Controlling the Direction of Photoinduced Energy Transfer in Multicomponent Species

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Abstract: Luminescence spectroscopy provides evidence for the efficient photoinduced energy transfer between the Ru^{II}-based metal-to-ligand charge-transfer (MLCT) chromophore and anthracene moieties in two multicomponent, rack-type species that contain Ru^{II}-polypyridine and anthracene subunits. Furthermore, the *direction* of such an energy transfer can be controlled: the energy-transfer process occurs from the Ru-based chromophore to the anthracene in a rigid matrix at 77 K, whilst in fluid solution at room temperature it occurs from the anthracene subunit to the Ru-based chromophore. The switch in the direction of the energy-transfer process arises from the quite different intrinsic lifetimes of the luminophores and the relatively small energy gap between the lowest energy excited states located in each subunit. The combination of such properties allows a thermal activation of an uphill energy transfer which switches the direction of the intercomponent process. This finding is of interest for the design, based on this relatively unexplored photophysical property, of novel artificial supramolecular systems that are capable of processing information at the molecular level.

Keywords: energy transfer · luminescence · molecular devices · multicomponent species · ruthenium

Introduction

Photoinduced electronic-energy transfer plays a key role in many processes of paramount importance, for example, photosynthesis.[1] Recently, knowledge about the intimate nature of the energy-transfer process has been further increased by the development of properly designed artificial multicomponent species. Such multicomponent systems allowed the disentanglement, control, and fine tuning of the effects of different parameters (i.e. distance and orientation of donors and acceptors, driving forces, role of the spacers in mediating electronic coupling) on the efficiency and rate of the process.[2] These achievements have also prompted the synthesis of artificial multicomponent systems, based on energy transfer, which behave as antenna systems for light conversion purposes,[2c, 2f, 3] photochemically driven enzymes or "photozymes",[4] chemical transformation reactors powered by infrared light,[5] luminescent chemical sensors,[6] and elements of information devices.[7]

Within this framework, directional control of electronic energy migration within a multicomponent structure is expected to open new perspectives for artificial functions operating at the molecular level. For example, input of information in the form of electronic energy could be directed to different sites ("exits") of the molecular arrangements, which would give rise to an output of information that could be different not only in the energy domain but also in the space domain (for a schematization, see Figure 1).

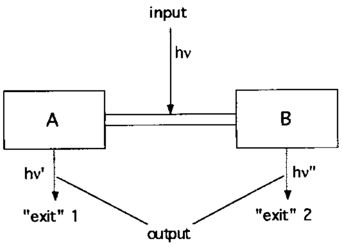

Figure 1. The input of information in the form of photons is captured by the multichromophore system AB. The electronic energy collected is then redirected to different exits as a function of the direction of the energy-transfer process between the subunits A and B.

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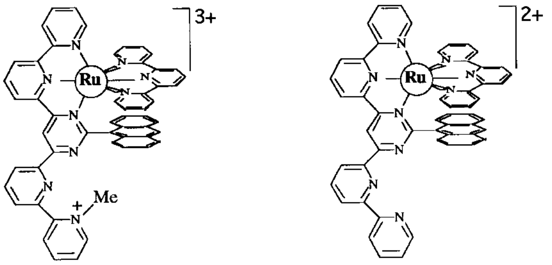
Basically, a multicomponent system that features a means to control the direction of photoinduced energy transfer consists of two chromophores with a predetermined and fixed spatial relationship, and whose energy order of the respective lowest lying excited states can be reversed. The same result can be obtained by taking advantage of quite different intrinsic lifetimes of the chromophores if their relevant excited states are lying close to one another and are suitably coupled. In this case, the lowest excited states of the chromophores would be in thermodynamic equilibrium and a thermally activated process could control the direction of the intercomponent process.[8] It is quite convenient that the two chromophores are intrinsically luminescent, in that this simplifies the study of the energy-transfer process by means of luminescence spectroscopy.

As a first step in this direction, we report here the photophysical properties of two new multicomponent systems that contain Ru^{II}-polypyridine and anthracene chromophores as active components. The structural formulas of these species, **1** and **2**, are shown in Figure 2. The properties of the chromophores are sufficiently different from one another so that the direction of the intercomponent energy-transfer process within the systems is reversed on passing from a fluid solution at room temperature to a rigid matrix at 77 K.



