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Solvent Switching of Intramolecular Energy Transfer in Bichromophoric Systems: Photophysics of (2,2'-Bipyridine)tetracyanoruthenate(II)/Pyrenyl Complexes

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Received February 19, 2003

The supramolecular systems $[\text{Ru}(\text{Pyr}_n\text{bpy})(\text{CN})_4]^{2-}$ ($n = 1, 2$), where one and two pyrenyl units are linked via two-methylene bridges to the $[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-}$ chromophore, have been synthesized. The photophysical properties of these systems, which contain a highly solvatochromic metal complex moiety, have been investigated in water, methanol, and acetonitrile. In all solvents, prompt and efficient singlet–singlet energy transfer takes place from the pyrene to the inorganic moiety. Energy transfer at the triplet level, on the other hand, is dramatically solvent dependent. In water, the metal-to-ligand charge transfer (MLCT) emission of the Ru-based chromophore is completely quenched, and rapid (200 ps for $n = 1$) irreversible triplet energy transfer to the pyrene units is detected in ultrafast spectroscopy. In acetonitrile, the MLCT emission is practically unaffected by the presence of the pyrenyl chromophore, implying the absence of any intercomponent triplet energy transfer. In methanol, triplet energy transfer leads to an equilibrium between the excited chromophores, with considerable elongation of the MLCT lifetime. The investigation of the $[\text{Ru}(\text{Pyr}_n\text{bpy})(\text{CN})_4]^{2-}$ systems in methanol provided a very detailed and self-consistent picture: (i) The initially formed MLCT state relaxes toward equilibrium in 0.5–1.3 ns ($n = 1, 2$), as monitored both by ultrafast transient absorption and by time-correlated single photon counting. (ii) The two excited chromophores decay with a common lifetime of 260–450 ns ($n = 1, 2$), as determined from the decay of MLCT emission (slow component) and of the pyrene triplet absorption. (iii) These equilibrium lifetimes are fully consistent with the excited-state partition of 12–6% MLCT ($n = 1–2$), independently measured from preexponential factors of the emission decay. Altogether, the results demonstrate how site-specific solvent effects can be used to control the direction of intercomponent energy flow in bichromophoric systems.

Introduction

The design and synthesis of supramolecular systems with predetermined pathways for electron and energy transfer is an important goal of current photochemical research.^{1–7}

Supramolecular systems containing polypyridine complexes of d⁶ metals [Ru(II), Os(II), Re(I)] and aryl chromophores (naphthalene, anthracene, pyrene) covalently linked

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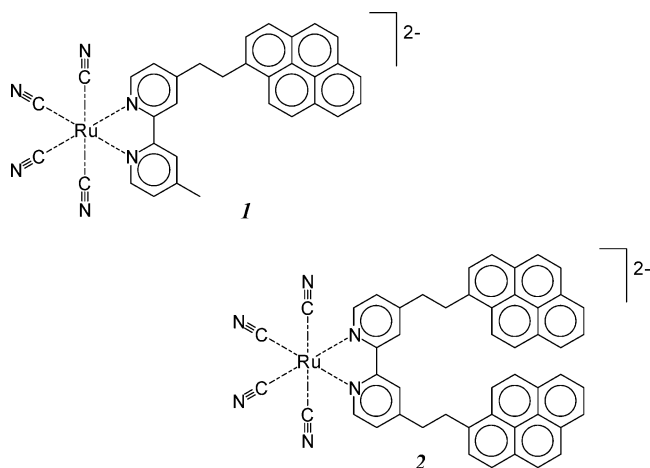
by various types of bridges (aliphatic, conjugated) have been recently under intense study. The main aim of such studies is to produce systems with remarkably long-lived emission.^{8–20} Two types of excited states are involved in the photophysics of such systems: (i) the lowest metal-to-ligand charge transfer (MLCT) state of the metal polypyridine unit; (ii) the lowest $\pi-\pi^*$ triplet state of the aryl unit. The photophysical properties, governed by intramolecular energy transfer processes between the inorganic and organic moieties, are crucially determined by the relative energies of the two types of excited states.⁴

In the systems studied so far, the relative energy of the excited states involved in the energy transfer process is synthetically established. Under these conditions, a large synthetic effort is required to obtain systematic variations in the driving force of the energy transfer process. An alternative strategy to the design of supramolecular systems with tunable driving force is to take advantage of the phenomenon of the second sphere donor–acceptor (SSDA) interactions^{21,22} to modify in a predictable way the energies of the excited states of the metal complex component. Metal complexes with ligands that possess peripheral basic or acid sites are able to establish specific interactions of the donor–acceptor type with the environment and in particular with the solvent.^{21,22} Mixed cyano–polypyridine complexes of Ru(II) are typical examples in which SSDA interactions between the cyanides and the solvent produce a pronounced solvatochromic behavior, both in absorption and in emission: the larger the acceptor character of the solvent (as measured by the Gutmann acceptor number²³), the higher becomes the oxidation potential of the metal center and the higher the energy of the metal-to-bipyridine MLCT excited states.^{22,24–31} As discussed elsewhere,²⁸ the extent of solva-

tochromism depends on the number of cyanide ligands. Thus, the ideal metal-containing candidate for the design of such tunable supramolecular systems would be a tetracyano bipyridine complex. The photophysical properties of $[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-}$ have been studied in detail and found to be extremely solvent-sensitive.^{24,28}

Exploiting the solvent effects on the inorganic chromophore, it should be possible to tune in a predictable way the driving force for intercomponent energy transfer. And in favorable cases, one could even use the solvent to switch the direction of energy transfer between the inorganic and organic chromophore in the supramolecular system. To this purpose, the organic unit should be chosen so as to have its triplet energy within the tunability range of the MLCT state of the tetracyano complex. From this viewpoint, pyrene seems to be a good candidate among the aromatic hydrocarbons. For a number of ruthenium polypyridine complexes bearing attached pyrenyl units a dramatic increase of the excited-state lifetime of MLCT ruthenium triplet has been observed, due to a thermal equilibrium between the lowest triplet of the two chromophores.^{4,8,9,16,19}

In this paper we report on the synthesis and the photophysical properties of the supramolecular systems $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$ (**1**) and $[\text{Ru}(\text{Pyr}_2\text{bpy})(\text{CN})_4]^{2-}$ (**2**), where one and two pyrenyl units are covalently linked to the $[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-}$ chromophore via dimethylene bridges.



