).[4b] The performance of this molecular switch is illustrated in the schematic drawing in Figure 1.

The best model complex for the donor part of this heteronuclear complex Ru-azotpy-Os is the homonuclear Ru complex, Ru-azotpy-Ru. The fact that the reduced form of this complex, Ru-azotpy•−-Ru, is still nonluminescent implies that the excited-state lifetime of the Ru-based unit in the heteronuclear complex is quite short. This is an unfavorable property for the utilization of the excited state for subsequent processes such as energy transfer. Furthermore, in the reduced form of this complex, a significant portion of the excited electrons must be localized in one of the terminal tpy ligands, as implied by the absorption spectrum of the reduced species. This lengthens the effective separation between the donor and the acceptor, which is also a factor working against efficient energy-transfer processes.[19] However, the fact that the energy transfer still occurs with a moderate 70% efficiency implies that the rate for the energy transfer processes is quite fast. Very fast energy transfer processes ($>10^{10}\ s^{-1}$) were observed even for several terpyridine-based heteronuclear Ru/Os complexes,[20] with a larger metal–metal separation than that in the case described here, resulting in an efficient intramolecular energy transfer. The nonluminescent nature of the donor chromophore in this case excludes the possibility of a Förster-type Coulombic mechanism for the energy transfer, which requires the overlap of the donor luminescence and the acceptor absorption,[21] leaving the Dexter-type electron-exchange mechanism[22] as the likely interaction for the energy transfer. The Dexter mechanism is considered also to be responsible for energy transfer in other related Ru/Os–tpy complexes.[19, 20b, 23]

Conclusion

In conclusion, Ru and Os tpy-type dinuclear complexes bridged by azotpy work as switches responding to redox stimuli. The original homonuclear species show no luminescence, apparently because the excited electron is trapped in the π* of azotpy. On the other hand, the reduced species behave more or less as the reference compounds $[M(tpy)_2]^{2+}$; Os-azotpy•−-Os becomes luminescent at room temperature and Ru-azotpy•−-Ru at 77 K. As such, these homodinuclear complexes work as a redox-responsive molecular photoswitch. For the heteronuclear Ru-azotpy-Os, intramolecular energy transfer can be switched on and off reversibly by the redox reaction as schematically shown in Figure 1. Thus, this heterodinuclear complex is a redox-responsive switch for intramolecular energy transfer.

Now that the switching behavior has been confirmed for the azotpy-based complexes, we are in a position to explore the preparation and the properties of linearly extended (tri-, tetrametallic, and so on) complexes bridged by more than one ditopic azotpy ligand. A system can be envisaged in which excitation energy is delivered to a designated site in response to redox stimuli by using these extended complexes.

Experimental Section

General method: Solvents and reagents were of reagent grade quality and used as received unless otherwise specified. Dimethylformamide (DMF) used on photophysical and electrochemical studies was distilled from P_2O_5. 4′-Nitro-2,2′:6′,2″-terpyridine,[6] $[Ru(tpy)Cl_3]$,[24] and $[Os(tpy)(H_2O)_3][PF_6]_3$[8] were prepared according to literature procedures.

The ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer in $CDCl_3$ or CD_3CN. Mass spectra were recorded on JEOL JMS-D-300, JEOL JMS-600H, or a Bruker Daltonics BIFLEX III spectrometers. Elemental analyses were carried out on a FISONS Instruments EA 1108 Elemental Analyzer. Absorption and emission spectra were measured with a Shimadzu UV-2500PC spectrophotometer and Shimadzu RF-5300PC spectrofluorophotometer, respectively. Cyclic voltammetry was conducted in N_2-purged DMF containing 0.1M TBAP as supporting electrolyte with a Nikko Keisoku NPGFZ-2501-A potentiogalvanostat or BAS electrochemical analyser model 720A. A glassy carbon or a platinum disk was used as the working electrode, an Ag/Ag^+ electrode as the reference, and a Pt wire as the counter electrode. All redox waves were referenced to internal ferrocene added at the end of each experiment. Redox potentials are quoted versus the ferrocene/ferrocenium couple ($Fc/Fc^+ = 0.0$ V). Spectroelectrochemical experiments were performed on 10μM samples in N_2-purged DMF containing 0.1M TBAP in a spectrofluorimetric cell (optical path 1 cm), with a Pt mesh, an Ag/Ag^+, and a Pt wire separated with an absorbent cotton, as the working, reference, and counter electrodes, respectively.