1 **2**

Figure 2. Structural formulae of **1** and **2**, the two new multicomponent systems that contain Ru^{II}-polypyridine and anthracene chromophores as active components.

Abstract in Italian: *In due nuove specie multicomponenti costituite da diverse subunità cromoforiche, ovvero complessi polipiridinici di Ru^{II} e antraceni, si verificano efficienti processi di trasferimento energetico fotoindotti, la cui direzione può essere controllata. Il trasferimento energetico avviene infatti dal cromoforo basato sul metallo alla subunità antracenica a 77 K in matrice rigida e dalla subunità antracenica al cromoforo metallico a temperatura ambiente in soluzione fluida. L'inversione della direzione del trasferimento energetico è dovuta ai tempi di vita intrinseci, notevolmente diversi, dei luminofori coinvolti ed alla piccola differenza di energia tra gli stati eccitati a piû bassa energia di ciascuna subunità. La combinazione di tali proprietà permette l'attivazione termica di un processo di trasferimento energetico endoergonico che può invertire la direzione del processo stesso. I risultati qui discussi sono di interesse per la progettazione di nuovi sistemi supramolecolari artificiali capaci di elaborare l'informazione a livello molecolare, basati su una proprietà fotofisica relativamente poco esplorata.*

Results

The *N*-monomethylated ligand 2-(9-anthryl)-4-(2′,2″-bipyrid-6′-yl)-6-[2′-methylpyridinium-2″-yl)-pyrid-6′-yl]pyrimidine (L_P) was prepared as its hexafluorophosphate salt from 2-(9-anthryl)-4,6-bis(2′,2″-bipyrid-6′-yl)]pyrimidine (L)[10] by means of the protection procedure designed for multichelating polypyridine ligands[11] and recently adopted for a closely related ligand.[12] The compound $[(terpy)Ru(L_P)]^{3+}$ (**1**; terpy = 2,2′,2″-terpyridine) was synthesized by the reaction of L_P with $[Ru(terpy)Cl_3]$.[13] The new compound $[(terpy)Ru(L)]^{2+}$ (**2**) was then prepared from **1** by demethylation with diazabicyclooctane. Both the new Ru^{II} compounds were purified and characterized as their hexafluorophosphate salts. Details of the synthesis and characterization of all the new species will be reported elsewhere.[14]

The absorption spectra of **1** and **2** are dominated by intense bands in the UV region (ε in the range $10^4-10^5\,M^{-1}cm^{-1}$) and by moderately intense bands in the visible (ε in the range $10^3-10^4\,M^{-1}cm^{-1}$). Both metal complexes are luminescent at room temperature in acetonitrile ($\lambda_{max} = 715-730$ nm; $\Phi \approx 10^{-3}$) and at 77 K in a rigid butyronitrile matrix ($\lambda_{max} = 685$ nm for both the complexes). Their luminescence spectra do not depend on the excitation wavelength. The luminescence lifetimes are monoexponential and are in the 10^{-8} to 10^{-7} s range at room temperature and several orders of magnitude longer at 77 K. Under all the experimental conditions, the excitation spectra of each compound matched their respective absorption spectra.

The absorption and photophysical data of **1** and **2** are collected in Table 1. Figure 3 shows the absorption spectra in acetonitrile solution and Figure 4 shows the emission spectra of **1** in fluid solution at room temperature as well as in a rigid matrix at 77 K.

Table 1. Absorption and luminescence data of the compounds **1** and **2**[a]

	Absorbance[b] λmax [nm] (ε [$M^{-1}cm^{-1}$])	Luminescence, 298 K λ_{max} [nm]	τ [ns]	Φ	Luminescence, 77 K[c] λ_{max} [nm]	τ [μs]
1	250 (86000) 320 (37800) 480 (8200) 530 (7600)	730	60	4.1×10^{-3}	685	510
2	250 (96200) 330 (43300) 470 (12000) 510 (11500)	715	30	1.5×10^{-3}	685	680

[a] Data were recorded in deaerated acetonitrile solution, unless otherwise stated. [b] Only some characteristic maxima are reported. [c] In butyronitrile.

