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Photoinduced Intercomponent Energy Transfer in a New Heterometallic Dinuclear Complex of Ru(II) and Os(II) with a 3,5-Bis(2-pyridyl)-1,2,4-triazole Cyclohexyl-Bridged Spacer

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Introduction

Design and synthesis of polynuclear metal complexes based on luminescent and redox-active building blocks are attractive topics for both theoretical and applicative reasons.[1] In particular, development of this field would contribute to the design of metal-based supramolecular systems featuring made-to-order energy migration and redox patterns, which could play a role in light-energy conversion schemes,[1,2] information treatment, and signal processing.[3]

In a recent paper we reported the synthesis and the photophysical and electrochemical properties of new homometallic dinuclear compounds containing the $Ru(bpy)_2^{2+}$ and $Os(bpy)_2^{2+}$ building blocks (bpy = 2,2′-bipyridine).[4] In those systems, the metal-based building blocks were arranged in dinuclear structures by the use of a novel bridging ligand, based on 3,5-bis(2-pyridyl)-1,2,4-triazole moieties connected by a cyclohexyl derivative spacer (dpt-cy-dpt, Figure 1). We learned from that study that only a weak interaction (if any) can occur between the components across the dpt-cy-dpt bridge. However, no information could be obtained on the allowedness of intercomponent energy and/or electron transfer processes in these species. To investigate the latter topic we have now synthesized the heterometallic dinuclear compound of formula $[(bpy)_2Ru(dpt\text{-}cy\text{-}dpt)Os(bpy)_2]^{4+}$ (**1**), by taking advantage of the so-called "complexes as ligands/complexes as metals" synthetic strategy.[5]

Here we report the synthesis of **1** and demonstrate that photoinduced energy transfer occurs in this species. This result indicates that dpt-cy-dpt and other related spacers are suitable bridges to build up polynuclear metal complexes featuring photoinduced intercomponent energy- and electron-transfer processes.

Experimental Section

The first step (i) of the synthetic procedure was to prepare the "complex-ligand" mononuclear species $[(bpy)_2Ru(dpt\text{-}cy\text{-}dpt)]^{2+}$ (**2**), which is also a new complex, by an equimolecular reaction between $Ru(bpy)_2Cl_2$[6] and dpt-cy-dpt.[4] In the second step (ii), **2** is used as a ligand to react with the "complex-metal" $Os(bpy)_2Cl_2$:[7] this reaction affords **1** in good yield (70%) and purity. The procedure is schematized in Figure 1. Details are given in the supplementary material.

The equipment used for spectroscopic, photophysical, and electrochemical measurement has been previously described.[4,5b]

Results and Discussion

Electrochemistry. Previous studies on the parent homometallic dinuclear species have shown that the bridging ligand used in **1** allows only a very weak interaction between the metal-containing subunits.[4] Therefore, **1** can be considered a supramolecular species made of $Ru(bpy)_2(dpt)^{2+}$ and $Os(bpy)_2(dpt)^{2+}$ components connected to each other by the cyclohexyl-derivatized spacer. The absorption and electrochemical properties of the title compound are therefore expected to be the superposition of the absorption and electrochemical properties of the single components. On this assumption, two oxidation processes are expected for **1**, concerning oxidation of the Os(II) center followed by oxidation of the Ru(II) center at higher potential, in agreement with the literature data[8,9] and with the results on parent dinuclear species.[4] Indeed, cyclic voltammetry (CV) and differential pulse voltammetry (DPV) of **1** showed two reversible one-electron oxidation processes occurring at +0.79 V and +1.30 V *vs* SCE (Table 1), which by comparison with data of the parent compounds are confidentially assigned to oxidation of the osmium and ruthenium centers, respectively.

On reduction, two successive, reversible reduction peaks at −1.33 and −1.51 V are shown in CV and DPV experiments. The analysis of the half-height widths and intensities of the DPV peaks, as well as the comparison with the peaks of the oxidation pattern, points out that each reduction peak comprises two one-electron reductions concerning two noninteracting sites.[5b,d,10] The first peak is assigned to independent first reduction of one Ru-coordinated bpy and one Os-coordinated bpy, and the second peak is assigned to independent first reduction of the remaining bpy ligands. As also demonstrated in other polypyridine metal complexes, reduction of bypiridine ligands is only hardly affected by replacing Ru with Os. Reduction of dpt-cy-dpt does not occur within the potential window investigated (> −1.80 V *vs* SCE).