Bis-[2,6-bis(2-pyridyl)-4-pyridyl]diazene (azotpy): A solution of 4′-nitro-2,2′:6′,2″-terpyridine (100 mg, 0.36 mmol) in a mixture of conc. aqueous NaOH (200 mg in 0.2 mL) and benzene (5 mL) was heated to 80 °C under N_2 with vigorous stirring. Zn powder (0.5 g) was added and the solution was vigorously stirred for an additional 3 h at 80 °C. The reaction mixture was hot-filtered and the residue was washed well with hot benzene and hot chloroform. Evaporation of the filtrate yielded a crude product (90 mg), to which 2-methoxyethanol was added. The solution was heated to boiling

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point and then left to cool to room temperature. The resulting precipitate was collected, washed with methanol, and dried in vacuo to give a yellow-brown powder (47 mg, 53%). M.p. 357.9–360.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 40 °C): $\delta = 8.87$ (s, 4H; H-3′), 8.78 (dd, $J = 4.9$, 1.0 Hz, 4H; H-6), 8.68 (dd, $J = 8.1$, 1.0 Hz, 4H; H-3), 7.89 (dt, $J = 7.8$, 1.8 Hz, 4H; H-4), 7.38 (dt, $J = 6.0$, 1.2 Hz, 4H; H-5); high-resolution MS (FAB): *m/z* calcd: 492.1811; found 492.1819; elemental analysis calcd (%) for $C_{30}H_{20}N_8$ (492.2): C 73.16, H 4.08, N 22.75; found: C 72.73, H 4.06, N 22.73.

[(tpy)Ru(azotpy)Ru(tpy)][PF$_6$]$_4$ (Ru-azotpy-Ru): A solution of [Ru(tpy)-Cl_3] (80 mg, 0.18 mmol) and $AgBF_4$ (106 mg, 0.54 mmol) in acetone (25 mL) was heated at reflux under N_2 for 2 h.[7] The reaction mixture was cooled to room temperature and filtered to remove AgCl. The filtrate was evaporated and *N*,*N*-dimethylacetamide (30 mL) was added to the resulting residue. This solution was added to a solution of azotpy (32 mg, 0.065 mmol) in *N*,*N*-dimethylacetamide (10 mL), and this mixed solution was heated at 120 °C under N_2 for 13 h. The reaction mixture was cooled to room temperature and filtered through Celite, and the filtrate was evaporated and the residue dried. The resulting solid was dissolved in the minimum amount of acetonitrile and excess aqueous NH_4PF_6 (400 mg) was added. The precipitate was collected by filtration, washed with water and diethyl ether, and the dense purple powder (132 mg) was purified by chromatography on silica with acetonitrile/0.4 M aqueous KNO_3 (5:1) as eluent to give a dense purple powder (45 mg), which was crystallized from methanol to yield a dense brown-purple powder (23 mg, 20%). M.p. > 375 °C; ^{1}H NMR (400 MHz, CD_3CN, 20 °C): $\delta = 9.40$ (s, 4H), 8.82 (d, $J =$ 8.3 Hz, 4H), 8.75 (d, $J = 7.8$ Hz, 4H), 8.54 (d, $J = 7.8$ Hz, 4H), 8.51 (t, $J =$ 8.3, 8.1 Hz, 2H), 8.05 (dt, $J = 7.8$, 1.5 Hz, 4H), 7.97 (dt, $J = 7.8$, 1.5 Hz, 4H), 7.46–7.48 (overlapping d (4H) and d (4H), $J = 5.9$, 5.6 Hz), 7.29 (dt, $J = 6.6$, 1.5 Hz, 4H), 7.20 (dt, $J = 6.6$, 1.5 Hz, 4H); ^{13}C NMR (100 MHz, CD_3CN, 20 °C): $\delta = 158.57$, 157.92, 156.45, 155.58, 153.62, 153.39, 139.32, 139.23, 137.62, 128.85, 128.38, 125.72, 125.51, 124.79, 117.78; MS (MALDI-TOF): *m/z* (%): 1452 (66) $[M - 2PF_6]^+$, 1307 (100) $[M - 3PF_6]^+$, 1162 (75) $[M - 4PF_6]^+$; elemental analysis calcd (%) for $C_{60}H_{50}F_{24}N_{14}O_4P_4Ru_2$ (tetrahydrate): C 40.14, H 2.70, N 10.92; found: C 39.90, H 2.50, N 10.54.

