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Extending Excited-state Lifetimes by Interchromophoric Triplet-state Equilibration in a Pyrene-Ru(II)diimine Dyad System

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The Future of Supramolecular Chemistry

In the last few years, supramolecular chemistry has become a key issue in many aspects of chemistry. A large community of researchers is assembling, covalently and non-covalently, simple “building blocks” to achieve large and complicated functional structures. New properties can in fact emerge when suitable molecules interact with each other, and the organization of “smart” components has led to the construction of nanosized architectures that can perform interesting functions upon an external input. More recently, the self-assembly principle moved from simple molecules in solution to surfaces in attempts to create molecular machines, switches, motors, wires, or in other words, photochemical or electrically driven devices. The next challenge will be the interface of such nanosystems with the macroworld or perhaps the creation of a complete molecular-based assembly able to give a readable and useful external signal.

The control of the assemblies, in terms of modulation of the strength of interaction, size, shape, directionality, organization on surfaces, can certainly be called supramolecular. More recently, such self-assembly has involved not only simple molecules but also nanoclusters such as gold or semiconductive nanoparticles.

Not only are these topics currently being pursued in our group, but also they represent how we see the future of supramolecular chemistry. Along this line, we intend to design and study the interactions and the functions of different types of nanosized objects, bridged by “molecular wires”, and triggered by light or electrons. Currently, we describe a simple molecular approach consisting of a pyrene-bridge-ruthenium system.



Professor Dr Luisa De Cola was born in Messina, Italy, where she studied Chemistry and received her “Laurea” (110/110 cum laude) in 1983. She was a postdoctoral research fellow (NIH and Coulter Electronics) at the Virginia Commonwealth University, Richmond, USA (1984–1986) (Postdoctoral Adviser: Professor L. M. Vallarino). Then, she joined the National Research Council F.R.A.E. CNR of Bologna as Associate Researcher (1986–1989). In 1990, she became Assistant Professor at Dipartimento di Chimica “G. Ciamician”, in the group of Professor Vincenzo Balzani, University of Bologna (Italy). In 1998, she has been appointed Full Professor (chair of Molecular Photonic Materials) at University of Amsterdam (The Netherlands). She has experience in the design, synthesis,

photochemical and photophysical properties of large (supra)molecular systems such as polynuclear compounds linked by saturated and conjugated bridging ligands, dendrimers, and molecular switches. In general, the purpose of the work has been the development of functional systems able to respond to an external stimulus such as light. She has industrial collaborations with Philips Research, and with Roche Diagnostics on (electro)luminescent materials.

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Professor Dr Frédéric Fages received his engineering degree in Physics & Chemistry from ENSCPB, Bordeaux, in 1983 and a PhD (Doctorat d'Etat) degree from the University Bordeaux 1 in 1988 with Henri Bouas-Laurent. He took up a position as Chargé de Recherche at CNRS in 1983, becoming Professor at the University Bordeaux 1 in 1998. The main focus of his research activity was the design of supramolecular systems with tunable fluorescence properties and the study of self-assembled gels from low-molecular-mass organogelators. In 1989, he was an Alexander-von-Humboldt postdoctoral fellow in the group of Kurt Schaffner and Alfred Holzwarth at Max-Planck-Institut für Strahlenchemie, Mülheim an der Ruhr, Germany, where he worked on light-harvesting antenna complexes for artificial photosynthesis. In September 2002, he joined the Laboratory of Organic Chemistry and Molecular Materials (UMR 6114 CNRS) at the Faculty of Sciences of Luminy, University Aix-Marseille II, where his research group works on the synthesis and study of conjugated nanostructured materials for optoelectronic applications.

Dr René M. Williams was born in 1965 in Amsterdam, where he also did his doctoral exam in 1990, on "Perylenebisimides, colorful compounds with a big potential", synthesis and photophysical characterization of perylenebisimide-bridge-electron donor systems. In 1990, he started as a researcher at the "Chemiewinkel" of the UvA, within the framework of social service, working on the long-term effects of paper deacidification. He started his PhD in 1991 research in the group of Professor Dr J. W. Verhoeven in the Organic Chemistry department of the UvA, where, on 10 June 1996, he received his doctorate with the thesis entitled: "Fullerenes as electron accepting components in supramolecular and covalently linked electron transfer systems". He then obtained a Marie-Curie fellowship, working at Max-Planck Institut für Strahlenchemie in Mülheim an der Ruhr, in the group of Professor Dr S. E. Braslavsky. He worked on "laser-induced optoacoustic spectroscopy" of *cis-trans* isomerization reactions of biological systems and photochromic compounds and, together with Silvia, wrote a chapter of a book: Photomovement—Molecular Basis. He did a second postdoc at Columbia University in the city of New York, in the group of Professor Dr N. J. Turro, working on an industrial project involving glass fibers: "Triplet sensitization effects on phosphine oxide photoinitiators used in photopolymerization". Here, he mainly focused on time-resolved electron paramagnetic resonance (TR-EPR). Since 1 December 1999, he has been working as a Lecturer/Assistant Professor in the Molecular Photonic Materials group of Professor Dr Luisa De Cola in the Institute of Molecular Chemistry in Amsterdam. Here, he specializes on photoinduced processes such as electron and energy transfer in molecular, supramolecular and nano systems.