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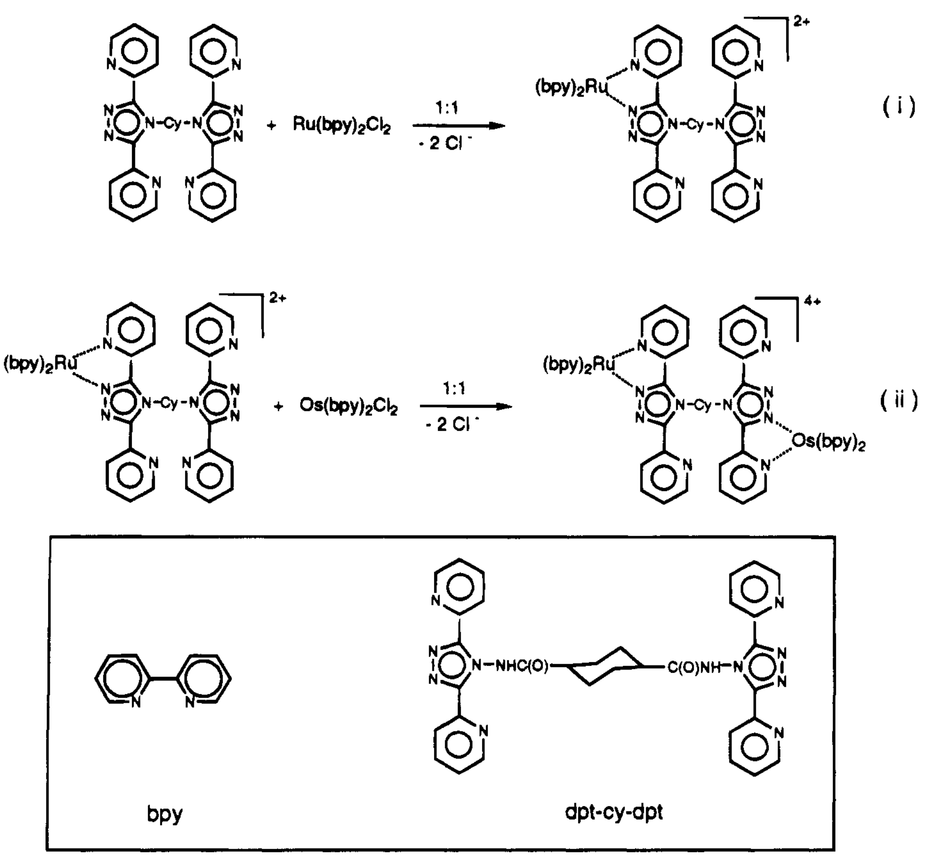

Figure 1. Structural formulas of the ligands and schematic procedure for the synthesis of **1**.

Table 1. Absorption Spectra, Luminescence, and Electrochemical Properties of the New Complex **1** and of Its Parent Dinuclear Species[a]

complexes		abs at 298 K λ_{max}, nm	luminescence				electrochemistry	
			298 K		77 K[b]			
no.	formula	(ϵ, 10^{-3} M^{-1} cm^{-1})	λ_{max}, nm	τ, ns	λ_{max}, nm	τ, μs	oxidn, V vs SCE	redn, V vs SCE
1	$(bpy)_2Ru(dpt\text{-}cy\text{-}dpt)Os(bpy)_2^{4+}$	450 (22.0)	620 724	56[c] 34[e,f]	580 715[g]	4.85[c] 0.90[e]	+0.79, +1.30	−1.33,[d] −1.51[d]
3	$(bpy)_2Ru(dpt\text{-}cy\text{-}dpt)Ru(bpy)_2^{4+}$	446 (25.0)	638	95	578	4.37	+1.33[d]	−1.30,[d] −1.54[d]
4	$(bpy)_2Os(dpt\text{-}cy\text{-}dpt)Os(bpy)_2^{4+}$	477 (15.6)	725	38	716	0.95	+0.84[d]	−1.27,[d] −1.58[d]

[a] Acetonitrile air-equilibrated solutions, unless otherwise noted. For 3 and 4, see also ref 4. Luminescence maxima are not corrected for photomultiplier response. Experimental errors are as follows: absorption maxima, ± 2 nm; extinction coefficients, 15%; luminescence maxima, ± 4 nm; luminescence lifetimes, 15%; redox potentials, ± 20 mV. [b] In MeOH/EtOH 4/1 (v/v) rigid matrix. [c] Measured for λ_{em} = 580 nm. [d] Dielectronic peak. [e] Measured for λ_{em} = 750 nm. [f] A longer−lived component is present in the tail of the decay trace, but its lifetime could not be measured because of the low intensity. [g] Maximum obtained by subtracting from the 77 K luminescence spectrum of **1** the 77 K luminescence spectrum of **2**, normalized at 580 nm.