This work provides a clear example of solvent control on intercomponent energy transfer in supramolecular systems. In particular, the solvent can be used to switch the direction of energy transfer between the organic and the inorganic

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component. In appropriate solvents, equilibrium between the excited components can be achieved and fine-tuned.

Experimental Section

Materials. $K_4[Ru(CN)_6] \cdot 3H_2O$ (Alfa) and 4,4'-dimethyl-2,2'-bipyridine (Me_2bpy , Aldrich) were commercial products and used as received. $K_2[Ru(4,4'-Me_2bpy)(CN)_4]$ complex was prepared by following the same procedure published for the analogous $K_2[Ru(bpy)(CN)_4]$.³¹ The synthesis of the ligands $Pyrbpy$ and Pyr_2bpy has been described elsewhere.^{16,32} Spectrograde organic solvents (Merck Uvasol) were used. Other chemicals were all of reagent grade quality.

Preparation of the Compounds. The syntheses of the complexes were carried out starting from the tetrabutylammonium (TBA^+) salt of $Ru(CN)_6^{4-}$. This salt was obtained from the potassium salt by ion exchange on cationic SP Sephadex C-25 resin.

$(TBA)_2[Ru(Pyrbpy)(CN)_4]$. In a typical synthesis, a mixture of 460 mg (0.37 mmol) of $(TBA)_4Ru(CN)_6$ and 147 mg (0.37 mmol) of $Pyrbpy$ in 50 mL of 5/1 MeOH/DMF was heated. To the boiling solution 75 μ L of 18 M H_2SO_4 was added. The color of the solution turned from pale to bright yellow. The reaction mixture was refluxed, under argon, for 30 h. After cooling, the solution was evaporated to dryness. The residue was washed with small portions of cold water (3×3 mL) to remove some unreacted $(TBA)_4[Ru(CN)_6]$ and then purified by gel-filtration chromatography using a Sephadex LH20 column and methanol as eluent. Elution with methanol gave a main yellow-orange fraction followed by a fraction containing the unreacted ligand. The eluted solution containing the product was rotary evaporated to dryness, and the resulting violet solid was dried under vacuum. Yield: 60%. 1H NMR (methanol- d_4): δ 9.38 (d, 1H), 9.32 (d, 1H), 8.38–7.78 (m, 11 H), 7.26 (d, 1H), 7.18 (d, 1H), 3.60 (t, 2H), 3.12 (t, 16 H), 3.05 (t, 2H), 2.15 (s, 3H), 1.60 (m, 16 H), 1.38 (m, 16 H), 0.95 (t, 24H). MS (MALDI-TOF, α -cyano-4-hydroxycinnamic acid as a matrix): m/z = 1088.3 ($[M + H]^+$ requires m/z = 1090).

$(TBA)_2[Ru(Pyr_2bpy)(CN)_4]$. The procedure was the same as for $(TBA)_2[Ru(Pyrbpy)(CN)_4]$ using Pyr_2bpy instead of $Pyrbpy$ and pure DMF as reaction solvent. Yield: 80%. 1H NMR (methanol- d_4): δ 9.36 (d, 2H), 8.09–7.06 (m, 22 H), 3.35 (t, 4H), 3.12 (t, 16 H), 2.78 (t, 4H), 1.60 (m, 16 H), 1.38 (m, 16 H), 0.95 (t, 24H). MS (MALDI-TOF, α -cyano-4-hydroxycinnamic acid as a matrix): m/z 1300.4 ($[M + H]^+$ requires m/z = 1304).

Apparatus and Procedures. NMR spectra were measured using a Varian 300 spectrometer (300 MHz).

UV-vis spectra were recorded with a Perkin-Elmer LAMDA40 spectrophotometer. Luminescence spectra were taken on a Spex Fluoromax-2 or on a Perkin-Elmer MPF 44E spectrofluorometer (77 K measurements), equipped with Hamamatsu R928 tubes. The 298 K luminescence spectra were corrected for instrumental response. Emission lifetimes were measured by time-correlated single-photon counting techniques, using a PRA 3000 fluorescence spectrometer equipped with a hydrogen discharge pulsing lamp (50 kHz, half-width 2 ns), a model 1551 cooled photomultiplier, and a Norland model 5000 MCA card. The decays were analyzed by means of Edinburgh FLA 900 software (estimated error on the lifetime = ± 0.1 ns).

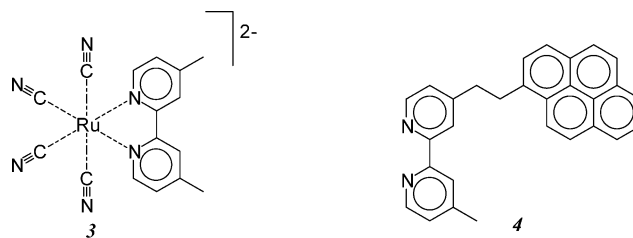
Nanosecond flash photolysis transient absorption experiments were performed with a Continuum Surelight Nd:YAG laser as excitation source by using an apparatus previously described.³³

Ultrafast transient absorption measurements were performed using the apparatus that has been described previously.³⁴

All measurements were carried out on deaerated solutions.

Results

The spectroscopic and photophysical behavior of the supramolecular systems $[Ru(Pyrbpy)(CN)_4]^{2-}$ and $[Ru(Pyr_2bpy)(CN)_4]^{2-}$ can be compared with that of the $[Ru(Me_2bpy)(CN)_4]^{2-}$ model complex (**3**) and of the Pyr_nbpy ($n = 1, 2$)



free ligands (**4**, $n = 1$), which constitute the models for the Ru-based and pyr-based units, respectively. A complete photophysical characterization of the Pyr_nbpy ligands is reported in a recent study.¹⁹ As far as the metal complex (**3**) is concerned, its spectroscopic and photophysical properties are expected to be very similar to those of the unsubstituted $[Ru(bpy)(CN)_4]^{2-}$ complex.^{24,30} In particular, as the behavior is expected to be extremely dependent on solvent,²⁴ solvents of widely different acceptor properties were chosen for this study: water, methanol, and acetonitrile (acceptor numbers 58.4, 41.3, and 19.3, respectively).