The synthesis and the spectroscopic properties of a bichromophoric ruthenium trisbipyridyl-1,4-diethynylenebenzene-pyrene system (Ru-b-Py) and the corresponding pyrene ligand (b-Py) are reported. The ruthenium model systems Ru-b-OH, Ru-b-Ph are also presented. UV-Vis absorption and emission at room and low temperature and time-resolved spectroscopy are discussed. For the Ru-b-Py dyad, a mixing of the ³MLCT state of the ruthenium-based component and the triplet state of pyrene, ³Py, is observed. Time-resolved transient absorption studies performed on the Ru-b-Py and on the b-Py ligand show that the lowest energy absorption is due to the population of the triplet state localized on the pyrene-component. Time-resolved studies also evidenced a relatively slow forward triplet equilibration rate, in the order of $2 \times 10^5 \text{ s}^{-1}$ (5 μs), and an even slower back energy transfer rate, $3.3 \times 10^4 \text{ s}^{-1}$, still faster than the intrinsic decay time of the pyrene (200 μs).

Keywords: Supramolecular photochemistry; Energy transfer; Room temperature phosphorescence

INTRODUCTION

Influencing excited-state lifetimes by interchromophoric interactions is an important theme in supramolecular photochemistry with the aim

of tuning photophysical properties for specific functions, such as diagnostic labeling or energy conversion [1–7].

In that connection, transition metal complexes, and in particular ruthenium complexes containing diimine ligands, have been the subject of continuing interest as luminescent labels or photosensitizers for photochemical reactions [8,9]. This is partly because they possess low-lying excited states such as metal-to-ligand charge transfer (MLCT) excited states that in most cases lead to luminescence in the visible region. Furthermore, due to an extremely efficient intersystem crossing (often $\eta = 1$), the lowest excited state is a triplet MLCT, and therefore its deactivation (formally spin forbidden) occurs on a rather long timescale (nano- to microsecond regime). It has been shown that for Ru(II) complexes of pyrene-tethered bipyridine ligands, the excited-state lifetimes can be prolonged further up to ca. 150 μs in solution at room temperature [10–13]. Such a result can be rationalized in terms of triplet-state equilibration involving reversible electronic energy transfer between the ³MLCT state of the complex and the triplet $\pi-\pi^*$ state of the pyrene chromophore. This particular feature is due to the quasi-isoenergetic position of the triplet states of the pyrene and Ru(II) units within the supramolecular dyad. Actually, the lifetime is modulated not only by the relative triplet energy of

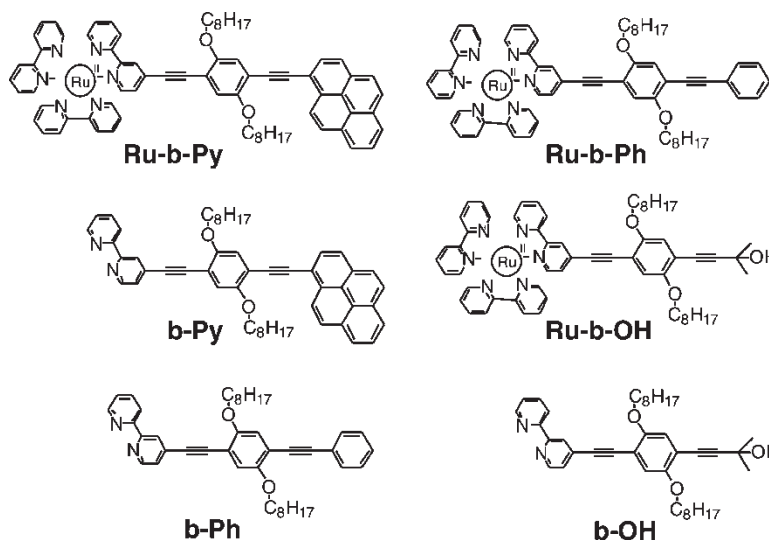


FIGURE 1 Structures of the ligands and the ruthenium complexes discussed in this study and their abbreviations. **Ru-b-Py** is the bichromophoric Rutheniumtrisbipyridyl-1,4-diethynylenebenzene-Pyrene system. **Ru-b-OH** and **Ru-b-Ph** are the model systems for the ruthenium complex (C_8H_{17} = n-octyl).

