Inorg. Chem. **1998,** *37,* 6084−6089

Design of Long-Lived Ru(II) Terpyridine MLCT States. Tricyano Terpyridine Complexes

Maria Teresa Indelli, Carlo Alberto Bignozzi, and Franco Scandola*

Dipartimento di Chimica, Università di Ferrara, 44100 Ferrara, Italy

Jean-Paul Collin

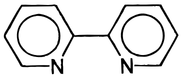
Laboratorie de Chimie Organo-Minérale, Institut de Chimie, Université de Strasbourg,
67008 Strasbourg, France

Received January 21, 1998

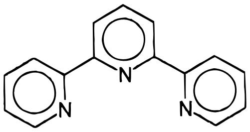
The photophysics of $Ru(tpy)(CN)_3^-$ and $Ru(ttpy)(CN)_3^-$ (where tpy = 2,2′:6′,2″-terpyridine and ttpy = 4′-(*p*-tolyl)-2,2′:6,2″-terpyridine) has been studied in detail. The complexes exhibit strongly solvatochromic behavior. Emission energies correlate linearly with solvent acceptor number, consistent with the metal-to-ligand charge transfer (MLCT) nature of the emission and the occurrence of second-sphere donor−acceptor interactions at the cyanide ligands. On the other hand, the correlation of emission lifetimes is clearly biphasic, with a sharp maximum found for solvents of intermediate acceptor number. Such a behavior is explained in terms of competition between a direct deactivation channel and an indirect, thermally activated decay pathway, with relative efficiencies depending strongly on MLCT state energy. A gain of 2 orders of magnitude in lifetime is obtained using the tricyano complexes ($Ru(tpy)(CN)_3^-$, $\tau = 48$ ns in DMSO; $Ru(ttpy)(CN)_3^-$, $\tau = 40$ ns in CH_3CN) instead of the corresponding bis-terpyridine species ($Ru(tpy)_2^{2+}$, $\tau = 250$ ps in CH_3CN; $Ru(ttpy)_2^{2+}$, $\tau = 860$ ps in CH_3CN). This shows how an appropriate choice of ancillary ligands can be used to improve the properties of photosensitizers containing the Ru(II)−terpyridine chromophoric unit.

Introduction

Metal polypyridine complexes are widely used as building blocks ("molecular components") for the design of supramolecular species performing complex light-induced functions ("photochemical molecular devices").[1−4] Particularly important in this context are the polypyridine complexes of d^6 metals. With their strong metal-to-ligand charge transfer (MLCT) absorption and long-lived, emitting ^{3}MLCT excited states, such complexes are ideal candidates as "photosensitizer" molecular components (i.e., units that interface the device with light and support intercomponent excited-state electron or energy transfer processes).[1] As to the ligands, bidentate ligands of the 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) type and tridentate ligands of the 2,2′:6′,2″-terpyridine type (tpy) are common.[4]

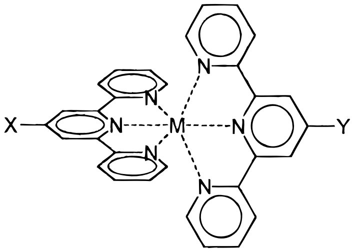


bpy



tpy

From a purely structural point of view, tpy-type ligands are definitely superior to the bidentate ones.[3] In fact, in the design of well-defined supramolecular systems by synthetic assembly of mononuclear building blocks, the occurrence of isomers is a major problem. Now, at difference with most species containing bidentate ligands, octahedral tpy-type complexes (**1**) are achiral (thus avoiding complications due to stereoisomers) and can be connected to other molecular components through the tpy 4′-position while maintaining the C_{2v} symmetry of the ligand (thus avoiding complications due to geometrical isomerism).



(1)

Along with these structural advantages, however, tpy complexes have a serious drawback of a photophysical nature. The lifetime of the ^{3}MLCT excited states is known[5] to be strongly dependent on (i) the energy of the state ("energy gap law") and (ii) the proximity of higher-energy metal-centered (^{3}MC) excited states (which can provide an additional, thermally activated decay path). Now, at difference with bis-chelating bpy-type ligands, the bite angles of a tris-chelating ligand such as tpy are not ideally suited for octahedral coordination. This results in a relatively weak ligand field at the metal, low energy of the

---

[1] Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Horwood: Chichester, U.K., 1991; Chapters 5 and 6.

[2] Scandola, F.; Bignozzi, C. A.; Indelli M. T. In *Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds*; Kalyanasundaram, K., Grätzel, M., Eds.; Kluwer: Dordrecht, 1993; p 161.

[3] Chambron, J.-C.; Coudret, C.; Collin, J.-P.; Guillerez, S.; Sauvage, J.-P.; Barigelletti, F.; Balzani, V.; De Cola, L.; Flamigni, L. *Chem. Rev.* **1994**, *94*, 993.