Discussion

The absorption spectra of **1** and **2** (Figure 3) are typical of Ru^{II}-polypyridine complexes.[15] The intense UV bands at $\lambda \approx 320$ nm can be mainly assigned to spin-allowed $\pi-\pi^*$ transitions which involve the polypyridine L_P and L ligands (ligand-centered (LC) transitions), on the basis of the absorption properties of L,[16] whereas the visible bands are

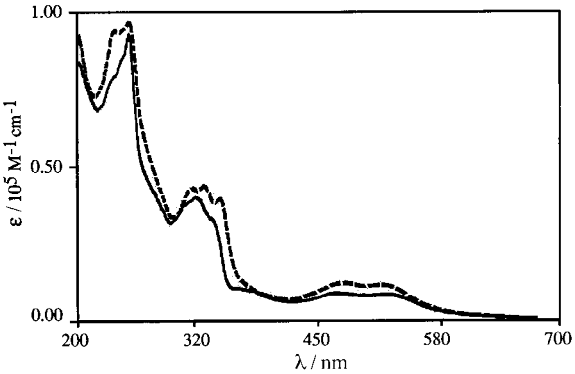


Figure 3. Absorption spectra of **1** (solid line) and **2** (dashed line) in acetonitrile fluid solution.

mainly due to spin-allowed metal-to-ligand charge-transfer (MLCT) transitions. The additional, very strong bands at $\lambda \approx$ 250 nm receive a contribution from the transition populating the ^1B_a state of the anthracene subunit.[17] The structured absorption bands that populate the ^1L_a level of the anthracene subunits expected at $\lambda \approx 320$ nm are partially obscured by the polypyridine-centered transitions.

Because of the presence of two different polypyridine ligands in both the complexes, two MLCT transitions at low energies are possible. The lowest absorption bands of **1** and **2** can be safely assigned to Ru$\rightarrow$L$_P$ and Ru$\rightarrow$L CT transitions, respectively, on the basis of i) the energy (Table 1) and ii) the comparison between the redox properties of $[Ru(terpy)_2]^{2+}$, **2**, and **1**. As far as point (i) is concerned, for both **1** and **2** the energy of the CT transition is significantly lower than that of the lowest CT transition in $[Ru(terpy)_2]^{2+}$ ($\lambda_{max} = 460$ nm[15]). With respect to point (ii), the first reductions in acetonitrile, localized in a terpy ligand in $[Ru(terpy)_2]^{2+}$ and in L and L$_P$ in the new compounds under study, take place at -1.29 V,[18] -0.89 V, and -0.82 V versus SCE, respectively, thus indicating that L and L$_P$ are more readily reduced than terpy. The slight red-shift of the lowest energy maximum of **1** compared to **2** (Table 1), which is attributed to the presence in L$_P$ of a methylated nitrogen capable of inducing further stabilization of the π^* orbital of the ligand, is in agreement with the redox data.

The luminescence of **1** and **2** in fluid solutions (Figure 4, Table 1) is assigned to triplet Ru$\rightarrow$L$_P$ and Ru$\rightarrow$L CT levels, respectively. This assignment is based on the emission energies, lifetimes, quantum yields, and spectral bandwidths, typical of Ru^{II}-polypyridine MLCT emitters.[15] The difference in energies of the emission spectra of the two complexes is in agreement with this interpretation, in that the lowest energy of the emission of **1** fits well with the reduction properties of the ligands (see above). The match between the excitation and the absorption spectra of **1** and **2** and the absence of anthracene fluorescence is particularly interesting in that it demonstrates that the light energy absorbed by the anthracene subunits is transferred with unitary efficiency to the ^{3}MLCT level of the Ru^{II} chromophores under these experimental conditions.

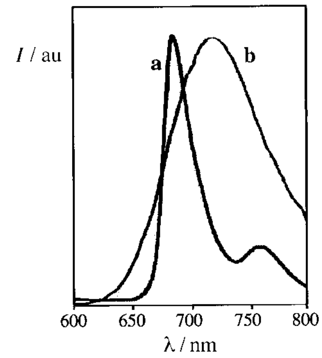


Figure 4. Emission spectra of **1** a) in a butyronitrile rigid matrix at 77 K and b) in fluid solution at room temperature.