the pyrene and Ru(II) chromophores but also by the nature of the covalent bridge connecting these two units and the relative orientation of the two chromophores. In the case of dyads in which the pyrene component is directly connected to the bpy ligand via a single C–C bond, orbital parentage also plays a role. In these cases, it was observed that emission was the result not of triplet equilibration but of intra-ligand charge transfer (ILCT) states leading to complex luminescence features [14–17].

In order to further evaluate the influence of the conjugated bridge on the excited-states properties of pyrene-Ru(II) dyads, the ligand **b-Py** was synthesized in which a phenylene ethynylene linker acts as a rigid tether ensuring extended π -conjugation between the two terminal units. The case of a related photoactive dyad was reported in which the pyrene and Ru(II) end-units are bridged by a single ethynylene moiety [18]. Moreover, the photophysical properties of π -conjugated metal-organic systems were reported and the results demonstrated the dramatic influence of the metal on the optical and electronic properties of the conjugated polymers [19].

Here, we report on the synthesis and the spectroscopic properties of a series of ligands and their ruthenium complexes. In particular, bpy (2,2'-bipyridine) connected in the 4 position to a terminal group such as a pyrene chromophore, **b-Py**, a benzene moiety, **b-Ph**, or an sp^3 carbon atom bearing a terminal alcohol function, **b-OH**, and their corresponding ruthenium complexes (Fig. 1) are discussed.

The photophysical properties of the pyrene-containing complex (**Ru-b-Py**) are shown and

compared with those of ruthenium reference systems, **Ru-b-Ph** and **Ru-b-OH** (Fig. 1).

RESULTS AND DISCUSSION

Synthesis

A preliminary account describing the synthesis of the ligand **b-Py** has been reported previously [20]. The synthesis involved a sequence of Pd-mediated cross-coupling reactions of ethynyl derivatives and the corresponding haloarenes. The full description of the synthesis of the ligands will be described elsewhere. The ruthenium complexes were prepared according to a classical procedure. The ligands were reacted with one molar equivalent of the $Ru(bpy)_2Cl_2$ precursor in refluxing ethanol (freshly distilled) under a nitrogen atmosphere for 20 h.

Electronic Absorption Spectra

The UV–Vis absorption spectra in THF of all the ruthenium complexes investigated are shown in Fig. 2. The most significant absorption maxima and the molar extinction coefficients (ϵ) are summarized in Table I.

As expected, the complexes show 1MLCT absorption bands in the visible region due to the $Ru \rightarrow bpy$ transitions. The lowest absorption band, assigned to the MLCT transition involving the substituted bipyridines [15], is red-shifted (470 nm) compared with the reference $Ru(bpy)_3^{2+}$ complex (450 nm). The bathochromic shift is consistent with the substitution of one of the bipyridyl unit with a strongly conjugating group. In the visible region, the **Ru-b-Py** complex shows, besides the MLCT