Absorption and Luminescence Properties. The absorption spectrum of **1** (Table 1 and the figure in the supplementary material) is dominated by a strong band in the UV region (λ_{max} = 280 nm, ϵ = 75 000 M^{-1} cm^{-1}), mainly due to a $\pi \rightarrow \pi^*$ transition centered on the bpy ligands and by a moderately strong band in the visible region (λ_{max} = 450 nm, ϵ = 22 000 M^{-1} cm^{-1}). A tail is also apparent at lower energies. The band peaking at 450 nm is due to overlapping Ru → bpy and Os → bpy charge transfer (CT) transitions. The sum divided by two of the absorption spectra of the homometallic dinuclear species $[(bpy)_2Ru(dpt\text{-}cy\text{-}dpt)Ru(bpy)_2]^{4+}$ (**3**) and $[(bpy)_2Os(dpt\text{-}cy\text{-}dpt)Os(bpy)_2Cl_2]^{4+}$ (**4**) gives a spectrum quite similar to the experimental spectrum of **1**, confirming the band attribution in **1** and the fact that the metal units are only very weakly coupled.

1 exhibits two emission features both at room temperature in acetonitrile solution and at 77 K in MeOH/EtOH 4/1 (v/v) rigid matrix, with lifetimes in the range 10^{-8}−10^{-6} s (Table 1, Figure 2). In both cases, emission are attributed to triplet Ru → bpy CT (the one at higher energy) and to triplet Os → bpy CT (the one at lower energy) levels. The dual nature of the luminescence is furtherly confirmed by the dependence of the emission spectra on the excitation wavelength. In fact, comparison of luminescence spectra (both at room temperature and 77 K) taken with a different excitation wavelength (for example, 420 or 500 nm) has shown that the lower-energy component of the emission is enhanced with respect to the higher-energy component for a longer excitation wavelength.

Photoinduced Intercomponent Processes. The contemporary presence of Ru → bpy CT and Os → bpy CT excited states, each one located in a different subunit of the dinuclear structure, makes possible the occurring of an electronic energy transfer process from the (upper-lying) triplet Ru-based excited chromophore to the (lower-lying) triplet Os-based one.[11,12] The

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(11) Singlet−singlet energy transfer is considered less probable because in mononuclear Ru(II) and Os(II) polypyridine complexes light excitation causes the population of the lowest energy triplet level with 100% efficiency[12a−c] on the subpicosecond time scale.[12d−f] We assume that in the present system the actual result of light excitation is population with unitary efficiency of the lowest energy ^{3}MLCT level of the component where light absorption has taken place.

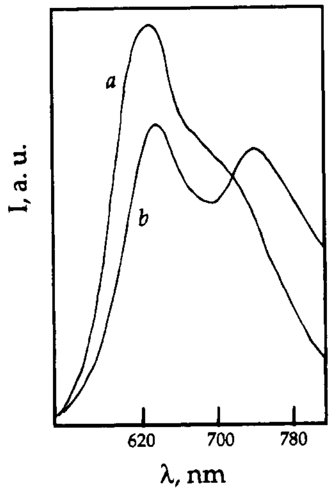

Figure 2. Luminescence spectra of isoabsorptive air-equilibrated acetonitrile solutions of **1** (*b*) and of a 1:1 mixture of **3** and **4** (*a*) at the isosbestic point (469 nm) at room temperature. Excitation wavelength is 469 nm.

efficiency and rate of such a process depends on the distance and the electronic coupling between the sites, which can be mediated by the spacer,[13,14] and on the driving force.[15] To investigate the quenching process, we compared the emission spectrum of a 1:1 mixture of **3** and **4** (solution *a*) and the emission spectrum of an isoabsorptive (at 469 nm, the isosbestic point, that was also the excitation wavelength) solution of **1** (solution *b*) (Figure 2). In this manner, light excitation was equally distributed between the Ru and Os centers in both the experiments. In this condition, the intensity of the Ru-based emission centered at 630 nm of *a* reduces to about $^2/_3$ in *b*, while at the same time the intensity of the Os-based emission results enhanced of about the same quantity. This indicates that quenching of the Ru-based emission is followed by sensitization of the Os-based luminescence, suggesting the occurrence of an intramolecular electronic energy transfer from Ru → bpy to Os → bpy level.[16]