The room-temperature photophysical properties of **1** and **2** also warrant some additional comments. Luminescence in fluid solution at room temperature is rarely found[15] for bis-tridentate Ru^{II} complexes. In fact, usually in these species a triplet metal-centered (^{3}MC) state lies close to the (potentially luminescent) ^{3}MLCT level, and the thermally activated population of the ^{3}MC state promotes fast radiationless decay to the ground state, which makes a radiative process uncompetitive.[19] The photophysical data (Table 1) indicate that **1** and **2** are among the strongest Ru^{II} emitters that contain bis-tridentate polypyridine ligands. In particular, to the best of our knowledge, **1** is the Ru^{II} complex of this family that exhibits the highest luminescence quantum yield ever reported. We attribute this property to the simultaneous presence of two factors:

i) the larger energy gap between ^{3}MC and ^{3}MLCT excited states compared to other similar systems, as a result of the stabilization of the latter state. This larger energy gap reduces the efficiency of the thermally activated process which deactivates luminescence;

ii) the larger coupling between donor and acceptor orbitals of the MLCT state in the complexes studied here, because of the contribution of the pyrimidine ring to the acceptor orbital. Pyrimidine-centered π^* orbitals are more coupled with metal dπ orbitals than pyridine-based π^* orbitals in metal complexes, and, as a consequence, the rate constant for the radiative decay from ^{3}MLCT to the ground state is increased in **1** and **2** with respect to, for example, $[Ru(terpy)_2]^{2+}$.

The situation is totally different in a rigid matrix at 77 K (Table 1, Figure 4). Under this condition, the emission spectra of **1** and **2** are practically identical (Table 1), although they exhibit different decays. From the emission spectra and lifetimes, we can attribute the 77 K emission of both complexes to a phosphorescence process centered in the anthracene subunits. The spectra are indeed typical of anthracene phosphorescence, as has been recently reported for a related mixed Ru^{II}-polypyridine/anthracene species.[20] The luminescence lifetimes are shorter than typical triplet anthracene lifetimes;[21] most likely because of an increased spin-orbit coupling induced in the anthracene moieties by the proximity of the metal-based chromophores.

The excitation spectra of **1** and **2** also match the relative absorption spectra under these experimental conditions. In particular, irradiation in the MLCT bands in the visible region leads to anthracene phosphorescence, which indicates that efficient energy transfer occurs from the Ru^{II}-based chromophores to the anthracene subunits.

The reason for the different photophysical properties (and direction of energy-transfer processes) of the complexes studied here under different experimental conditions resides in the nature of the luminophores. The lowest energy levels of each luminophore of the multicomponent species **1** and **2** are indeed quite different. In particular, the ^{3}MLCT levels of Ru$^{\mathrm{II}}$-polypyridine subunits have relatively short intrinsic lifetimes (they rarely exceed 1 μs at room temperature),[15, 22] whereas the lifetimes of the lowest energy triplet of anthracene derivatives is greater by several orders of magnitude.[21] Furthermore, the energy of the MLCT states depends on the nature of the matrix, while the anthracene-based excited states are usually independent of the matrix.

The energy of the lowest energy triplet of the anthracene subunits in **1** and **2** is assumed to lie at $\lambda = 685$ nm, the highest-energy feature of the 77 K emission (anthracene-based) of the complexes (Figure 4, Table 1). To estimate the energy of the ^{3}MLCT states of **1** and **2**, the following reasoning is used: From an inspection of the photophysical data of a large number of Ru$^{\mathrm{II}}$-polypyridine MLCT emitters,[15] the ^{3}MLCT emitting level at 77 K is typically $\approx 1200\ \mathrm{cm^{-1}}$ over emission maximum in the fluid solutions at room temperature. If a similar effect is assumed for **1** and **2**, the ^{3}MLCT states of the studied species at 77 K are expected to lie at $\lambda \approx 660$ nm, which is slightly higher than that of the anthracene triplet. This energy level scheme also explains the different lifetimes of the anthracene-based phosphorescence of **1** and **2** (Table 1): the anthracene triplet is mixed with the closely lying ^{3}MLCT levels and the mixing is stronger in **1** because of a smaller energy gap (the lowest energy ^{3}MLCT level in **1** is at lower energy than in **2** and is, therefore, closer to the anthracene triplet responsible for the emission), thus justifying the shorter lifetime of **1**.