UV-Vis Absorption Spectra. The absorption spectra of $[Ru(Pyrbpy)(CN)_4]^{2-}$ and $[Ru(Pyr_2bpy)(CN)_4]^{2-}$ in methanol solution are shown in Figure 1 together with spectra of the $[Ru(Me_2bpy)(CN)_4]^{2-}$ and $Pyrbpy$ model units. The spectra of the multicomponent systems are exactly those expected for 1/1 and 1/2 mixtures of $[Ru(Me_2bpy)(CN)_4]^{2-}$ and $Pyrbpy$, indicating that the electronic interaction between the chromophores of the supramolecular systems is very weak. The spectra are dominated by the intense and structured bands of the pyrene unit in the UV region and by MLCT $Ru(II) \rightarrow bpy$ transitions, typical of the $Ru(II)$ polypyridine complexes, in the visible region.

Paralleling the behavior observed for the model complex, the energy of MLCT bands is extremely sensitive to the solvent which shifts to the red in solvents with low acceptor numbers. The absorption of the pyrene unit, on the other hand, is practically insensitive to the solvent. The absorption spectra of the dyad $[Ru(Pyrbpy)(CN)_4]^{2-}$ in various solvents are shown in Figure 2.

The energies of the lowest MLCT band maximum, λ_{max}^{abs} (298 K), for the model complex $[Ru(Me_2bpy)(CN)_4]^{2-}$ and for $[Ru(Pyrbpy)(CN)_4]^{2-}$ are collected in Tables 1 and 2, respectively.

Emission Measurements. The emission properties of $[Ru(Pyrbpy)(CN)_4]^{2-}$ and $[Ru(Pyr_2bpy)(CN)_4]^{2-}$ are extremely

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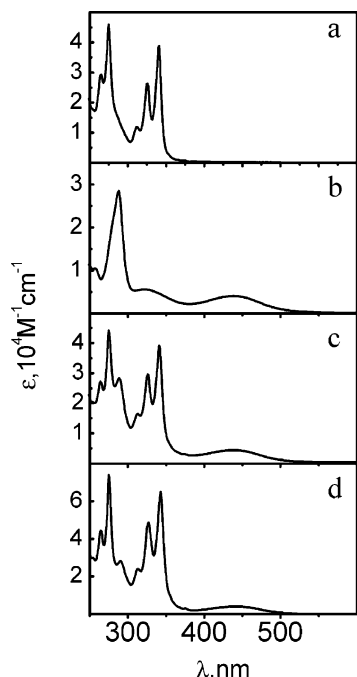


Figure 1. Absorption spectra of (a) Pyrbpy, (b) $[\text{Ru}(\text{Me}_2\text{bpy})(\text{CN})_4]^{2-}$, (c) $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$, and (d) $[\text{Ru}(\text{Pyr}_2\text{bpy})(\text{CN})_4]^{2-}$ in MeOH solution at room temperature.

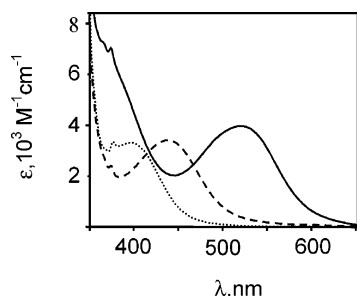


Figure 2. Absorption spectra of $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$ in CH_3CN (continuous line), MeOH (dashed line), and H_2O (dotted line) at room temperature.

solvent dependent. In H_2O the systems are practically nonemitting whereas in MeOH and in CH_3CN solutions at room temperature they exhibit the intense MLCT emission typical of a Ru-based unit. The band shape, energy position, and quantum yield of this emission are identical to those measured in the same solvent for the $[\text{Ru}(\text{Me}_2\text{bpy})(\text{CN})_4]^{2-}$ complex. As for $[\text{Ru}(\text{Me}_2\text{bpy})(\text{CN})_4]^{2-}$, the energy of the MLCT emission is strongly solvent-dependent which shifts, as expected, in the same direction as absorption. In Figure 3 the room-temperature emission spectra in MeOH of $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$ and $[\text{Ru}(\text{Pyr}_2\text{bpy})(\text{CN})_4]^{2-}$ are compared with those of the models. It is important to note that, in all solvents investigated, the typical fluorescence of the pyrene unit is not observed. The excitation spectra of the supramolecular systems match very closely the corresponding absorption spectra.

In CH_3CN the emission decay of both $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$ and $[\text{Ru}(\text{Pyr}_2\text{bpy})(\text{CN})_4]^{2-}$ is monoexponential, with a lifetime practically coincident with the value found for the $[\text{Ru}(\text{Me}_2\text{bpy})(\text{CN})_4]^{2-}$ model (7 ns). In MeOH solutions, however, a clearly nonexponential behavior is observed for

Table 1. Spectroscopic and Photophysical Properties of $[\text{Ru}(\text{Me}_2\text{bpy})(\text{CN})_4]^{2-}$

	solvent (acceptor no.) ^a		
	H_2O (58.4)	MeOH (41.3)	CH_3CN (19.3)
$\lambda_{\text{max}}^{\text{abs}}$ (298 K), ^b nm	392	439	530
$\lambda_{\text{max}}^{\text{em}}$ (298 K), ^c nm	600	640	780
τ (298 K), ^d ns	115	30	7
$10^{-3}E^{0-0}$, ^e cm^{-1}	19.3	17.7	15.3

^a Acceptor numbers were taken from ref 23. ^b Lowest-energy band. ^c Corrected data. ^d Deaerated solution. ^e Excited-state energy estimated from the onset (5% relative intensity) of the room-temperature emission spectrum.

Table 2. Spectroscopic and Photophysical Properties of $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$

	solvent (acceptor no.) ^a		
	H_2O (58.4)	MeOH (41.3)	CH_3CN (19.3)
$\lambda_{\text{max}}^{\text{abs}}$ (298 K), ^b nm	392	439	530
$\lambda_{\text{max}}^{\text{em}}$ (298 K), ^c nm	600 ^d	640	780
τ (298 K), ^e ns	<1	1.2, 260 ^f	7

^a Acceptor numbers were taken from ref 23. ^b Lowest-energy band. ^c Corrected data. ^d Very weak emission. ^e Deaerated solution. ^f Short and long component of the biexponential decay.