Luminescence lifetime analysis confirms the quenching process. In fact, the luminescence decay of **1** at 600 nm (the Ru-based emission) yields a lifetime of 56 ns, which when compared with the lifetime of the parent homometallic dinuclear Ru compound **3** (95 ns, Table 1) suggests that another deactivation pathway adds in **1** to the deactivation pathways of the Ru-based emission in **3**. As far as the luminescence decay of **1** measured at 760 nm (i.e.; the Os-based emission) is concerned, a biphasic behavior is expected, as also pointed out by one of the reviewers. In fact, the Os luminescent level should be formed directly by light excitation *and* by energy transfer from the Ru → bpy CT level. However, we were able to obtain only one reliable decay constant, virtually equivalent to the Os emission lifetime in **4** (Table 1). A second, longer-lived component could be detected in the tail of the luminescence decay, but it substantially merges with the noise in the single photon counting experiments and cannot be measured with sufficient confidence. Preferential population of the Os-bpy level by the light excitation (excitation wavelength, 337 nm) and similarity between the expected lifetimes are probably at the origin of the difficulties in making in evidence the biphasic behavior.

The intercomponent process is apparently forbidden at low temperature in rigid matrix. In fact, the two emission bands of **1** at 77 K exhibit the same lifetimes of the separated metal-based components (Table 1).

The rate constant k_q for Ru-based luminescence quenching at room temperature can be calculated from the equation $k_q = 1/\tau - 1/\tau_0$, where τ and τ_0 are the luminescence lifetimes of the Ru-based component in **1** and **3**, respectively. From this equation, k_q is determined to be 0.8×10^7 s^{-1}. Intermolecular energy transfer from the Ru → bpy CT level of $Ru(bpy)_3^{2+}$ to the Os → bpy CT level of $Os(bpy)_3^{2+}$ is almost diffusion controlled in fluid solution,[17] indicating that the order of magnitude of the energy-transfer rate in the encounter complex is larger than 1×10^9 s^{-1}. The small value of the rate constant in **1** can be attributed to the separation and restricted orientations between donor and acceptor partners imposed by the semirigid bridging ligand. In fact, the shortest through-space center-to-center distance between the metal-based components, *r*, approximates 11 Å (estimated from CPK models for a folded conformation). Other conformers with similar (or lower) energies can exist, but they all exhibit longer center-to-center distances.

As far as the mechanism of the process is concerned, a detailed discussion would be rather speculative and out of the aim of this note. Anyway, some considerations deserve to be made. First, sensitization of the Os-based emission alone is not sufficient to indicate direct energy transfer as the sole mechanism for the Ru-based emission quenching in **1**. In principle, the observed quenching could be due to the reductive electron transfer schematized in eq 1 (see also Figure 3, process *II*; for simplicity reason, only one bpy ligand for each metal is reported, and the real oxidation states of the metals, as well as the charges of the compound, are neglected).

$$\text{bpy}^{-}\text{—Ru}^{+}\text{—dpt-cy-dpt—Os—bpy} \rightarrow \text{bpy}^{-}\text{—Ru—dpt-cy-dpt—Os}^{+}\text{—bpy} \quad (1)$$

From the excited-state energy of the Ru-based unit (2.14 eV, estimated by 77 K emission spectrum) and the redox potentials shown in Table 1, it can be observed that such a process is slightly exergonic ($\Delta G = -0.02$ eV). Once formed, the product of the electron-transfer process *II* could undergo a further electron transfer (process *III* of Figure 3), which is probably faster than process *II* because of a higher driving force. The final product of the total process *II* + *III* is again the triplet Os → bpy CT level, so justifying sensitization of the Os-based luminescence.