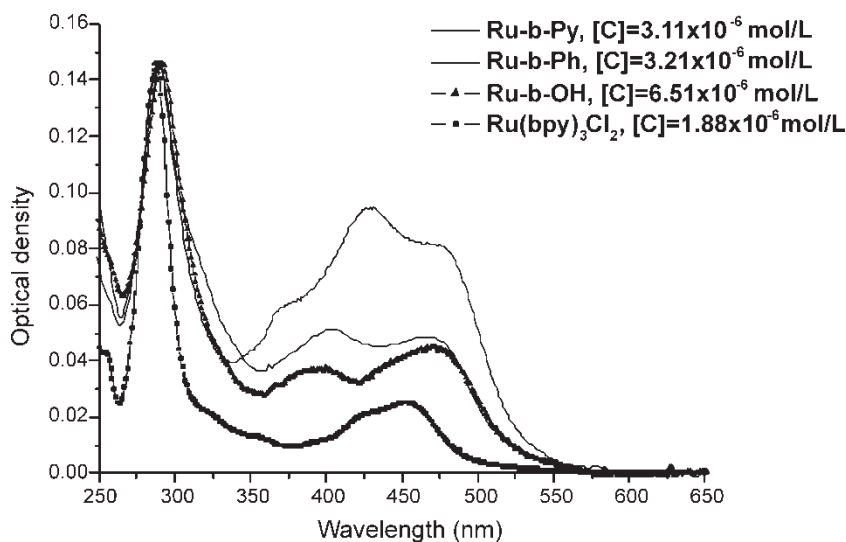


FIGURE 2 UV-Vis absorption spectra of **Ru-b-OH** (6.5×10^{-6} M) and **Ru-b-Ph** (3.2×10^{-6} M) and **Ru-b-Py** (3.2×10^{-6} M) compared with $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (1.9×10^{-6} M) in THF solution.

bands, a band at 430 nm which can be assigned to a pyrene $\pi-\pi^*$ transition, as confirmed by comparison with the absorption spectrum of **b-Py** obtained after addition of an excess of Zn(II) (Fig. 3). As expected, the transition at 430 nm is not observed in the spectra of **Ru-b-Ph** and **Ru-b-OH** compounds (Fig. 2) or the corresponding ligands that lack the pyrene chromophore (Fig. 3).

The UV region is dominated by the characteristic ligand centered, ^1LC , $\pi-\pi^*$ transitions of the unsubstituted bпыs, at 290 nm, at a slightly lower energy for the substituted ones. Furthermore, for the ligands **b-OH** and **b-Ph**, low-lying ^1LC transitions due to the extended electronic delocalisation are observed with maxima at 362 and 370 nm, respectively.

In the **b-Py** compound, containing the pyrene moiety, the absorption spectrum related to the pyrene unit is also influenced by the substitution. Whereas pyrene normally shows characteristic bands with a good, fine structure between 200 and 350 nm, the spectrum assigned to the pyrene moiety is relatively unstructured and is also bathochromically shifted to 415 nm, with a tail going to 450 nm. The spectra were also recorded in butyronitrile

and in acetonitrile, but no solvent effects were observed.

Luminescence Spectroscopy

Representative room-temperature emission spectra of the compounds are depicted in Fig. 4 (deaerated butyronitrile solutions). Emission data are summarized in Table II.

Upon excitation at 480 nm, the typical $^3\text{MLCT}$ emission for heteroleptic ruthenium complexes around 650 nm is observed for **Ru-b-Ph**, **Ru-b-OH**, and for **Ru-b-Py** also, a sharp pyrene phosphorescence feature at 680 nm is present. The excitation spectra are independent of observation wavelength (645 or 680 nm) and are in accordance with the absorption spectra. The emission intensity is very sensitive to the presence of oxygen, and deoxygenating the solutions results in an increase in the emission quantum yields of a factor of 1.5 and 8 for **Ru-b-OH** and **Ru-b-Ph**, respectively. In the case of **Ru-b-Py**, deaerating the solution also causes a change in the shape of the emission spectrum. In fact, the presence of oxygen leads to the disappearance of the pyrene emission at 680 nm, leaving the less oxygen-sensitive 645 nm emission as predominant (see Fig. 5).

The emission spectrum of **Ru-b-Py** obtained by excitation at a short wavelength ($\lambda_{\text{ex}} = 370$ nm) presents a residual emission around 450 nm. Such fluorescence could in principle be assigned to a small impurity of the ligand in our complex. However, addition of excess zinc chloride did not lead to charge-transfer emission characteristic of the zinc (II)-pyrene-containing bipyridine complex [20].

TABLE I Absorption characteristics of the complexes in THF

	λ_{max}^* (nm)	ε^\dagger ($\text{M}^{-1} \text{cm}^{-1}$)
Ru-b-OH	470 (396, 291)	— [‡]
Ru-b-Ph	470 (404, 290)	15,000
Ru-b-Py	470 (430, 375, 290)	26,200

* Other transitions are shown in parentheses. [†] At the absorption maximum. [‡] Not determined due to low solubility.