[(tpy)Ru(azotpy)][PF$_6$]$_2$ (Ru-azotpy): A solution of [Ru(tpy)Cl_3] (80 mg, 0.18 mmol) and $AgBF_4$ (106 mg, 0.54 mmol) in acetone (25 mL) was heated at reflux under N_2 for 2 h.[7] The reaction mixture was cooled to room temperature and filtered to remove AgCl. The filtrate was evaporated, and *N*,*N*-dimethylacetamide (30 mL) was added to the resulting residue. This solution was added to a solution of azotpy (107 mg, 0.22 mmol) in *N*,*N*-dimethylacetamide (20 mL), and this mixed solution was heated at 120 °C under N_2 for 12 h. The reaction mixture was cooled to room temperature and filtered through Celite, and the filtrate was evaporated and the residue dried. The resulting solid was dissolved in the minimum amount of acetonitrile and excess aqueous NH_4PF_6 (500 mg) was added. The precipitate was collected by filtration, washed with water and diethyl ether, and the dense reddish-purple powder (214 mg) was purified by chromatography on silica with acetonitrile/toluene (from 2:3 to acetonitrile only) as eluent followed by crystallization by diffusing toluene into an acetonitrile solution to yield a dense reddish-purple powder (140 mg, 69%). Although ^{1}H NMR data suggested the presence of some impurities, we proceeded to the next step. MS (ES): *m/z* (%): 972 (100) $[M - PF_6]^+$.

[(tpy)Os(azotpy)Os(tpy)][PF$_6$]$_4$ (Os-azotpy-Os): A solution of [Os(tpy)-$(H_2O)_3$][PF_6]$_3$ (100 mg, 0.11 mmol) and azotpy (24 mg, 0.049 mmol) in ethyleneglycol (24 mL) was heated at 150 °C under N_2 for 1 h.[25] The reaction solution was cooled to room temperature and excess aqueous NH_4PF_6 (500 mg) was added. The precipitate was collected by filtration, washed with water and diethyl ether, and dried in vacuo. The dense purple powder (104 mg) was purified by preparative TLC on silica with acetonitrile/0.4 M aqueous KNO_3 (3:1) as eluent to give a dense brown-purple powder (34 mg, 36%). M.p. > 375 °C; ^{1}H NMR (400 MHz, CD_3CN, 20 °C): $\delta = 9.39$ (s, 4H), 8.85 (d, $J = 8.3$ Hz, 4H), 8.76 (d, $J = 7.8$ Hz, 4H), 8.52 (d, $J = 7.8$ Hz, 4H), 8.06 (t, $J = 8.3$, 8.1 Hz, 2H), 7.91 (dt, $J = 7.8$, 1.5 Hz, 4H), 7.82 (dt, $J = 7.8$, 1.5 Hz, 4H), 7.35 (d, $J = 5.6$ Hz, 8H), 7.24 (dt, $J = 6.6$, 1.5, 1.2 Hz, 4H), 7.13 (dt, $J = 6.6$, 1.5, 1.2 Hz, 4H); ^{13}C NMR (100 MHz, CD_3CN, 20 °C): $\delta = 160.55$, 160.03, 156.46, 155.06, 154.98, 153.86, 153.76, 139.24, 139.18, 137.27, 128.75, 128.54, 125.64, 123.58, 117.40; MS (MALDI-TOF): *m/z* (%): 1775 (46) $[M - PF_6]^+$, 1630 (97) $[M - 2PF_6]^+$, 1485 (100) $[M - 3PF_6]^+$; elemental analysis calcd (%) for $C_{60}H_{54}F_{24}N_{14}O_6P_4Os_2$ hexahydrate: C 35.54, H 2.68, N 9.67; found: C 35.36, H 2.55, N 9.37.