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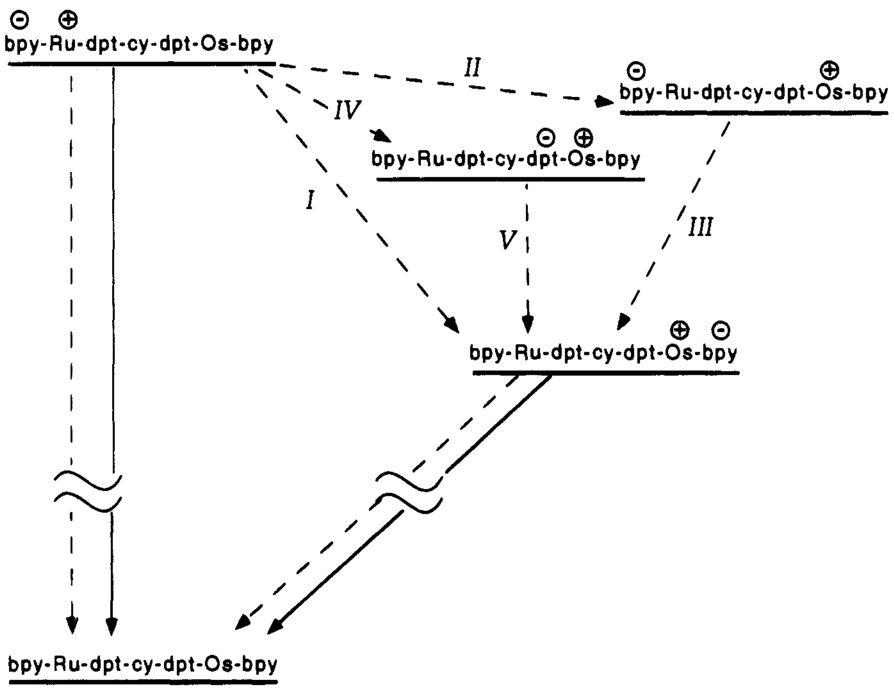

Figure 3. Schematic representation of the deactivation processes of Ru → bpt CT excited state discussed in the text. Solid and dashed lines indicate radiative and radiationless processes, respectively. For simplicity reason, only one bpy ligand for each metal is reported, and the real oxidation states of the metals, as well as the charges of the compound, are neglected. The energy levels are not in scale.

Another pathway for energy transfer should also be considered. In fact, a rough estimation of the energy level of the Os → dpt CT excited state[18] suggests that energy transfer from Ru → bpy CT level to Os → dpt CT excited state (Figure 3, process *IV*) could be exergonic and compete with the other deactivation processes. Once formed, Os → dpt CT would relax promptly to Os → bpy CT (Figure 3, process *V*; note that *V* is a deactivation process between excited states of the same subunit, and should occur in the subpicosecond timescale[12d–f]), once more yielding sensitization of Os → bpy CT emission as the final result. Actually, intermediate energy excited states have been demonstrated to be effectively involved in bimolecular electron-transfer processes, when particular reorganization energy and driving force parameters are fitted.[21]

It should be noted that the quenching processes represented in Figure 3 are expected to have different driving forces, reorganization energies, and electronic factors. Therefore, it would be necessary to study a family of similar, suitably designed dinuclear species to evaluate the importance of each process in **1**. Work toward this direction has been planned in our laboratories.

Conclusion

Photoinduced intercomponent energy transfer occurs in $[(bpy)_2Ru(dpt\text{-}cy\text{-}dpt)Os(bpy)_2]^{4+}$ from the higher-lying Ru → bpy CT level to the lower-lying Os → bpy CT excited state, with a rate constant of $0.8 \times 10^7\ s^{-1}$. This result indicates that dpt-cy-dpt and other related spacers can be used to build up polynuclear metal complexes featuring photoinduced intercomponent energy- and electron-transfer processes.

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Supplementary Material Available: Detailed synthesis of the new compounds **1** and **2** and a figure showing the absorption and emission (at 77 K) spectra of **1** are given (2 pages). Ordering information is given on any current masthead page.

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(18) The Os → dpt CT level is difficult to determine with a good approximation, but it can be tentatively estimated by the following considerations. (i) The first reduction potential of the compound $Ru(1M3ptr)_3{}^{3+}$ in acetonitrile (1M3ptr = 1-methyl-3-(pyridin-2-yl)-1,2,4-triazole) has been reported to be −1.75 V *vs* SCE;[19] such a potential is assigned to reduction of the triazole ligand and approximately gives the energy of the π^* orbital of this ligand in metal(II)-polypyridine compounds. (ii) If one considers the π^* energy level of 1M3ptr in $Ru(1M3ptr)_3{}^{2+}$ as a good model for the π^* energy level of dpt in the $Os(bpy)_2(dpt)^{2+}$ unit,[20] $\Delta E = e(E_{ox}(Os) - E_{red}(dpt)) = {\sim}2.54$ eV for the latter complex. (iii) On the basis of the linear relationship between ΔE and the energy of the corresponding MLCT excited state in Ru- and Os-polypyridine compounds,[8,9] one would gain ~2.07 eV for the energy level of the Os → dpt CT excited state of **1**. Because of the assumptions we have made in points i–iii, however, the energy of the Os → dpt CT excited state so obtained should be taken with much care.

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