[4] Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759.

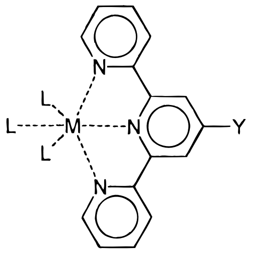
[5] Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.

10.1021/ic980060u CCC: $15.00 © 1998 American Chemical Society
Published on Web 10/24/1998

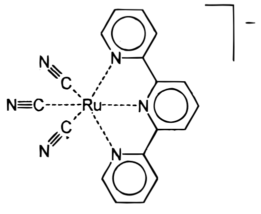
MC states, and an efficient thermally activated decay pathway.[6] As a consequence, tpy complexes tend to have relatively short-lived MLCT states and to be weak emitters (e.g., as compared to analogous bpy complexes). For example, while the ^{3}MLCT state of $Ru(bpy)_3^{2+}$ is long-lived ($\tau = 890$ ns) and highly luminescent ($\Phi = 0.059$),[5] that of $Ru(tpy)_2^{2+}$ has an extremely short lifetime ($\tau = 250$ ps) and is practically nonluminescent ($\Phi \leq 5 \times 10^{-6}$) at room temperature.[3] This is a severe drawback for the use of Ru(II) terpyridine complexes as photosensitizer units. All but very fast intercomponent processes are inefficient in supramolecular systems containing such units, and picosecond spectroscopy is required.[7,8] Alternatively, low temperatures can be used to reach convenient excited-state lifetimes, but this entails other experimental problems and may rule out the occurrence of thermally activated intercomponent processes.[9,10]

Rational strategies can be devised to increase the excited-state lifetime of Ru(II) tpy-type complexes. Since one of the main origins of the short lifetime is the small energy gap between the emitting ^{3}MLCT state and the upper-lying ^{3}MC states, increasing such an energy gap would be beneficial. In bis-tpy complexes of type **1**, substitutions at the 4′-positions of the ligands can be used for that purpose. The effect of substitution at the *chromophoric* ligands is, however, a complex one.[11] Both electron donor and electron acceptor substituents are found to decrease the energy of the ^{3}MLCT state, but their effect on the energy of the MC states is such that the largest gap and, thus, the longer lifetime are obtained when the two substituents X and Y are of opposite type. With such a strategy, lifetimes as long as 50 ns can be obtained.[11] When the tpy ligands are connected through their 4′-positions with π-delocalizing fragments, remarkable lifetime enhancements are observed.[12−15] Again, this can be rationalized in terms of stabilization of the ^{3}MLCT upon delocalization, although the concomitant decrease in excited-state distortion and, thus, in the Franck−Condon factors for radiationless decay probably add to the effect.

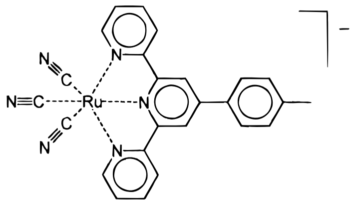
As an alternative strategy to the design of long-lived Ru(II) terpyridine complexes, one could think of synthesizing monoterpyridine complexes of type **2**, and of using the *ancillary* ligands, L, to tune the relative energies of ^{3}MLCT and ^{3}MC states. To give rise to high-energy ^{3}MC states and low-energy ^{3}MLCT, an ideal ancillary ligand should simultaneously (i) provide a strong ligand field (i.e., be in a high position in the spectrochemical series) and (ii) provide high charge density on the metal (i.e., be in a low position in the ligand electrochemical series[16,17]). Among several plausible candidates, *cyanide* is a good compromise between these two requirements. It should be pointed out, however, that the properties of cyanide as a ligand are known to be strongly dependent on solvent, through second-sphere donor−acceptor interactions at the free nitrogen end.[17] This complicates the prediction of the effect of cyanide ancillary ligands on the lifetime of Ru → tpy MLCT states and implies that any experimental check must include a careful examination of the solvent dependence of the photophysical behavior. We report here on the photophysical behavior of $Ru(tpy)(CN)_3^-$ (**3**)[18] and $Ru(ttpy)(CN)_3^-$ (where ttpy = 4′(p-tolyl)-2,2′:6,2″-terpyridine), (**4**). The terpyridine complex was available from a preliminary study.[18] The tolyl-substituted species has been specifically synthesized, as a model for rodlike binuclear systems containing the $Ru(tpy)(CN)_3^-$ chromophore bound to a rigid polyphenylene spacer.



