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Intramolecular Electronic Energy Transfer in a Pyrene-Labeled Ruthenium(II)-Trisbipyridine Hemicage Complex

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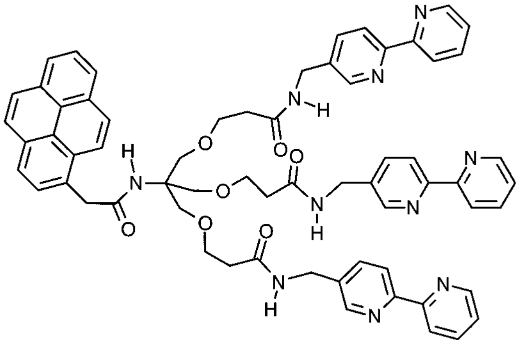
Introduction

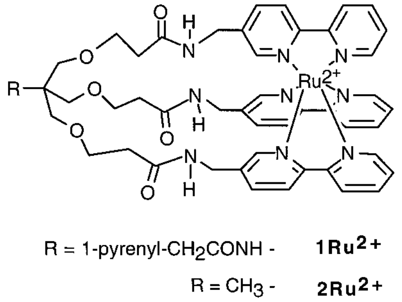
The design of luminescent polypyridine−ruthenium(II) complexes is a subject of paramount interest owing to their potential as versatile light-harvesting units for the elaboration of multicomponent supramolecular systems endowed with photo- and electroactive properties.[1−3] Particularly interesting are those systems that present a long-lived MLCT (metal-to-ligand charge transfer) excited state[4,5] for many applications, such as luminescence-based sensing or photochemical conversion and storage of solar energy.[6−11] $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) represents the archetype of such complexes, and the lifetime of its ^{3}MLCT triplet state is about 1 μs in deaerated acetonitrile at room temperature.[4] Several design strategies were reported to allow a substantial elongation of that triplet lifetime. Suitable hemicaging or caging of the $[Ru(bpy)_3]^{2+}$ structure using, respectively, tripod-like or macrobicyclic ligands incorporating three bpy units, was demonstrated to prevent excited-state ligand photodissociation, thereby providing for increased excited-state lifetime and photostability toward ligand ejection.[12,13] Recently, it has been observed that reversible triplet energy transfer can occur between pyrene and a Ru(II) polypyridine complex, which results in a dramatic increase of the excited-state lifetime of the latter.[14−18]

To our knowledge, there is no example in the literature of hemicage Ru(II) polypyridine complex systems labeled with a pendant aromatic chromophore. In that connection we envisaged the synthesis of the fluorescent tripodal ligand **1** (Scheme 1), which was anticipated to allow the preparation of the pyrene-tethered hemicaged Ru(II) complex, **1**Ru^{2+}. Recently, the study of a series of fluorescently labelled tripod-like chelators[19,20] confirmed that attachment of the photosensitive group to the bridgehead carbon atom of the tripod did not interfere with metal cation binding and warranted excited-state communication between the chromophore and the hemicaged metal.[19,20b]

Scheme 1. The Pyrene-Labeled Tripodal Ligand **1**



Scheme 2. Schematic Structure of the Ruthenium(II)−Trisbipyridine Hemicage Complexes



Here we describe the synthesis of compound **1** and the preparation and photophysical study of **1**Ru^{2+}. To investigate the effect of the tripodal structure on the excited-state behavior of **1**Ru^{2+}, we report also on the model ligand compound **2** and its monuclear **2**Ru^{2+} complex (Scheme 2).

Experimental Section

All solvents for syntheses were purified using standard procedures. Spectroscopic grade acetonitrile (Carlo Erba) was used as supplied. Mass spectrometry was performed with either a VG analytical Autospec-Q (FAB) or a Micromass TofSpec E (MALDI-TOF). The 5-aminomethyl-2,2′-bipyridine **4** and $Ru(DMSO)_4Cl_2$ were synthesized by following published procedures.[21−23] The syntheses of the tripod ligand **2** and the pyrene-containing triacid compound **3** were previously described.[20]

Electronic absoption spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. The emission and luminescence excitation