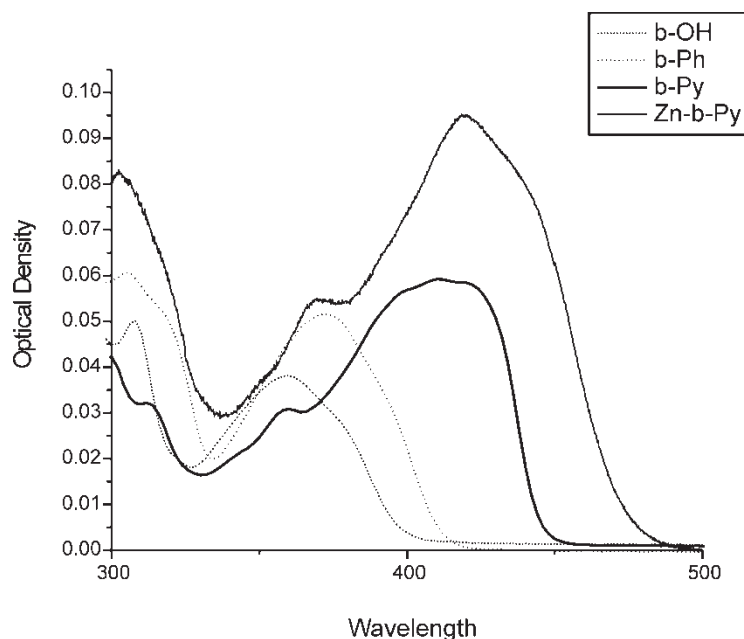


FIGURE 3 UV-Vis absorption spectra of **b-OH**, **b-Ph**, **b-Py** and the Zn(II) complex of **b-Py** in THF solution.

Furthermore, the excited-state lifetime measured in the emission maximum is far too short ($\tau = 300$ ps) to be attributed to the free ligand ($\tau = 2$ ns). Therefore, we can rule out the hypothesis of an impurity, and we believe that this residual emission is due to a non-complete energy transfer from the excited singlet $\pi-\pi^*$ state of the pyrene-based component to the lower excited state. Some reports in the literature, where the fluorescence of the ligand is not totally quenched upon ruthenium [21,22] or rhenium [19,23] complexation, corroborate our observation.

The luminescence quantum yields were determined in tetrahydrofuran (THF), butyronitrile (BCN)

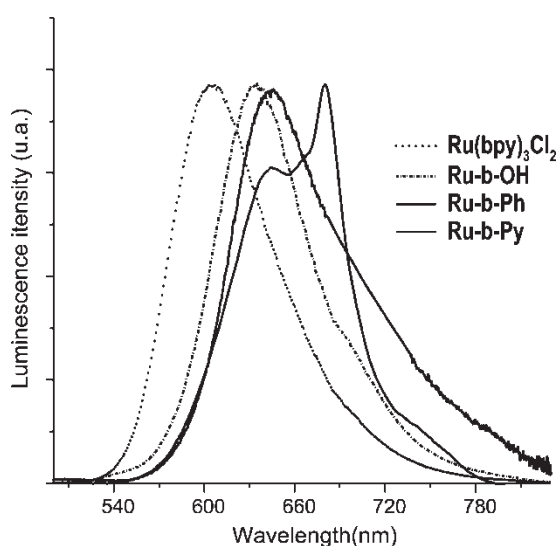


FIGURE 4 Emission spectra of $\text{Ru}(\text{bpy})_3\text{Cl}_2$, **Ru-b-OH**, **Ru-b-Ph** and **Ru-b-Py** in deaerated butyronitrile solution at room temperature ($\lambda_{\text{ex}} = 480$ nm).

and acetonitrile (ACN), and were relatively low (see Table II). The emission quantum yields were smaller than those reported in the literature for similar compounds, and almost as low as for the terpyridyl systems [18,24].

Time-resolved emission spectra obtained for **Ru-b-Py** clearly show the conversion of the ruthenium-based emission into the more structured pyrene phosphorescence (Fig. 6). The shift of the maximum in time is estimated to occur on a $5 \mu\text{s}$ timescale, as determined with a smaller incremental time delay.

A comparison of scaled emission spectra at different delay (0 and $50 \mu\text{s}$) shows the change in emission contribution of the two chromophores (Fig. 6). The lifetime of the emission centered around 680 nm is longer than that centered around 645 nm. For **Ru-b-Py**, we observe a biexponential emission decay with a short component of $3 \mu\text{s}$ and a longer component of about $20-40 \mu\text{s}$ (see Table III). The relative amplitudes of these emissions vary slightly as a function of observation wavelength. The contribution of the short component varies from 80% ($\lambda_{\text{obs}} = 650$ nm) to 70% ($\lambda_{\text{obs}} = 750$ nm). The contribution is in agreement with the relative weight of each band, calculated from the steady-state luminescence spectrum, at room temperature, by gaussian deconvolution.