(2)



(3)



(4)

Experimental Section

Materials. The $K[Ru(tpy)(CN)_3]$ complex was prepared as described previously.[18]

$K[Ru(ttpy)(CN)_3]$ was prepared following a simplified procedure of the previously published method.[18] $Ru(ttpy)Cl_3$ (0.2 g, 0.38 mmol) and $AgBF_4$ (0.22 g, 1.13 mmol) were heated to reflux in acetone (50 mL) for 2 h. The resulting purple suspension was filtered to remove precipitated AgCl, and a methanolic solution of KCN (0.5 g in 50 mL) was added to the filtrate. Then the solution was refluxed under argon overnight. After cooling, the solvents were evaporated and the residue was subjected to chromatography over Al_2O_3 using successively *n*-propyl alcohol (500 mL), ethanol (500 mL), and methanol (1 L) as eluents. The brown fractions yielded 65 mg of pure sample (32%). ^{1}H NMR (200 MHz, CD_3CN): δ 8.95 (d, 2H, 5 Hz), 8.30 (s, 2H), 8.12 (d, 2H, 7.5 Hz), 7.78 (d, 2H, 7.5 Hz), 7.62 (dd, 2H, 7 and 7 Hz), 7.33 (dd, 2H, 6 and 6 Hz), 7.07 (d, 2H, 8 Hz), 2.32 (s, 3H). FAB-MS (negative mode): $m/z = 503.0$ ($M - K^+$ requires 503).

Tetrabutylammonium salts of the complexes were used in nonaqueous solvents. These salts were obtained from the potassium salts by ion exchange on cationic CM Sephadex C-25 resin. Spectrograde organic solvents (Merck Uvasol) were used without further purification.

---

(6) Calvert, J. M.; Caspar, J. V.; Binstead, R. A.; Westmoreland, T. D.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 6620.

(7) Barigelletti, F.; Flamigni, L.; Balzani, V.; Collin, J.-P.; Sauvage, J.-P.; Sour, A.; Constable, E. C.; Cargill Thompson, A. M. W. *J. Am. Chem. Soc.* **1994**, *116*, 7692.

(8) Indelli, M. T.; Scandola, F.; Flamigni, L.; Collin, J.-P.; Sauvage, J.-P.; Sour, A. *Inorg. Chem.* **1997**, *36*, 4247.

(9) Collin, J.-P.; Guillerez, S.; Sauvage, J.-P.; Barigelletti, F.; De Cola, L.; Flamigni, L.; Balzani, V. *Inorg. Chem.* **1991**, *30*, 4230.

(10) Indelli, M. T.; Scandola, F.; Collin, J.-P.; Sauvage, J.-P.; Sour, A. *Inorg. Chem.* **1996**, *35*, 303.

(11) Maestri, M.; Armaroli, N.; Balzani, V.; Constable, E. C.; Cargill Thompson, A. M. W. *Inorg. Chem.* **1995**, *34*, 2759.

(12) Benniston, A. C.; Grosshenny, V.; Harriman, A.; Ziessel, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1884.

(13) Grosshenny, V.; Harriman, A.; Ziessel, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2705.

(14) Barigelletti, F.; Flamigni, L.; Guardigli, M.; Sauvage, J. P.; Collin, J. P.; Sour, A. *Chem. Commun.* **1996**, 1329.

(15) Hammarstrom, L.; Barigelletti, F.; Flamigni, L.; Indelli, M. T.; Armaroli, N.; Calogero, G.; Guardigli, M.; Sour, A.; Collin, J. P.; Sauvage, J. P. *J. Phys. Chem. A* **1997**, *101*, 9061.

(16) Lever, A. B. P *Inorg. Chem.* **1990**, *29*, 1271. Fielder, S. S.; Osborne, M. C.; Lever, A. B. P.; Pietro, W. J. *J. Am. Chem. Soc.* **1995**, *117*, 6990.

(17) Scandola, F.; Indelli, M. T. *Pure Appl. Chem.* **1988**, *60*, 973.

(18) Timpson, C. J.; Bignozzi, C. A.; Sullivan B. P.; Kober, E. M.; Meyer T. J. *J. Phys. Chem.* **1996**, *100*, 2915.

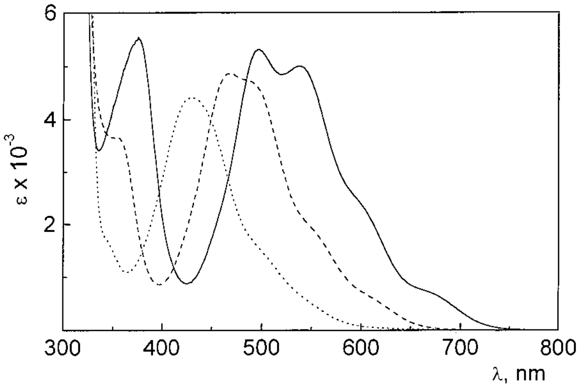


Figure 1. Absorption spectra of $Ru(tpy)(CN)_3^-$ in water (···), ethanol (− − −), and in CH_3CN (—).