At room temperature in fluid solution, the charge-transfer states are stabilized by a fast reorganization of the solvent so that their energy is lowered,[23] thus further approaching the energy level of the anthracene triplet. However, such a stabilization seems to be insufficient to invert the energy order of ^{3}MLCT and triplet anthracene levels at room temperature, as suggested by the onset of the MLCT emission of **1** at room temperature (Figure 4).

On the basis of the above discussion, intercomponent energy transfer from the ^{3}MLCT level(s) of the Ru$^{\mathrm{II}}$-polypyridine chromophores to the anthracene triplet, as indicated by the luminescence spectra at 77 K, is fully reasonable. Such an energy transfer should also occur at room temperature, so that the electronic energy collected by all the chromophores of the multicomponent species **1** and **2** upon light excitation is rapidly funneled to the anthracene subunits also in this condition. However, even if the stabilization upon solvent rearrangement that occurs in fluid solution is ignored, the lowest energy ^{3}MLCT states of **1** and **2** should lie no more than $600\ \mathrm{cm^{-1}}$ above the lowest energy anthracene level. The Boltzmann distribution indicates that at 298 K the upper-lying ^{3}MLCT states are populated for at least 4 % in both complexes. By taking into account the much faster intrinsic deactivation rates of the ^{3}MLCT states with respect to the intrinsic deactivation rates of the anthracene triplet, thermal activation is enough to irreversibly drive an uphill energy-transfer from the anthracene subunit(s) to the Ru-based chromophores.[24] The process is also assisted by the relatively fast solvent reorganization associated with energy transfer in fluid solution.

In a rigid matrix at 77 K, the MLCT states are very poorly populated, and the electronic energy collected by **1** and **2** decays by anthracene phosphorescence. The situation is schematized in Figure 5. This interpretation is a reminder of the reversible energy-transfer processes that occur in some Ru$^{\mathrm{II}}$/arene complexes.[25]

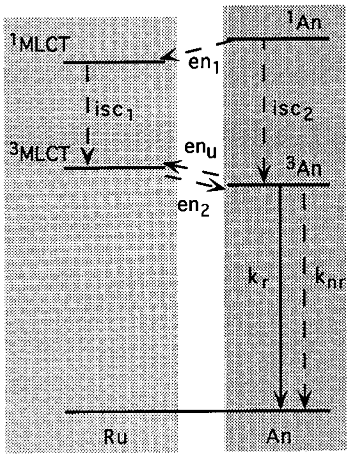


Figure 5. Schematization of the deactivation processes that occur in **1** and **2**. For simplicity, only the lowest energy singlet and triplet levels of the Ru$^{\mathrm{II}}$-polypyridine chromophores (^{1}MLCT and ^{3}MLCT) and of the anthracene subunits (^{1}An and ^{3}An) are represented. For the sake of clarity, the levels that belong to each individual subunit are grouped together vertically. The processes en$_1$ and en$_2$ are energy-transfer processes in a multicomponent approach. The process en$_u$ is uphill energy transfer. At room temperature, ^{3}MLCT and ^{3}An are in thermal equilibrium and ^{3}MLCT acts as a sink for the energy because its k' values (the decay rates of ^{3}MLCT that directly lead to the ground state, not shown in Figure) are much higher than the k values of ^{3}An. At 77 K, en$_u$ is negligible so that ^{3}An phosphorescence occurs.

Conclusions

We have demonstrated that the direction of the efficient photoinduced energy-transfer in two new multicomponent species is temperature-controlled. This leads to luminescence outputs that have different energies, lifetimes, and subunit origins, which means they are different in the energy, time, and space domains.[26] The control of the direction of the intercomponent energy-transfer process suggests the feasibility of the design of novel artificial supramolecular systems that are capable of elaborating information at the molecular level based on this relatively unexplored photophysical property.

Experimental Section

Absorption spectra were performed with a Kontron Uvikon860 spectrophotometer. Luminescence spectra and luminescence decays at 77 K were obtained by a Perkin Elmer LS-5B fluorimeter equipped with a Hamamatsu R928 photomultiplier. The emission spectra were corrected for phototube response by means of a calibrating lamp. Luminescence decays at room temperature were measured by an Edinburgh FL 900 time-correlated single-photon-counting spectrometer. Luminescence quantum yields were calculated by the optically diluted method,[9a] with $[Os(bpy)_3]^{2+}$ as the quantum yield reference ($\Phi = 0.0066$ in deaerated acetonitrile solution[9b]). Experimental uncertainties are as follows: absorption maxima, ±2 nm; extinction coefficients, 10 %; emission maxima, ±4 nm; emission lifetimes, 10 %; emission quantum yields, 20 %.