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Table 1. Spectroscopic and Photophysical Data in Acetonitrile at 298 K

	absorption				emission		
	λ_{max} (nm)	ϵ_{max} (M^{-1} cm^{-1})	state	chromophore	λ_{max} (nm)	τ (ns)	Φ_{em}
1	342	35 000	^1L_a	pyrene	375	200	0.55
	279	shoulder	$\pi-\pi^*$	bpy			
	275	shoulder	^1B_b	pyrene			
	242	100 000	^1B_a	pyrene			
2	279	55 000	$\pi-\pi^*$	bpy			
1Ru^{2+}	451	9000	MLCT	Ru	606	2100[a]	0.040
	343	29 000	^1L_a	pyrene			
	291	73 000	$\pi-\pi^*$	Ru			
	277	60 000	^1B_b	pyrene			
	243	70 000	^1B_a	pyrene			
2Ru^{2+}	453	9700	MLCT		604	980	0.043
	291	75 000	$\pi-\pi^*$				
1-Et pyrene	341	43 800	^1L_a		375	193	0.64
	274	60 000	^1B_b				
	241	85 000	^1B_a				
$[Ru(bpy)_3]^{2+}$	452	13 600	MLCT		609	890	0.063
	288	76 600	$\pi-\pi^*$				

[a] Degassed using freeze−pump−thaw technique.

spectra, corrected for the lamp spectrum, were obtained with a Jobin Yvon Spex Fluorolog FL 111 spectrofluorimeter. Phosphorescence emission spectra were obtained with a Hitachi F4500 spectrophotometer. Emission quantum yields for argon-degassed acetonitrile solutions of the complexes were determined relative to an aqueous solution of $[Ru(bpy)_3]^{2+}$ (Strem Chemicals, 99%) using $\phi_{em} = 0.042$ as a reference.[24] Excited-state lifetimes were determined by laser flash spectroscopy, using an excimer laser (Lambda Physik EMG 100, 308 nm pulses of duration 10 ns and energy 150 mJ) as pump for a tunable dye laser (Lambda Physik FL 2000, pulses of duration 8 ns and energy 10 mJ).[25] The detection system consisted of a Jobin Yvon H25 monochromator, a Hamamatsu R955 photomultiplier, and a Le Croy 9362 digital oscilloscope. The laser intensity was attenuated to avoid biphotonic effects. The measurements were performed at room temperature. The analysis was carried out within the first millimeter of the sample excited by the laser pulse, using 10 mm length quartz cells. The concentration of the acetonitrile solutions was such that the absorption optical density was around 0.8 at the excitation wavelength of the laser. Unless otherwise stated, solutions were deaerated by bubbling 15 min with argon before experimentation.

Tris[*N*-(2,2′-bipyridyl-5-ylmethyl)aminocarbonylethoxymethyl]-*N*′-pyren-1-ylmethylcarbonylaminomethane (1). A mixture of triacid **3** (0.52 g, 0.9 mmol), dicyclohexylcarbodiimide (0.83 g, 4 mmol), and *N*-hydroxysuccinimide (0.46 g, 4 mmol) in freshly distilled DMF (10 mL) was stirred at room temperature for 24 h. After filtration of the precipitated dicyclohexylurea, the amine **4** (0.745 g, 4 mmol) in DMF (10 mL) was added to the filtrate, and the mixture was stirred at 50 °C for 4 days. After cooling and removal of the solvent, the yellow-green oily crude compound was subjected to column chromatography on alumina, eluting with dichloromethane/methanol (95:5, v/v). Ligand **1** was obtained as a beige solid (0.82 g, 84%), mp 224 °C: ^1H NMR ($CDCl_3$) δ 8.60 (t, 3H, N*H*), 8.4−6.9 (m, 30H, Ar), 6.10 (s, 1H, N*H*), 4.20 (d, 6H, bpy-C*H*$_2$), 4.10 (s, 2H, pyrene-C*H*$_2$), 3.41 (s, 6H, C-C*H*$_2$-O), 3.39 (t, 6H, O-C*H*$_2$-CH$_2$), 2.03 (t, 6H, O-CH$_2$-C*H*$_2$); HR-MS (FAB$^+$) *m*/*e* 1081.47141 (calcd for $C_{64}H_{61}N_{10}O_7$, 1081.47247). Anal. Calcd for $C_{64}H_{61}N_{10}O_7{\cdot}2H_2O$: C, 69.44; H, 5.85; N, 12.52. Found: C, 68.91, H, 5.71, N, 12.62.

(1Ru)(PF$_6$)$_2$. A solution of ligand **1** (50 mg, 0.046 mmol) and $Ru(DMSO)_4Cl_2$ (22.3 mg, 0.046 mmol) in absolute ethanol (20 mL) was refluxed under argon atmosphere for 3 h. After removal of the solvent the residue was dissolved in H_2O and the solution was filtered. After addition of a saturated aqueous solution of NH_4PF_6 to the filtrate, the orange precipitate was filtered off, washed with water, and redissolved in acetonitrile. Slow addition of diethyl ether caused the precipitation of the compound, which was successively subjected to size-exclusion chromatography on Sephadex LH-20 eluted with a 4:4:1 mixture of acetone/CH_2Cl_2/MeOH and then to column chromatography on silica gel eluted with a 80:15:5 mixture of DMF/ethanol/H_2O saturated with NH_4PF_6. The orange, slow running fractions were collected and evaporated to dryness. The compound was dissolved in acetonitrile and precipitated by addition of ether to give (1Ru)(PF$_6$)$_2$ (15%): MS (MALDI-TOF) *m*/*e* 1325 (M − PF$_6$), 1180 (M − 2PF$_6$). Anal. Calcd for $C_{64}H_{61}N_{10}O_7P_2F_{12}{\cdot}4H_2O$: C, 49.74; H, 4.50; N, 9.06. Found: C, 49.95; H, 4.49; N, 8.80.