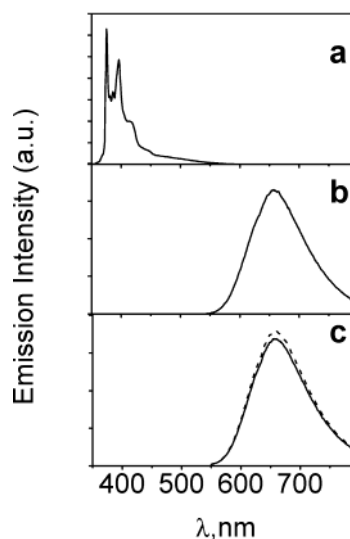


Figure 3. Emission spectra of (a) Pyrbpy, (b) $[\text{Ru}(\text{Me}_2\text{bpy})(\text{CN})_4]^{2-}$, (c) $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$ (continuous line), and $[\text{Ru}(\text{Pyr}_2\text{bpy})(\text{CN})_4]^{2-}$ (dotted line) in MeOH at room temperature.

both systems. The experimental decays measured for $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$ and $[\text{Ru}(\text{Pyr}_2\text{bpy})(\text{CN})_4]^{2-}$ in deaerated MeOH at room temperature are shown in Figure 4. For both systems the emission decay consists of two components: a major short-lived component with a lifetime (τ_1) of few nanoseconds; a minor long-lived component with a lifetime (τ_2) of hundreds of nanoseconds. The experimental values obtained from a biexponential fit are (preexponential factors in parentheses) the following: $\tau_1 = 1.2$ ns (88%) and $\tau_2 = 260$ ns (12%) for $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$; $\tau_1 = 0.6$ ns (94%) and $\tau_2 = 460$ ns (6%) for $[\text{Ru}(\text{Pyr}_2\text{bpy})(\text{CN})_4]^{2-}$.

The emission properties of the supramolecular systems were also studied in a rigid matrix at 77 K (1/1, EtOH/MeOH) and compared with those of the model complex (Figure 5). For both systems, in rigid matrix the emission becomes completely different with respect to that of Ru

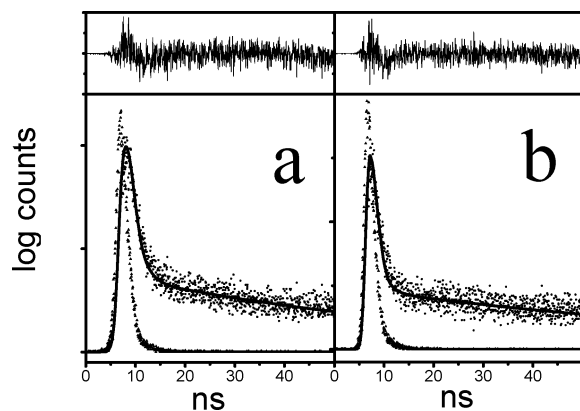


Figure 4. Experimental emission decays (with superimposed lamp profiles) of (a) $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$ and (b) $[\text{Ru}(\text{Pyr}_2\text{bpy})(\text{CN})_4]^{2-}$ in deaerated MeOH solution at room temperature. The solid lines represent fits of the data points to a two-exponential decay law; see text.

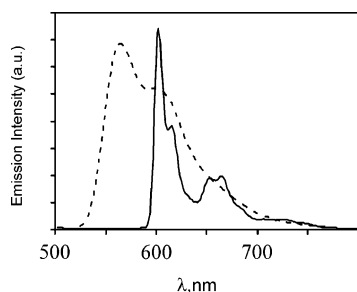


Figure 5. Emission spectra of $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$ (continuous line) and $[\text{Ru}(\text{Me}_2\text{bpy})(\text{CN})_4]^{2-}$ (dashed line) at 77 K in EtOH/MeOH rigid matrix.

model: a structured emission with a pronounced shift to the red was observed. The band shape, the energy position, and the comparison with the emission observed for the Pyrbpy free ligand clearly indicate that this emission is phosphorescence from the triplet state of the pyrene unit.

The relevant photophysical properties for the model complex $[\text{Ru}(\text{Me}_2\text{bpy})(\text{CN})_4]^{2-}$ and for $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$ are collected in Tables 1 and 2, respectively. The data for $[\text{Ru}(\text{Pyr}_2\text{bpy})(\text{CN})_4]^{2-}$ are practically identical to those reported for $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$,³⁵ except for the values of the lifetimes in methanol as reported above.

Transient Absorption Measurements. The supramolecular systems and the models were investigated by both ultrafast (femtosecond) and conventional (nanosecond) laser flash photolysis.

The transient behavior observed following 400 nm excitation in ultrafast spectroscopy is summarized in Figure 6. For the $[\text{Ru}(\text{Me}_2\text{bpy})(\text{CN})_4]^{2-}$ model in aqueous solution, the transient absorption consists of a broad, featureless band tail in the 460–750 nm range (Figure 6a). After a very fast initial change (partial decrease in the red portion, completed in about 10 ps) this absorption remains constant over the whole kinetic range of the experiment (ca. 1 ns). The behavior is practically the same in MeOH. With $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$ in aqueous solution, on the other hand, a clear evolution from