Apparatus and Procedures. The instruments and procedures used to obtain absorption and emission spectra were as described in a previous paper.[10]

The emission spectra were corrected for instrumental response by calibration with an NBS standard quartz-halogen lamp. Emission quantum yields were obtained using $Ru(bpy)_3^{2+}$ in water ($\Phi = 0.059$)[5] as a reference emitter. Emission lifetimes were measured by time-correlated single photon counting techniques, using a PRA 3000 nanosecond fluorescence spectrometer.[19]

Laser flash photolysis experiments were carried out using an Applied Photophysics detection system coupled with a Continuum Surelite II Q-switched Nd:YAG laser source. The third harmonic ($\lambda = 355$ nm, half-width 7 ns, maximum pulse energy 150 mJ) was used for excitation. The transient signals were recorded on a Lecroy 9360 digital storage oscilloscope and analyzed with routine software.

The excited-state absorption (ESA) spectrum of $Ru(tpy)(CN)_3^-$ was taken 15 ns after the start of the laser pulse, allowing for a 30% correction in intensity due to the finite laser flash duration. The absorbance changes were converted into molar absorptivity changes by using triplet benzophenone[20] as a laser actinometer following previously described procedures.[21] All measurements were carried out on deaerated solutions.

Results

The $Ru(tpy)(CN)_3^-$ complex (**3**) exhibits a pronounced solvatochromic behavior. The absorption spectra in water, ethanol (EtOH), and acetonitrile (CH_3CN) are shown in Figure 1. For these and other solvents, the energies of the lowest energy absorption band maximum, ν_{max}^{abs} (298 K), are collected in Table 1.[22]

At room temperature in fluid solution, $Ru(tpy)(CN)_3^-$ exhibits emission in all solvents, although with widely varying intensity (see below). Paralleling the behavior observed in absorption, the energy of the emission, ν_{max}^{em} (298 K), is strongly solvent-dependent (Table 1). The decay of the emission, which always follows an appreciably single exponential behavior, gives lifetime values, τ (298 K), that also depend strongly on the solvent (Table 1, Figure 2). The emission quantum yield in CH_3CN is 4.0×10^{-4}. The relative emission intensity in the other solvents parallels the variation in lifetimes.

In low-temperature rigid glasses, intense emission from $Ru(tpy)(CN)_3^-$ is observed. Emission energies, ν_{max}^{em} (77 K), and lifetimes, τ (77 K), change with the glassy solvent, although to a much lesser extent than at room temperature (Table 1).

In laser flash photolysis experiments performed in CH_3CN at room temperature, transient spectral changes are observed (positive absorption at $\lambda < 450$ nm and $\lambda > 580$ nm, bleaching at 460 nm $< \lambda <$ 580 nm). The decay of the transient spectral changes follows good first-order kinetics with a lifetime of 40 ns, coincident with that obtained from emission decay (Table 1). After correction for ground-state bleaching (see Experimental Section) the excited-state absorption (ESA) spectrum shown in Figure 3 is obtained.

The behavior of the tolyl-substituted complex, $Ru(ttpy)(CN)_3^-$ (**4**), has also been briefly investigated. The results are shown in Table 2.

Discussion

Spectroscopic and Photophysical Behavior. The visible spectrum of $Ru(tpy)(CN)_3^-$ is dominated by metal-to-terpyridine MLCT transitions. The highly solvatochromic behavior of this complex is in line with what is observed, as a general phenomenon, for mixed cyano−polypyridine complexes of d^6 metals.[18,23−31] The behavior can be explained primarily in terms of second-sphere donor−acceptor (SSDA) interactions[17] between the cyanides and the solvent. The larger the acceptor character of the solvent (indicated by the Gutmann acceptor number[22]), the higher becomes the oxidation potential of the metal center, and the higher is the energy of the metal-to-terpyridine MLCT states (Table 1). As discussed elsewhere,[18] the extent of solvatochromism in mixed cyano−polypyridine complexes, as measured by the slope of, e.g., absorption energy against the solvent acceptor number, depends on the number of cyanide ligands. Thus, the solvatochromism of $Ru(tpy)(CN)_3^-$ is intermediate between those of $Ru(bpy)_2(CN)_2$ and $Ru(bpy)(CN)_4^{2-}$.

The emission has the typical spectral and photophysical features of Ru(II) polypyridine MLCT transitions. It shifts with solvent, as expected, in the same direction as absorption (Table 1). The solvatochromic effect is somewhat smaller than for absorption, as is common in this type of system.[18,23−31] Besides the energy, also the lifetime and intensity of the emission are strongly solvent-dependent, as discussed in detail in the next section. In rigid glasses at 77 K, the emission is strongly blue-shifted and the solvent effects are much less pronounced with respect to room temperature (Table 1). This is consistent with what is observed for other Ru(II) cyano−polypyridine complexes[23] and is the consequence of the lack of solvent relaxation under these experimental conditions.