(2Ru)(PF$_6$)$_2$. Following the same procedure as above, (2Ru)(PF$_6$)$_2$ was obtained in 15% yield contaminated with a small amount of the binuclear complex $[(\mathbf{2})_2(Ru)_2]^{4+}$: FAB-MS *m*/*e* 2315 (2M − PF$_6$), 1084 (M − PF$_6$), 939 (M − 2PF$_6$). Anal. Calcd for $C_{47}H_{51}N_9O_6P_2F_{12}{\cdot}1H_2O$, $1(CH_3CH_2)_2O$: C, 46.36; H, 4.81; N, 9.54. Found: C, 46.01; H, 4.81; N, 9.80.

Results and Discussion

The synthesis of ligand **1** was performed by following a procedure similar to that reported for **2**.[20a] The mononuclear ruthenium(II) complex **1**Ru^{2+} was obtained by reaction of **1** with $Ru(DMSO)_4Cl_2$, as source of ruthenium(II),[23] in refluxing ethanol. The same methodology was utilized for the preparation of **2**Ru^{2+}.[26] For both Ru(II) complexes, proton NMR spectra at room temperature were rather complex, particularly in the aromatic proton resonances region. The aliphatic part showed single sets of unresolved, broadened peaks for the resonance signals of the diastereotopic methylene protons of the tripodal unit. Mass spectrometry was used to ascertain the structure of the complexes. FAB and MALDI-TOF mass spectra of **1**Ru^{2+} showed the $M^+ - PF_6^-$ and $M^+ - 2PF_6^-$ masses and revealed the absence of any stoichiometries other than 1:1. The FAB mass spectrum of **2**Ru^{2+} indicated the presence of small amounts of the binuclear $[(\mathbf{2})_2(Ru)_2]^{4+}$ species, which could not be separated from the mononuclear complex.

The electronic absorption spectrum of free ligand **1** in acetonitrile solution at room temperature showed a series of intense absorption bands in the UV region. They consisted of the superimposition of the absorption bands of the pyrene and bpy chromophores, identical to those found in the spectra of 1-ethylpyrene[27] and ligand **2**, respectively (Table 1). The lowest energy transition band in the spectrum of compound **1**, lying

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[26] The low synthetic yields are due to the fact that (i) the reactions were not optimized, and (ii) extensive purification, involving consecutive chromatographic steps, was necessary to remove polymeric species.

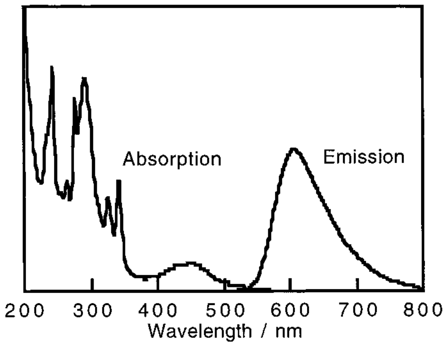

Figure 1. Absorption and luminescence spectra ($\lambda_{exc} = 452$ nm) of **1**Ru^{2+} in deaerated acetonitrile at room temperature.

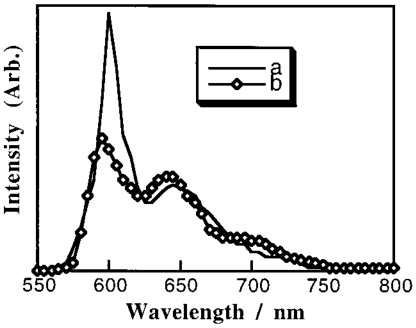

Figure 2. Phosphorescence (a) and total luminescence (b) spectra of **1**Ru^{2+} in 4:1 EtOH/MeOH at 77 K ($\lambda_{exc} = 342$ or 452 nm).

between 310 and 350 nm ($\lambda_{max} = 342$ nm), corresponds to the ^1L_a band of the pyrene nucleus, the forbidden ^1L_b transition band being not observed under these conditions. The UV−vis spectrum of the complex **1**Ru^{2+} in acetonitrile solution is composed of the absorption transition manifolds corresponding to the pyrene and the coordination center (Figure 1, Table 1). The absorption bands for pyrene were found identical to those recorded for the free ligand, a hypochromic effect being noticed for the ^1L_a band. The lowest energy transition in the visible region is due to the MLCT state of the Ru(II)-containing chromophore. The intense ligand centered $\pi-\pi^*$ states of the bipyridine are red-shifted relative to the free ligand and recorded at ca. 291 nm. The absorption spectra of **2**Ru^{2+} and $[Ru(bpy)_3]^{2+}$ reference complex show no significant differences.