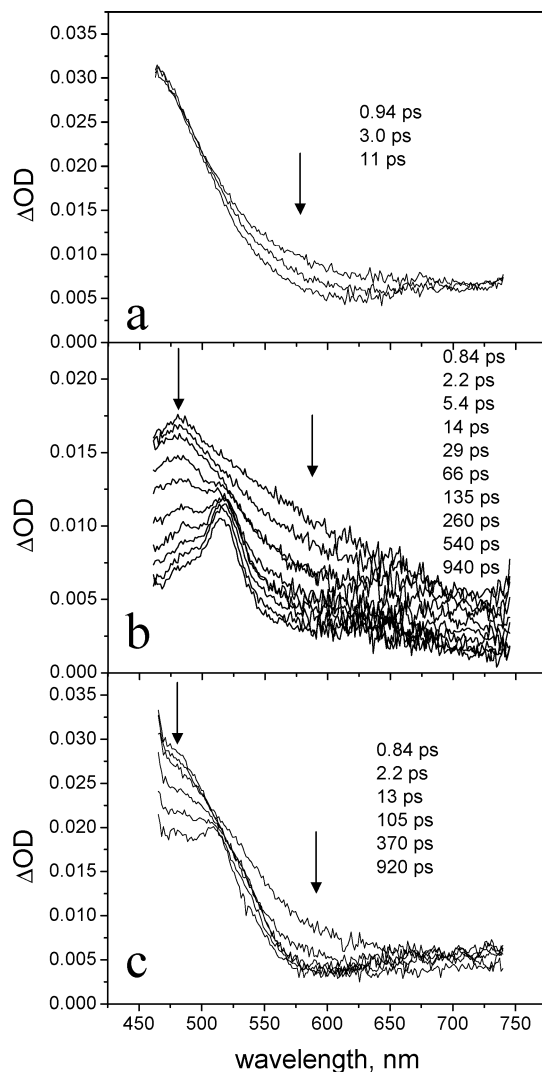


Figure 6. Transient spectral changes measured in ultrafast spectroscopy for (a) $[\text{Ru}(\text{Me}_2\text{bpy})(\text{CN})_4]^{2-}$ in H_2O , (b) $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$ in H_2O , and (c) $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$ in MeOH.

an initial spectrum similar to that of the $[\text{Ru}(\text{Me}_2\text{bpy})(\text{CN})_4]^{2-}$ model to a final spectrum characterized by a sharp maximum at 516 nm is observed (Figure 6b). The behavior is qualitatively the same in MeOH (Figure 6c), although the formation of the maximum at 516 nm is slower and is not yet completed at the end of the temporal window of the experiment. Kinetic analysis of the spectral changes at 480 nm yields lifetimes of 200 ps in H_2O and ca. 1.2 ns in MeOH.³⁶

Figure 7 shows the transient spectra obtained in nanosecond laser flash photolysis of deaerated MeOH solutions, immediately (ca. 10 ns) after the 355 nm excitation pulse.³⁷ For both $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$ (Figure 7c) and $[\text{Ru}(\text{Pyr}_2\text{bpy})(\text{CN})_4]^{2-}$ (Figure 7d) the spectrum is characterized by an intense absorption maximizing at 410 nm.³⁵ This absorption spectrum is very different from that of the model

(35) The identical behavior of $[\text{Ru}(\text{Pyr}_2\text{bpy})(\text{CN})_4]^{2-}$ and $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$ rules out the occurrence of photophysical processes involving the two pyrenyl units, such as, e.g., excimer formation.

(36) These values refer to the main component of the transient decays. The decays are appreciably biexponential, with an additional minor (<20%) short-lived (25–30 ps) component.

(37) The same spectral changes were observed using 532 nm as laser excitation.

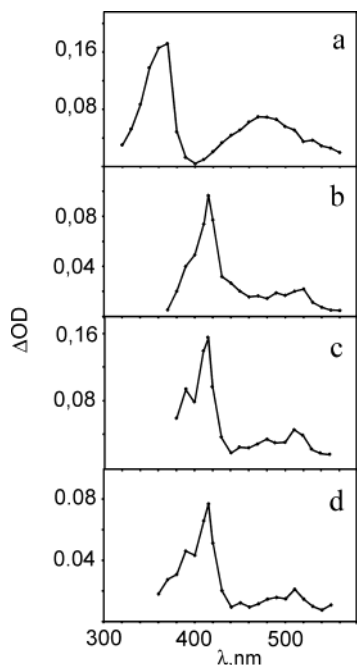


Figure 7. Transient absorption spectra in MeOH solution of (a) $[\text{Ru}(\text{Me}_2\text{bpy})(\text{CN})_4]^{2-}$, (b) Pyrbpy, (c) $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$, and (d) $[\text{Ru}(\text{Pyr}_2\text{bpy})(\text{CN})_4]^{2-}$ taken immediately after the laser pulse ($\lambda_{\text{exc}} = 355$ nm, half-width 8 ns).

complex $[\text{Ru}(\text{Me}_2\text{bpy})(\text{CN})_4]^{2-}$ (Figure 7a) and practically identical to that of the ligand model Pyrbpy (Figure 7b). In the whole spectral region, the decay of all these transient changes was well-modeled by first-order kinetics. The lifetimes for $[\text{Ru}(\text{Me}_2\text{bpy})(\text{CN})_4]^{2-}$ and Pyrbpy were 30 ns and 150 μs , respectively. The lifetimes obtained for $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$, 260 ns, and $[\text{Ru}(\text{Pyr}_2\text{bpy})(\text{CN})_4]^{2-}$, 450 ns, are coincident with those of the long component observed in the luminescence decays (vide supra). In H_2O , the transient behavior of $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$ was practically identical, in terms of spectral features and lifetime, to that observed for the Pyrbpy model in MeOH (Figure 7b).

Discussion

Energy Levels. The substantial additivity of the absorption spectra of the Ru-based and pyrenyl units (Figure 1) warrants a localized description of $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$ and $[\text{Ru}(\text{Pyr}_2\text{bpy})(\text{CN})_4]^{2-}$, with energy levels diagrams obtained as a superposition of those of the $[\text{Ru}(\text{Pyr}_2\text{bpy})(\text{CN})_4]^{2-}$ and Pyr_nbpy model systems. It is important to remember that the energy levels of the pyrenyl unit are practically insensitive to the solvent whereas those of the Ru-based unit are strongly solvent dependent because of second-sphere donor–acceptor interactions at the cyanides.^{21,22–30} This is clearly seen in the spectra of Figure 2, where the constancy of the pyrenyl feature at 375 nm contrasts with the highly solvatochromic behavior of the MLCT band. Therefore, a specific energy level diagram should be used when discussing the photophysical behavior in a particular solvent. The energy level diagrams for H_2O , CH_3CN , and MeOH are shown in Figure 8. In these diagrams the relevant energy values for the various excited states are obtained from spectroscopic and photophysical data of the component units. The energy of the

singlet states are estimated from absorption spectra. The pyrene triplet energy value ($E^T = 16.4 \times 10^3 \text{ cm}^{-1}$) is taken from the highest-energy maximum of the 77 K phosphorescence of the Pyrbpy ligand.¹⁹ The energy of the lowest triplet of Ru-based unit in the various solvents is estimated from the onset of the MLCT room-temperature emission of the $[\text{Ru}(\text{Me}_2\text{bpy})(\text{CN})_4]^{2-}$ model (Table 1). These diagrams hold for both $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$ and $[\text{Ru}(\text{Pyr}_2\text{bpy})(\text{CN})_4]^{2-}$, with the latter system having two isoenergetic pyrene-based triplets instead of one.