The ESA spectrum of $Ru(tpy)(CN)_3^-$ (Figure 3) consists of a prominent band at 550 nm. Given the nature of the MLCT excited state, and the practically nonabsorbing nature of the ruthenium−cyanide moiety, this ESA spectrum essentially

---

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

(20) Bensasson, R.; Salet, C.; Balzani, V. *J. Am. Chem. Soc.* **1976**, *98*, 3722.

(21) Bignozzi, C. A.; Bortolini, O.; Chiorboli, C.; Indelli, M. T.; Rampi, M. A.; Scandola, F. *Inorg. Chem.* **1992**, *31*, 172.

(22) Gutmann, V. *The Donor-Acceptor Approach to Molecular Interactions*; Plenum: New York, 1980.

(23) Bignozzi, C. A.; Chiorboli, C.; Indelli, M. T.; Rampi Scandola, M. A.; Varani, G.; Scandola, F. *J. Am. Chem. Soc.* **1986**, *108*, 7872.

(24) Demas, J. N.; Addington, J. W.; Peterson, S. H.; Harris, E. W. *J. Phys. Chem. Soc.* **1977**, *81*, 1039.

(25) Belser, P.; von Zelewsky, A.; Juris, A.; Barigelletti, F.; Balzani, V. *Gazz. Chim. Ital.* **1985**, *115*, 723.

(26) Davila, J.; Bignozzi, C. A.; Scandola, F. *J. Phys. Chem.* **1989**, *93*, 1373.

(27) Kitamura, N.; Sato, M.; Kim, H. B.; Obata, R.; Tazuke, S. *Inorg. Chem.* **1988**, *27*, 651.

(28) Burgess, J. *Spectrochim. Acta* **1970**, *26A*, 1369.

(29) Indelli, M. T.; Bignozzi, C. A.; Marconi, A.; Scandola, F. *J. Am. Chem. Soc.* **1988**, *110*, 7381.

(30) Winkler, J. R.; Sutin, N. *Inorg. Chem.* **1987**, *26*, 220.

(31) Winkler, J. R.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1987**, *109*, 3470.

Table 1. Spectroscopic, Photophysical, and Redox Properties of $Ru(tpy)(CN)_3^-$ in Different Solvents

	solvent (acceptor no.)[a]							
	H_2O (58.4)	MeOH (41.3)	EtOH (37.1)	*n*-PrOH (33.5)	CH_3CN (19.3)	DMSO (19.3)	DMF (16.0)	acetone (12.5)
$\nu_{max}^{abs} \times 10^{-3}$ (298 K),[b] cm^{-1}	23.4	21.8	20.3	19.7	18.6	18.4	17.9	17.8
$\nu_{max}^{em} \times 10^{-3}$ (298 K), cm^{-1}	15.4	14.8	14.2	13.9	13.3	13.2	13.1	12.8
$\nu_{max}^{em} \times 10^{-3}$ (77 K), cm^{-1}	17.6[c,d]		16.4[e]				15.3[f]	
τ (298 K),[g] ns	<1	1.5	5.4	16	40	48	35	24
τ (77 K), μs	3.5		3.4				2.5	
E^{0-0} [h] $\times 10^{-3}$, cm^{-1} (eV)	17.0	16.4	15.9	15.5	14.9 (1.85)	14.9 (1.85)	14.7 (1.82)	14.5
$E_{1/2}$ [Ru^{III}/Ru^{II}],[i] V					0.56	0.55	0.49	
$^*E_{1/2}$ [$Ru^{III}/^*Ru^{II}$],[j] V					−1.29	−1.30	−1.33	

[a] Acceptor numbers were taken from ref 22. [b] Low-energy band. [c] High-energy band. [d] 9 M LiCl glass. [e] EtOH/MeOH (4:1) glass. [f] DMF/CH_2Cl_2 (9:1) glass. [g] Deaerated solution. [h] Excited-state energy estimated from the onset (5% relative intensity) of the room-temperature emission spectrum. [i] Vs SCE, from ref 18; the literature data in V vs Fc^+/Fc have been converted by adding 0.39 V. [j] Excited-state redox potentials obtained using the ground-state potentials ($E_{1/2}$) and excited-state energies (E^{0-0}).

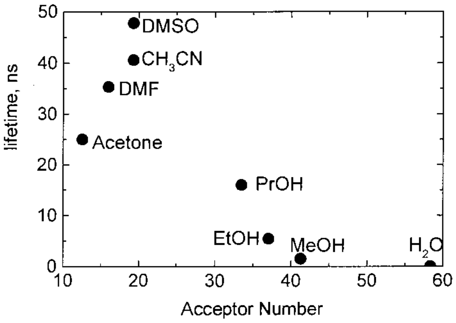


Figure 2. Correlation of the emission lifetime with the Gutmann acceptor number for $Ru(tpy)(CN)_3^-$.