Acknowledgments

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[1] a) D.-P. Hader, M. Tevini, *General Photobiology*, Pergamon, Oxford, **1987**; b) R. Van Grondelle, J. P. Dekker, T. Gillbro, V. Sundström, *Biochim. Biophys. Acta* **1994**, *1187*, 1; c) G. McDermott, S. M. Prince, A. A. Freer, A. M. Hawthornthwaite-Lawless, M. Z. Papiz, R. J. Cogdell, N. W. Isaac, *Nature* **1995**, *374*, 517; d) J. Kroepke, X. Hu, C. Muenke, K. Schulten, H. Michel, *Structure* **1996**, *4*, 581; e) M. Freemantle, *Chem. Eng. News* **1998**, October 26, 37.

[2] The literature on this topic is too large to be exhaustively cited. For some recent reviews or representative articles, see: a) T. J. Meyer, *Acc. Chem. Res.* **1989**, *22*, 163; b) F. Scandola, M. T. Indelli, C. Chiorboli, C. A. Bignozzi, *Top. Curr. Chem.* **1990**, *158*, 73; c) V. Balzani, F. Scandola, *Supramolecular Photochemistry*, Horwood, Chichester, **1991**, Chapt. 6; d) M. R. Wasielewski, *Chem. Rev.* **1992**, *92*, 435; e) D. Gust, T. A. Moore, A. L. Moore, *Acc. Chem. Res.* **1993**, *26*, 198; f) J.-M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, VCH, Weinheim, **1995**, Chap. 8; g) V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serroni, *Chem. Rev.* **1996**, *96*, 759; h) G. S. Sadler, W. F. Wacholtz, C. K. Ryu, R. S. Schmehl, *New J. Chem.* **1996**, *20*, 749; i) J.-P. Collin, P. Gaviña, V. Heitz, J.-P. Sauvage, *Eur. J. Inorg. Chem.* **1998**, 1.

[3] See, for example: a) N. Sabbatini, M. Guardigli, J.-M. Lehn, *Coord. Chem. Rev.* **1993**, *123*, 201; b) A. Hagfelt, M. Graetzel, *Chem. Rev.* **1995**, *95*, 49; c) C. Devasoss, P. Bharathi, J. S. Moore, *J. Am. Chem. Soc.* **1996**, *118*, 9635; d) C. A. Bignozzi, J. R. Schoonover, F. Scandola, *Prog. Inorg. Chem.* **1997**, *44*, 1; e) L. M. Dupray, M. Devenney, D. R. Striplin, T. J. Meyer, *J. Am. Chem. Soc.* **1997**, *119*, 10243; f) P. G. Van Patten, A. P. Shreve, J. S. Lindsey, R. J. Donohoe, *J. Phys. Chem. B* **1998**, *102*, 4209; g) V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni, M. Venturi, *Acc. Chem. Res.* **1998**, *31*, 26.

[4] J. E. Guillet, N. A. D. Burke, M. Nowokowska, H. Reese, D. M. Gravett, *Macromol. Symp.* **1995**, *98*, 53.

[5] D.-L. Jiang, T. Aida, *J. Am. Chem. Soc.* **1998**, *120*, 10 895.

[6] a) I. Klimant, O. S. Wolfbeis, *Anal. Chem.* **1995**, *67*, 3160; b) W. Xu, K. A. Kneas, J. N. Demas, B. A. De Graff, *Anal. Chem.* **1996**, *68*, 2605; c) G. Di Marco, M. Lanza, A. Mamo, I. Stefio, C. Di Pietro, G. Romeo, S. Campagna, *Anal. Chem.* **1998**, *70*, 5019; d) X. Song, J. Nolan, B. I. Swanson, *J. Am. Chem. Soc.* **1998**, *120*, 11 514.

[7] E. Ishow, A. Credi, V. Balzani, L. Mandolini, F. Spadola, *Chem. Eur. J.* **1999**, *5*, 984.