[(tpy)Ru(azotpy)Os(tpy)][PF$_6$]$_4$ (Ru-azotpy-Os): A solution of [Ru(tpy)-(azotpy)][PF_6]$_2$ (80 mg, 0.072 mmol) and [Os(tpy)$(H_2O)_3$][PF_6]$_3$ (66 mg, 0.072 mmol) in ethylene glycol (20 mL) was heated at 150 °C under N_2 for 1 h.[25] The reaction solution was cooled to room temperature and excess aqueous NH_4PF_6 (400 mg) was added. The precipitate was collected by filtration, washed with water and diethyl ether, and dried in vacuo. The dense purple powder (132 mg) was purified by preparative TLC on silica with acetonitrile/0.4 M aqueous KNO_3 (3:1) as eluent to give a dense brown-purple powder (25 mg, 19%). M.p. > 375 °C; ^{1}H NMR (400 MHz, CD_3CN, 20 °C): $\delta = 9.42$ (s, 2H), 9.38 (s, 2H), 8.85 (d, $J = 8.3$ Hz, 2H), 8.82 (d, $J =$ 8.3 Hz, 2H), 8.76 (dd, $J = 7.8$, 2.4 Hz, 4H), 8.54 (dd, $J = 8.3$, 7.8 Hz, 4H), 8.50 (t, $J = 8.3$, 7.8 Hz, 1H), 8.07 (t, $J = 8.3$, 7.8 Hz, 1H), 8.05 (dt, $J = 8.3$, 1.5 Hz, 2H), 7.97 (dt, $J = 7.8$, 1.5 Hz, 2H), 7.92 (dt, $J = 8.3$, 1.5 Hz, 2H), 7.82 (dt, $J = 7.8$, 1.5 Hz, 2H), 7.49 (d, $J = 5.4$ Hz, 2H), 7.46 (d, $J = 4.9$ Hz, 2H), 7.34–7.37 (overlapping d (2H) and d (2H), $J = 5.4$, 4.9 Hz), 7.28 (dt, $J = 6.6$, 1.0 Hz, 2H), 7.25 (dt, $J = 6.6$, 1.0 Hz, 2H), 7.21 (dt, $J = 6.6$, 1.5, 1.0 Hz, 2H), 7.14 (dt, $J = 6.6$, 1.5, 1.0 Hz, 2H); ^{13}C NMR (100 MHz, CD_3CN, 20 °C): $\delta =$ 160.47, 159.98, 158.61, 158.57, 157.72, 156.55, 156.37, 155.60, 154.98, 154.89, 153.91, 153.79, 153.57, 153.37, 139.31, 139.26, 139.21, 139.19, 137.50, 137.44, 128.79, 128.54, 128.36, 125.65, 125.47, 124.75, 123.60, 117.71, 117.50; MS (MALDI-TOF): *m/z* (%): 1540 (55) $[M - 2PF_6]^+$, 1395 (100) $[M - 3PF_6]^+$. The purity of Ru-azotpy-Os was carefully confirmed by TLC.

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