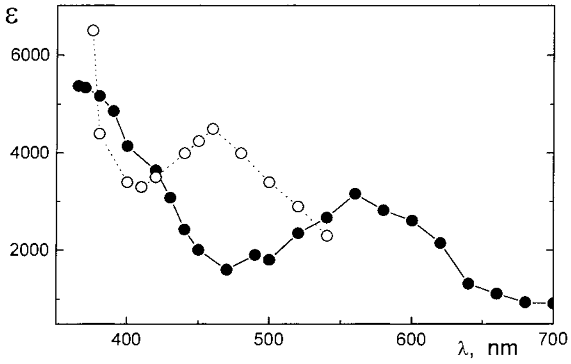


Figure 3. Excited-state absorption spectra of $Ru(tpy)(CN)_3^-$ (●) and $Ru(bpy)(CN)_4^{2-}$ (○) in CH_3CN.

Table 2. Spectroscopic and Photophysical Properties of $Ru(ttpy)(CN)_3^-$ in Different Solvents

	solvent (acceptor no.)[a]		
	H_2O (58.4)	EtOH (37.1)	CH_3CN (16.0)
$\nu_{max}^{abs} \times 10^{-3}$ (298 K),[b] cm^{-1}	22.5	20.2	18.3
$\nu_{max}^{em} \times 10^{-3}$ (298 K), cm^{-1}	15.3	14.0	13.2
$\nu_{max}^{em} \times 10^{-3}$ (77 K), cm^{-1}		16.1[c]	
τ (298 K),[d] ns	<1	7.9	40.0

[a] Acceptor numbers were taken from ref 22. [b] Low-energy band. [c] EtOH/MeOH (4:1) glass. [d] Deaerated solution.

corresponds to the spectrum of the tpy^- radical anion.[13] When compared with that of the corresponding monobipyridine complex,[32] the substantial red-shift corresponding to the larger delocalization of the terpyridine ligand is apparent (Figure 3).

From excited-state energies and ground-state oxidation potentials are obtained excited-state redox potentials of about −1.3 V vs SCE (Table 1). Thus, $Ru(tpy)(CN)_3^-$ is potentially a very strong excited-state reductant (compare, e.g., with −0.86 V for the standard $Ru(bpy)_3^{2+}$ photosensitizer).

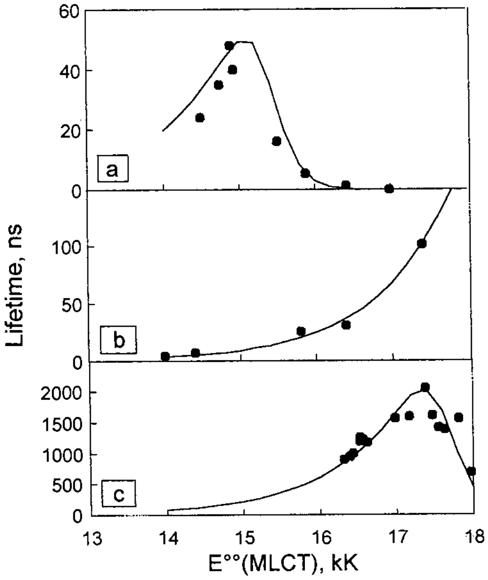


Figure 4. Plot of the emission lifetime vs solvent-dependent emission energy for $Ru(tpy)(CN)_3^-$ (a), $Ru(bpy)(CN)_4^{2-}$ (b), and $Ru(bpy)_2(CN)_2$ (c). The full-line curves are calculated using eqs 1 and 2 with the following sets of parameters: (a) $k° = 8 \times 10^{13}$ s^{-1}, $\alpha = 1.02$ cm, $k' = 1 \times 10^{10}$ s^{-1}, $E_{MC} = 16\,700$ cm^{-1}; (b) $k° = 5 \times 10^{14}$ s^{-1}, $\alpha = 1.02$ cm, $k' = 1 \times 10^{10}$ s^{-1}, $E_{MC} = 20\,000$ cm^{-1}; (c) $k° = 2 \times 10^{13}$ s^{-1}, $\alpha = 1.02$ cm, $k' = 1 \times 10^{10}$ s^{-1}, $E_{MC} = 19\,700$ cm^{-1}.