[8] Under this circumstance, it could be questioned whether a real change in the direction of energy transfer occurs, in that the electronic energy is in any case initially directed to the same, lowest-lying subunit. However, in case the luminescence output origins from the other subunit as a consequence of the thermally activated process, a reverse energy migration takes place within the excited state lifetime.

[9] a) J. N. Demas, G. A. Crosby, *J. Phys. Chem.* **1971**, *75*, 991; b) R. S. Lumpkin, T. J. Meyer, *J. Phys. Chem.* **1986**, *90*, 5307.

[10] G. S. Hanan, U. S. Schubert, D. Volkmer, E. Rivière, J.-M. Lehn, N. Kyritsakas, J. Fischer, *Can. J. Chem.* **1997**, *75*, 169.

[11] a) S. Serroni, G. Denti, *Inorg. Chem.* **1992**, *31*, 4251; b) S. Campagna, G. Denti, S. Serroni, A. Juris, M. Venturi, V. Ricevuto, V. Balzani, *Chem. Eur. J.* **1995**, *1*, 211.

[12] D. Bassani, J.-M. Lehn, K. Fromm, D. Fenske, *Angew. Chem.* **1998**, *110*, 2534; *Angew. Chem. Int. Ed.* **1998**, *37*, 2364;.

[13] B. P. Sullivan, J. M. Calvert, T. J. Meyer, *Inorg. Chem.* **1980**, *19*, 1404.

[14] Similar synthetic procedures have also been reported: a) G. S. Hanan, C. R. Arana, J.-M. Lehn, D. Fenske, *Angew. Chem.* **1995**, *107*, 1191; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1122; b) G. S. Hanan, C. R. Arana, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **1996**, *2*, 1292.

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

[16] a) A. Credi, V. Balzani, S. Campagna, G. S. Hanan, C. R. Arana, J.-M. Lehn, *Chem. Phys. Lett.* **1995**, *243*, 105. b) P. Ceroni, A. Credi, V. Balzani, S. Campagna, G. S. Hanan, C. R. Arana, J.-M. Lehn, *Eur. J. Inorg. Chem.* **1999**, 1409.

[17] M. Klessinger, J. Michl, *Excited States and Photochemistry of Organic Molecules*, VCH, New York, **1995**.

[18] V. Balzani, A. Juris, F. Barigelletti, P. Belser, A. von Zelewsky, *Riken Q* **1984**, *78*, 78.

[19] T. J. Meyer, *Pure Appl. Chem.* **1986**, *58*, 1193.

[20] G. J. Wilson, A. Launikonis, W. H. F. Sasse, A. W.-H. Mau, *J. Phys. Chem. A* **1997**, *101*, 4860.

[21] a) N. J. Turro, *Modern Molecular Photochemistry*, Benjamin-Cummings, Menlo Park, **1978**; b) *Handbook of Organic Photochemistry* (Ed.: J. C. Scaiano), *Vols. I* and *II*, CRC, Boca Raton, **1989**.

[22] For the term intrinsic lifetime we mean the excited-state lifetime of the "isolated" luminophore. Models for the intrinsic lifetimes of the metal-based and anthracene-based luminophores of **1** and **2** are the luminescence lifetimes of $[Ru(bpy)_3]^{2+}$ (≈ 1 µs, depending on the matrix[15]) and the transient triplet–triplet absorption spectrum lifetime of anthracene (in the range 10^{-4} to 10^{-3} s[21]).

[23] P. Chen, T. J. Meyer, *Chem. Rev.* **1998**, *98*, 1439.

[24] The anthracene triplet plays the role of "reservoir" of the MLCT excited state. This effect has already been used to lengthen the MLCT luminescence lifetime in Ru^{II}/arene complexes.[19, 25]

[25] a) W. E. Ford, M. A. J. Rodgers, *J. Phys. Chem.* **1992**, *54*, 1; b) G. J. Wilson, W. H. F. Sasse, A. W.-H. Mau, *Chem. Phys. Lett.* **1996**, *250*, 583; c) J. A. Simon, S. L. Curry, R. S. Schmehl, T. R. Schatz, P. Piotrowak, X. Jin, R. P. Thummel, *J. Am. Chem. Soc.* **1997**, *119*, 11 012.

[26] The difference in space domain, although it is correct in principle, should be treated with care when it refers to relatively small molecules.

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