Excitation into the pyrene ^1L_a absorption transition ($\lambda_{exc} = 342$ nm) of the free ligand **1** in acetonitrile solution gives rise to the typical fluorescence spectrum of this chromophore. The fluorescence quantum yield ($\Phi_{em} = 0.55$) and the singlet excited-state lifetime ($\tau = 200$ ns) are found similar to those of 1-ethylpyrene and triacid compound **3**,[20b] indicating the absence of any interaction between pyrene and the bpy units in the excited state (Table 1).

The emission spectra of **2**Ru^{2+} and $[Ru(bpy)_3]^{2+}$ exhibited similar features, e.g., structureless emission pointing at 604 nm and an emission lifetime of 980 ns. The emission quantum yield for **2**Ru^{2+} was slightly lower than that for $[Ru(bpy)_3]^{2+}$. These observations indicate that no particular stabilization of the MLCT state is occurring in **2**Ru^{2+}, in contrast to the case of previous hemicage Ru(II) trisbipyridine complexes.[12,13] Consistently, photochemical experiments did not point to any increase of photostability of **2**Ru^{2+} relative to $[Ru(bpy)_3]^{2+}$. Indeed the quantum yields for ligand photosubstitution in acetonitrile containing 0.01 M benzyl(triethyl)ammonium chloride were found to be the same order of magnitude for both complexes (ca. 0.03).[28] This was attributed to the poor conformational rigidity of the coordination sphere of **2**Ru^{2+}, thereby allowing strong nuclear distortion around the metal center during the lifetime of the excited complex.

Upon excitation of the bichromophoric **1**Ru^{2+} complex at 452 nm, the emission spectrum is found to be similar to that of the parent $[Ru(bpy)_3]^{2+}$ species, its maximum being located at 606 nm. Photoexcitation of the aromatic pyrene moiety leads to a spectrum composed of the emission band originating from the MLCT state, identical to that observed above, along with that of the locally excited $\pi\pi^*$ state of pyrene. The latter is found to be of very weak intensity ($\Phi_{em} < 0.001$) as compared to that given by the free ligand, consistent with the behavior of literature complexes in which singlet−singlet intramolecular energy transfer acts as an efficient deactivation process from singlet pyrene.[15] Furthermore the luminescence excitation spectrum observed at 606 nm closely matched the electronic absorption spectrum. The decay of the emission from the $[Ru(bpy)_3]^{2+}$ fragment in **1**Ru^{2+} is monoexponential,[29] a value of 2.1 μs being found for the ^{3}LMCT lifetime independently of the excitation wavelength (342 or 452 nm). The emission spectrum of **1**Ru^{2+}, recorded in a frozen matrix (ethanol/methanol, 4:1, v/v) at 77 K, shows the MLCT emission band of the ruthenium(II) moiety, independent of the excitation wavelength (Figure 2a). When using a phosphoroscope to remove short-lived emissions, the emission spectrum consists mainly of the characteristic emission bands of the triplet $\pi\pi^*$ state of pyrene, a value of 16 780 cm^{-1} being obtained for the 0−0 transition (Figure 2b). A triplet lifetime of 380 ms was recorded. These results are in keeping with those reported by Wilson et al.[15] on a Ru(II) trisbipyridine complex in which one of the bipyridine ligands is covalently linked to a pendant pyrene chromophore via a flexible, nonconjugated linker. It is thus inferred that the elongated lifetime of **1**Ru^{2+} relative to the parent $[Ru(bpy)_3]^{2+}$ species also stems from the occurrence of a reversible, intramolecular electronic energy transfer.[15]

This study illustrates the potential of hemicage ruthenium complexes of pyrene-tethered tripod ligands as promising photoactive systems in which efficient triplet−triplet energy transfer can lead to a significant elongation of the ^{3}MLCT lifetime. Future investigation could focus on the generation of a pyrene-labeled ruthenium(II)−trisbipyridine hemicage complex with increased stability toward excited-state dissociation.

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[29] The absence of any shorter component at the nanosecond time scale was confirmed using the single photon counting technique.[20b]