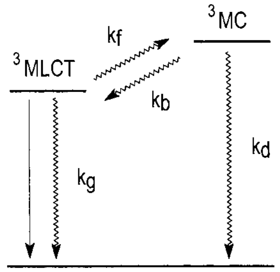
The spectroscopic and photophysical behavior of the tolyl-substituted complex, $Ru(ttpy)(CN)_3^-$ (**4**), is practically identical to that of the parent unsubstituted complex, except for a very small red-shift of all the absorption and emission energies, consistent with the slightly larger delocalization in the ttpy ligand.[9]

Solvent Dependence of Emission Lifetimes. The plot of the lifetime of $Ru(tpy)(CN)_3^-$ emission in various solvents at room temperature against the solvent acceptor number (Figure 2) or the linearly related excited-state energy (Figure 4a) has a rather peculiar, biphasic shape: the lifetime peaks (48 ns) for DMSO, and it drops sharply in going to solvents of both higher and lower acceptor properties (emission energies). This behavior can be interpreted within the generally accepted scheme for Ru(II) polypyridine photophysics (Scheme 1). According to this scheme, the emitting ^3MLCT state deactivates along two main competing channels: (i) direct radiationless transition to the ground state (k_g) and (ii) conversion to the lowest metal-centered (^3MC) excited state (k_f and k_b for forward and back

---

(32) The ESA spectrum of $Ru(bpy)(CN)_4^{2-}$ in acetonitrile (Figure 3) is identical to that previously obtained in water,[23] consistent with the assignment of the transition as a bpy-centered one.

Scheme 1



processes, respectively) and, from there, to the ground state (k_d).[5,6,33] In both cases, the lifetime contains a temperature-independent and a temperature-dependent term (eq 1).

$$1/\tau = k_g + k' \exp(-\Delta E_a/RT) \tag{1}$$

In eq 1, k' and ΔE_a have different meanings depending on which of two limiting regimes is obeyed: if $k_b > k_d$ (equilibrium limit), $1/\tau = k_g + (k_f/k_b)k_d$, $k' = k_d$, and $\Delta E_a = (E_{MC} - E_{MLCT})$; if $k_b < k_d$ (activation limit), $1/\tau = k_g + k_f$, and k' and ΔE_a are the frequency factor and activation energy of the ^{3}MLCT → ^{3}MC step (k_f). In any case, both channels are expected to be sensitive to changes in the energy of the ^{3}MLCT. As to k_g, the well-known energy gap law of radiationless transitions (eq 2) predicts an exponential *decrease* in deactivation rate with increasing ^{3}MLCT energy.[33]

$$k_g \approx k^\circ \exp(-\alpha E_{MLCT}) \tag{2}$$

For the thermally activated pathway, on the other hand, the decay rate is expected to *increase*, as long as the increase in the energy of the ^{3}MLCT state results in a decrease of the ^{3}MLCT-to-^{3}MC energy separation (or activation energy). These opposing effects provide a simple basis for the rationalization of a biphasic behavior.

The continuous line in Figure 4a is calculated on the basis of eqs 1 and 2 assuming for the sake of simplicity the equilibrium kinetic limit and constant energy for the ^{3}MC state as a function of solvent, and using a reasonable set of parameters ($k^\circ = 8 \times 10^{13}$ s^{-1}, $\alpha = 1.02$ cm, $k' = 1 \times 10^{10}$ s^{-1}, $E_{MC} =$ 16 700 cm^{-1}). While the above assumptions are arbitrary[34] and the set of parameters used is by no means unique, this crude calculation clearly shows the qualitative ability of the model to represent the data. The physical rationale is obvious: in the ascending branch (left), the excited-state decay is dominated by direct deactivation (and thus by energy gap law effects); in the descending branch (right), the decay is dominated by the ^{3}MC-mediated pathway (and thus by thermal activation); the central maximum spans the narrow solvent range where competition between the two pathways is efficient.[35]

In low-temperature glasses, the activated pathway is obviously absent and the lifetime has a completely different solvent dependence with respect to room temperature. Thus, in keeping with the energy gap law, water has the highest emission energy and the longest lifetime at 77 K (Table 1).

When the solvent dependences exhibited by various Ru(II) cyano−polypyridine complexes are compared (Figure 4a−c), no obvious regularity is apparent at first sight. The above-mentioned general scheme, however, can easily provide an interpretation of the experimental results, it being kept in mind that the ligand field strength (and thus the MC energy) follows the order tpy < bpy < CN$^-$, and the ligand electrochemical parameter E_L (and thus the MLCT energy) follows the order CN$^-$ < tpy ≈ bpy.[16,36]