In all solvents, the singlet state of the pyrene unit is by far higher in energy with respect to the singlet of the metal-based unit, so that the singlet–singlet energy transfer process from pyrene to Ru unit is always thermodynamically allowed. On the other hand, the tuning of MLCT triplet energy obtained through SSDA interactions with the solvent causes drastic changes in the relative energy order position of the triplets of the two chromophores. In water the pyrene triplet is the lowest state while in CH_3CN the order is inverted. In MeOH, the two triplets are very close, with the pyrene triplet expected to be slightly lower in energy (within the precision of the energy estimates).

Photophysics of the Supramolecular Systems. The observation that in all solvents the typical fluorescence of the pyrene unit is completely quenched is a clear indication that in these systems photoexcitation of the pyrene chromophore is followed by rapid singlet–singlet energy transfer with population of the MLCT singlet state. The efficiency of this process is unitary as demonstrated by the good matching of the excitation spectra with the absorption spectra of the supramolecular systems, including the pyrene absorption region. This agrees with the general behavior of ruthenium polypyridine complexes bearing pyrenyl chromophores.^{8,9,19,20} Since in Ru(II) polypyridine complexes intersystem crossing at the MLCT level is known to be ultrafast (subpicosecond) and 100% efficient, the important consequence of these results is that photoexcitation of the supramolecular systems, irrespective of the wavelength, is expected to produce quantitatively the triplet MLCT of the Ru-based chromophore.

On the basis of the comparison with the emission properties of the Ru model complex, the assignment of the room-temperature emission exhibited by the multicomponent systems to $^3\text{MLCT}$ excited state of the Ru-based unit is straightforward. Because the properties of this emission are strongly solvent dependent, the photophysical behavior in the various solvents will be discussed separately.

(a) Water. In aqueous solution the MLCT emission is completely quenched, indicating that an efficient triplet–triplet energy transfer process from the ruthenium-based unit to pyrene takes place. This behavior is as expected on the basis of the energy level diagram (Figure 8, left), where this process is highly exergonic ($\Delta E = 1900 \text{ cm}^{-1}$). The absence of any MLCT emission suggests that intercomponent energy transfer must take place in the subnanosecond time regime, and indeed, this process can be clearly seen in ultrafast spectroscopy. In Figure 6b, the initial spectrum is that of the Ru-based MLCT state (as shown by comparison with

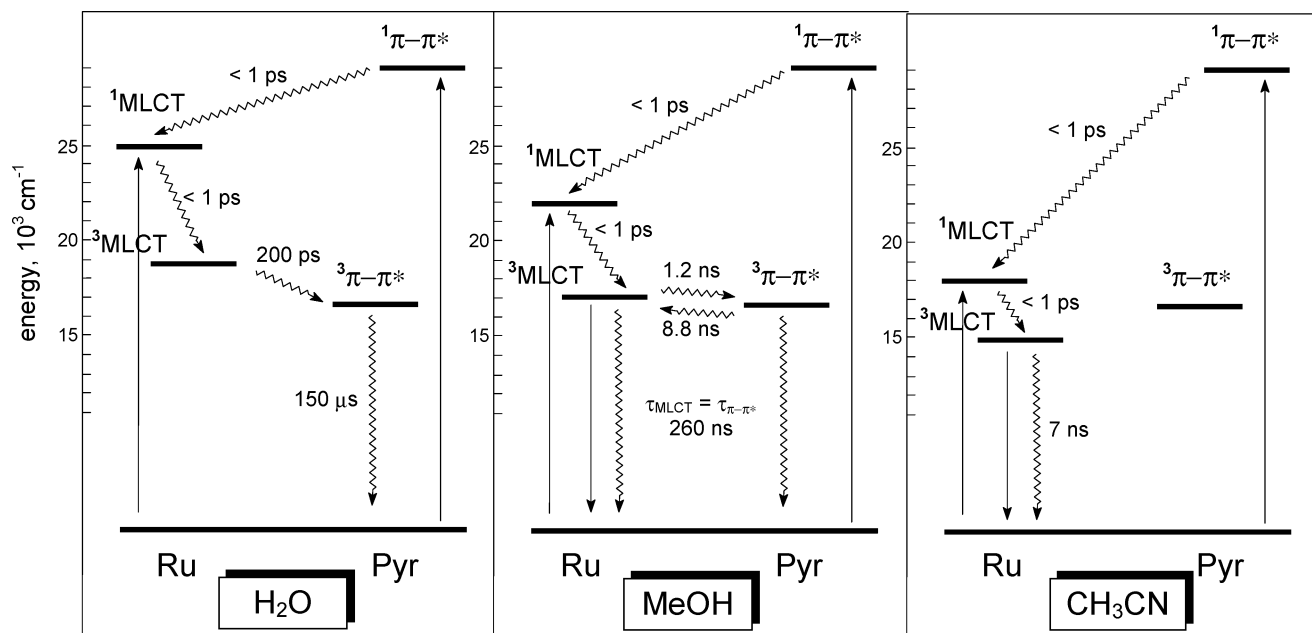


Figure 8. Schematic energy level diagram and photophysical processes for $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$ in H_2O , MeOH , and CH_3CN .

Figure 6a). In the first ca. 10 ps, Figure 6b shows small spectral changes characteristic of this chromophore (see again Figure 6a) that we tentatively assign to relaxation of the specific solvent interactions at the cyanides. Then, a sharp maximum at 516 nm develops with time. As shown by comparison with the ns spectrum of Figure 7b, this maximum is diagnostic of the production of the pyrenyl triplet state. The lifetime of the intercomponent energy transfer process is ca. 200 ps.^{38,39} In summary (Figure 8, left), the energetics in water is such that fast, irreversible triplet energy transfer from the Ru-based unit to the aryl moiety takes place. This type of situation has been previously reported for ruthenium polypyridine complexes bearing appended anthracene units.^{10b,19,40}

(b) Acetonitrile. In acetonitrile (Figure 8, right) the energy of the MLCT states is much lower, and the relative energy ordering of the Ru-based and pyrene triplets has been reversed with respect to water. In particular, triplet energy transfer to the pyrene would now be highly endoergic ($\Delta E = \text{ca. } 1100 \text{ cm}^{-1}$) and the properties of the Ru-based MLCT state should be practically unaffected. Indeed, both supramolecular systems exhibit MLCT emission with the same features (energy position, band shape, quantum yield, and lifetime) as that of the model complex.