For example, the monotonic increase in lifetimes with increasing solvent acceptor number (and emission energy) exhibited[23] by Ru(bpy)(CN)$_4^{2-}$ (Figure 4b) simply reflects the fact that here the ^{3}MC energy is much higher than in the previous case (a bpy and a cyanide replacing a tpy ligand) so that the branch controlled by the energy gap law spans the whole solvent range available. The behavior of Ru(bpy)$_2$(CN)$_2$, investigated in detail by Kitamura et al.,[27] on the other hand, is again biphasic (Figure 4c). Here, the energy of the ^{3}MC state is probably comparable to that in Ru(bpy)(CN)$_4^{2-}$, but the biphasic behavior arises from the generally higher energy of the ^{3}MLCT state (a bpy replacing two cyanide ligands) which reduced the ^{3}MC−^{3}MLCT energy gap. The solid lines in Figure 4b and Figure 4c have been calculated with two sets of parameters that reflect these pictures (same k' as above; $E_{MC} =$ 20 000 cm^{-1}, $k^\circ = 5 \times 10^{14}$ s^{-1} for Ru(bpy)(CN)$_4^{2-}$; $E_{MC} =$ 19 700 cm^{-1}, $k^\circ = 2 \times 10^{13}$ s^{-1} for Ru(bpy)$_2$(CN)$_2$). A comparison between the parameter values used in this (admittedly crude) rationalization indicates (a) that the overall experimental lifetime range, as well as the maximum lifetime value observed for each complex, is largely determined by what is formally regarded as a preexponential factor, k°, in the energy gap law, and (b) that such a factor apparently increases with the number of cyanides in the complex. This probably reflects the introduction into the system of cyanide high-energy vibrational modes and the strong coupling of such modes to the MLCT electronic transition.[37,38]

Conclusions

In this work, the use of cyanides as ancillary ligands to extend the lifetime of ^{3}MLCT excited states of Ru(II) terpyridine complexes has been explored. With respect to Ru(tpy)$_2^{2+}$ (τ = 250 ps, CH$_3$CN) or Ru(ttpy)$_2^{2+}$ (τ = 860 ps, CH$_3$CN), a gain of 2 orders of magnitude in the ^{3}MLCT lifetime is obtained in going to Ru(tpy)(CN)$_3^-$ (τ = 48 ns, DMSO) or Ru(ttpy)(CN)$_3^-$ (τ = 40 ns, CH$_3$CN). With lifetimes in this range, interesting perspectives arise for the use of structurally attractive Ru(II) terpyridine units as photosensitizer molecular components in supramolecular devices.

---

(33) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193. Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722.

(34) The equilibrium assumption is just arbitrary. That of constant MC energy would be, strictly speaking, incorrect as the strong second-sphere interactions with the solvent will certainly affect to some extent the ligand field strength of cyanide. It is used here simply to mean that the solvent dependence is probably much less pronounced for MC than for MLCT energies.

(35) In principle, the assignment of the right-hand branch of Figure 4a to a termally activated decay regime could be checked by temperature-dependent lifetime measurements. In practice, however, the emissions in this solvent range are too weak and short-lived to yield reliable activation energy values.

(36) The strong solvatochromism implies that cyanide should actually have a solvent-dependent E_L value. From the solvent-dependent electrochemistry of Ru(bpy)(CN)$_4^{2-}$,[23] using standard arguments,[16] the following E_L values for cyanide are obtained: −0.01 (DMF); 0.13 (H$_2$O). Thus, the order indicated is appropriate regardless of the solvent.

(37) The coupling of the CN vibrations has the same origin as solvatochromism, i.e., the decrease in π back-bonding occurring upon MLCT excitation. Direct proof can been obtained from time-resolved infrared spectra of related systems, showing that CN stretching frequencies in the MLCT excited state are substantially blue-shifted with respect to the ground state.[38]

(38) Schoonover, J. R.; Gordon, C. K.; Argazzi, R.; Woodruff, W. H.; Peterson, K. A.; Bignozzi, C. A.; Dyer, R. B.; Meyer, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 10996.

The presence of cyanides introduces strongly solvatochromic behavior in Ru(II) polypyridine complexes. For $\mathrm{Ru(tpy)(CN)_3^-}$ and $\mathrm{Ru(ttpy)(CN)_3^-}$, emission energy correlates linearly with solvent acceptor number, while a clearly biphasic dependence is observed for emission lifetimes as a function of emission energy. The lifetime solvent dependence can be readily explained in terms of a standard model involving competition between direct radiationless decay to the ground state and a thermally activated pathway through upper metal-centered states. The model applies to other mixed-ligand cyano polypyridine complexes as well.

The general question as to the effect of replacing a polypyridine ligand with cyanides on the lifetime of Ru(II) polypyridine complexes does not admit a simple answer. The prediction is complicated by the solvent dependence of lifetimes, their sensitivity to the energy of both MC and MLCT states, and the occurrence of intrinsic vibronic effects of cyanide on MLCT decay. In the case of Ru(II) terpyridine complexes, however, the effect is certainly one of lifetime enhancement, and its main reason is the lifting of the MC states accompanying the substitution of strong-field cyanide ligands for the weak-field terpyridine ligand.

Acknowledgment. Financial support from MURST and CNR (Italy), from CNRS (France), and from EEC (TMRX-CT96-0079) is gratefully acknowledged.

IC980060U