(c) Methanol. A particularly interesting behavior is observed in methanol. The main results obtained in this solvent can be summarized as follows.

(i) At room temperature the systems exhibit the typical MLCT emission with the same quantum yield of the Ru model complex, whereas at 77 K pyrene phosphorescence is only observed, even by excitation into the intense $^1\text{MLCT}$ absorption bands (Figure 5).

(ii) For both systems at room temperature, the MLCT emission shows a biexponential decay. The two components can be fitted by exponential curves having lifetimes of 1.2 and 260 ns, respectively, for $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$ and 0.6 and 460 ns for $[\text{Ru}(\text{Pyr}_2\text{bpy})(\text{CN})_4]^{2-}$. It is important to note that in both cases the long component is remarkably long-lived with respect to the emission lifetime of the Ru model complex ($\tau = 30 \text{ ns}$ in MeOH ; Table 1).

(iii) The transient absorption spectra (Figure 7) for both multicomponent systems closely resemble that observed for Pyrbpy ligand even when no excitation light is absorbed by pyrene moiety. The attribution of these transients to the triplet–triplet absorption of the pyrene moiety is straightforward. The transients are formed during the laser flash and decay as a single exponential with the same lifetime of the long-lived MLCT emission.

(iv) The ultrafast experiments on $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$ (Figure 6c) show that the initial featureless spectrum, characteristic of the Ru-based MLCT chromophore (see Figure 6a), rapidly converts to a spectrum with maximum at 516 nm, characteristic of the pyrenyl triplet state (see Figure 7b). The conversion has a lifetime of 1.1 ns, coincident with the fast component of the emission decay.

These findings clearly indicate that at room temperature the Ru-based MLCT triplet initially populated following excitation undergoes a fast energy transfer process to the pyrene-based $\pi-\pi^*$ triplet. The lifetime for this energy transfer process, as measured by ultrafast spectroscopy or from the fast component of the MLCT emission decay, is 1.2 ns for $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$ and 0.6 ns for $[\text{Ru}(\text{Pyr}_2\text{bpy})-$

(38) The fact that the decays are not single exponentials can be tentatively attributed to conformational effects. This behavior is common to other systems with flexible intercomponent bridge.³⁹

(39) Indelli, M. T.; Bignozzi, C. A.; Harriman, A.; Schoonover, J. R.; Scandola, F. *J. Am. Chem. Soc.* **1994**, *116*, 3768.

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(CN)₄]²⁻. Contrary to what happens in water, however, the energy transfer is reversible in MeOH, leading to a thermal equilibrium between the MLCT triplet and the π - π^* triplet. This is demonstrated by fact that a long-lived component of MLCT emission persists after the initial fast decay and that this long component decays with the same lifetime as the pyrene-based triplet observed in transient absorption. At room temperature, the equilibrium is substantially shifted toward the π - π^* triplet, as shown by the low preexponential factor of the long-lived MLCT emission and the almost quantitative presence of π - π^* triplet in nanosecond transient absorption. The slightly lower energy π - π^* triplet relative to the MLCT triplet is demonstrated by the fact that in going from room temperature to 77 K the MLCT luminescence is replaced by pyrene-like phosphorescence. A schematic representation of above-sketched picture is given in Figure 8 (center).

In a thermal equilibrium mechanism, the energy transfer rates for forward (k_f) and back (k_b) processes between Ru-based and pyrene triplets greatly exceed the intrinsic decays to the ground state ($k_f \gg 1/\tau_{Ru}$ and $k_b \gg 1/\tau_{pyr}$, where τ_{Ru} and τ_{pyr} are the intrinsic lifetimes of the triplets). Under these conditions, the deactivation rate of the equilibrium mixture of the two triplets (k_{eq}) to the ground state is given by the following equation, according to standard kinetic analysis:

$$k_{eq} = \alpha \frac{1}{\tau_{pyr}} + (1 - \alpha) \frac{1}{\tau_{Ru}} \quad (1)$$

Here α and $1 - \alpha$ are the equilibrium fractional concentrations. These concentrations can be obtained from the MLCT emission decay profiles: the preexponential factor of the short component is proportional to the fraction of the MLCT emission that disappears and populates the pyrene triplet (α) while that of the long component is proportional to the fraction that remains at the equilibrium ($1 - \alpha$). The experimental values obtained are $\alpha = 0.88$ and $\alpha = 0.94$ for [Ru(Pyrbpy)(CN)₄]²⁻ and [Ru(Pyr₂bpy)(CN)₄]²⁻, respectively. Assuming $\tau_{Ru} = 30$ ns and $\tau_{pyr} = 150$ μ s (from the measured decays of the [Ru(Me₂bpy)(CN)₄]²⁻ and Pyr_nbpy models), these α values yield an equilibrium lifetime of 252 ns for [Ru(Pyrbpy)(CN)₄]²⁻ and 503 ns for [Ru(Pyr₂bpy)(CN)₄]²⁻. The agreement between these calculated figures and the measured values is gratifying.

For each supramolecular species, the experimentally determined room-temperature partition between the two triplets can be translated into an equilibrium constant and a thermodynamic driving force. The values obtained are $K_{eq} = 7.3$ and $\Delta G = -410$ cm⁻¹ for [Ru(Pyrbpy)(CN)₄]²⁻ and $K_{eq} = 15.7$ and $\Delta G = -570$ cm⁻¹ for [Ru(Pyr₂bpy)(CN)₄]²⁻.⁴¹ Since the energy gap between the triplets of the two chromophores is expected to be the same for the two systems, the fact that the equilibrium constant of [Ru(Pyr₂bpy)(CN)₄]²⁻ is practically twice that of [Ru(Pyrbpy)(CN)₄]²⁻ is to be attributed to the statistical factor caused by the presence of

two degenerate pyrene-based triplet levels in the former system. In terms of ΔG values, this means that $\Delta H \approx -410$ cm⁻¹ for both species, while a term $T\Delta S = R \ln 2$ adds ca. -140 cm⁻¹ in the case of [Ru(Pyr₂bpy)(CN)₄]²⁻. In principle, the ΔH value obtained from the equilibrium behavior should be compared with the ΔE value obtainable from spectroscopic measurements (Table 1 and Figure 5). In practice, the uncertainty in the spectroscopic estimates (especially of the MLCT E^{0-0} values) is too large, relative to the small energy differences involved, to make such a comparison meaningful.

It should be pointed out that an analogous statistical factor should apply to the rate constants for intercomponent energy transfer (³MLCT \rightarrow π - π^* in Figure 8). As a matter of fact, the lifetime for this process (as measured by the fast component of the MLCT emission decay) is shortened by a factor of ca. 2 in going from [Ru(Pyrbpy)(CN)₄]²⁻ to [Ru(Pyr₂bpy)(CN)₄]²⁻.

The excited-state equilibrium established by [Ru(Pyrbpy)(CN)₄]²⁻ and [Ru(Pyr₂bpy)(CN)₄]²⁻ in MeOH is analogous to that observed for a number of Ru(II) tris(polypyridine) complexes bearing covalently attached pyrenyl chromophores.^{8,9,19,20} As in those cases, the main practical result is a remarkable elongation of the emission lifetime of the Ru-based component relative to the simple molecular species, at constant emission quantum yield.⁴² It is worthwhile to note that the elongation in lifetime depends on the number of pyrenyl units attached to the chromophore: the lifetime doubles in going from [Ru(Pyrbpy)(CN)₄]²⁻ to [Ru(Pyr₂bpy)(CN)₄]²⁻.⁴³ This is in line with the linear trend recently reported in the literature for Ru(II) polypyridine complexes with a variable number of appended pyrenyl chromophores.¹⁶

Conclusions

This work shows how site-specific solvent effects can be used to tune the energy levels of a bichromophoric system (dyad) so as to control the direction of energy flow. Within a single dyad, an appropriate selection of the solvent permits one to go from a system where the energy resides on the Ru-based chromophore (CH₃CN, Figure 8, right) to the opposite situation where the energy flows irreversibly to the pyrene unit (H₂O, Figure 8, left), through an intermediate regime where an equilibrium between the excited states of the two units is obtained (MeOH, Figure 8, center). These three types of behavior can also be obtained with conventional systems based on tris(polypyridine)ruthenium(II) complexes but at the price of synthesizing three different dyad systems, e.g., with pendant naphthalene, pyrene, and anthracene groups.^{10b,44,45}

(42) The constancy of the emission quantum yield arises by compensation between the decrease in population and the increase in lifetime of the emitting state. This is true provided that the intrinsic lifetime of the aryl unit is much longer than that of the Ru-based chromophores.

(43) Indeed, it can be demonstrated from eq 1 that equilibrium constant and equilibrium lifetime are proportional, provided that $K \gg 1$ and $\tau_{pyr} \gg \tau_{Ru}$.

(44) Analogously, shift from aryl-based to metal-based emission output has also been reported for a single species, but in that case significant temperature changes were required.⁴⁵

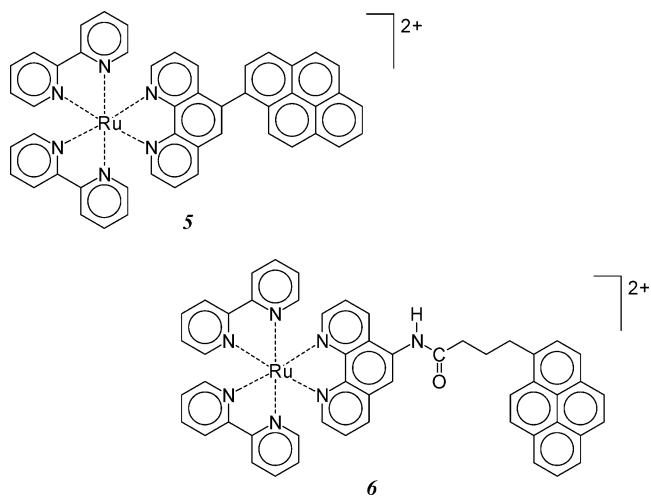
(41) These equilibrium constant values, together with the measured rate constants of the forward energy transfer step, permit the calculation of $\tau = 8.8$ and 9.4 ns for the back energy transfer process. The constancy of these values is a further internal check of the validity of the model.

In MeOH, where the equilibrium regime has been studied in detail, the results show a remarkable degree of internal consistency. In particular, (i) the relaxation of the initially formed MLCT state toward equilibrium gives comparable kinetics when monitored by ultrafast transient absorption or by time-correlated single photon counting emission, (ii) coincident equilibrium lifetimes are obtained by monitoring the decay of MLCT emission (slow component) or of the pyrene triplet absorption, and (iii) the measured equilibrium lifetimes coincide with those predicted on the basis of excited-state partition, independently measured from pre-exponential factors of emission decay.

The rate constants of intercomponent energy transfer measured in this work can be compared with a few values available in the literature for related systems. Tyson et al.^{9b} measured $2.8 \times 10^{10} \text{ s}^{-1}$ for compound **5**, and Ford and Rodgers⁸ obtained $1.3 \times 10^8 \text{ s}^{-1}$ for compound **6**. We find $5 \times 10^9 \text{ s}^{-1}$ for $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$ (**1**) in MeOH. Since all the systems are in a comparable equilibrium regime, the driving forces of the processes are probably similar.⁴⁶ Therefore, it is reasonable to ascribe the differences in rate mainly to electronic coupling effects. Indeed, the ordering

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(46) The fact that the driving force is kinetically relevant for this type of energy transfer processes is demonstrated by the increase in rate observed for $[\text{Ru}(\text{Pyrbpy})(\text{CN})_4]^{2-}$ in going from MeOH to H_2O .



of decreasing rates qualitatively follows the increasing length of the covalent linkage between the polypyridine ligand and the attached pyrene group.

Acknowledgment. Financial support from the EC (Contract G5RD-CT-2002-00776, MWFM), MURST (Cofin 1999), EC (TMR Network on Nanometer size complexes, Contract ERBFMRX-CT98-0226), and CNR (Agenzia 2000) is gratefully acknowledged.

IC034185X