For the other complexes, the excited-state lifetimes are monoexponential and are much longer than the $\text{Ru}(\text{bpy})_3^{2+}$ reference compound. It is known, however, that ruthenium complexes containing a phenylethynylene-substituted bipyridine exhibit a long excited-state lifetime in deaerated solution due to delocalization effects [25-27].

TABLE II Emission quantum yields in deaerated solutions of the complexes ($\lambda_{\text{ex}} = 480 \text{ nm}$), together with the maximum of the most intense emission peaks

	THF	λ_{max} (nm)	BCN	λ_{max} (nm)	ACN	λ_{max} (nm)
Ru-b-OH	0.017	645	0.011	649	0.014	652
Ru-b-Py	0.008	645, 678	0.008	650, 680	–	652, 680
Ru-b-Ph	0.030	646	0.005	647	0.002	651

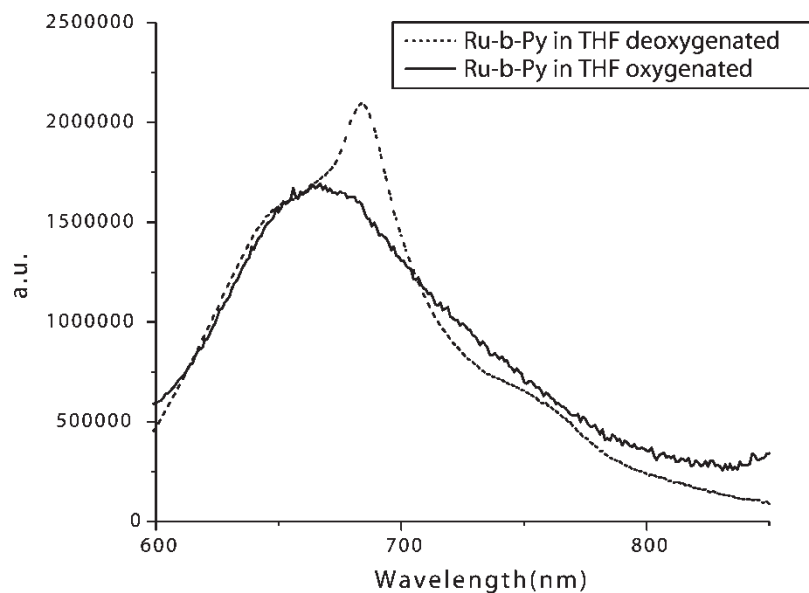
The model complex **Ru-b-OH** displays a slight solvent effect on the emission lifetime, ranging from 3 to 4 μs . **Ru-b-Ph** shows a similar lifetime (see Table III) comparable with the short component of **Ru-b-Py**.

The excited-state emission lifetimes are summarized in Table III.

Emission spectra at 77 K were recorded for all the complexes, and representative spectra are shown in Fig. 7. **Ru-b-Ph** and **Ru-b-OH** display the normal features of $^3\text{MLCT}$ emission (625 nm) for polypyridine complexes [28]. For the **Ru-b-Py** system, the pyrene phosphorescence is very clearly observed at about 675 nm.

The steady-state and time-resolved emission data suggest that deactivation of the $^3\text{MLCT}$ excited state via triplet energy transfer occurs to the lower lying [$\Delta E(\text{RT}) = 919 \text{ cm}^{-1}$; $\Delta E(77 \text{ K}) = 1250 \text{ cm}^{-1}$] ^3LC excited state localized on the pyrene moiety [22]. The intensity ratio of bands at 640 nm and 680 nm varies slightly as a function of the excitation wavelength, indicating that an intersystem crossing from the singlet excited state of pyrene plays a minor role. Similar behavior was observed at 77 K for other ruthenium complexes containing the pyrene chromophore [11,12,15].

Schmehl *et al.* made the same observation in the case of a ruthenium complex containing a pyrene chromophore directly bound to a phenanthroline [15]. The authors concluded that there is a weak interaction between the pyrene and the rest of the system, on account of the large torsion angle between the pyrene unit and phenanthroline. This is not the case for **Ru-b-Py**. In fact, the absorption spectrum of **Ru-b-Py** (Fig. 2) shows an interaction between terminal units of the complex. This is even more evident in the emission maximum strongly shifted to the red ($\lambda_{\text{max}} \approx 590 \text{ nm}$ for pyrene and $\lambda_{\text{max}} \approx 680 \text{ nm}$ for the pyrene-localized emission of **Ru-b-Py**). The bathochromic shift of the pyrene phosphorescence is a consequence of the conjugation of the system. The same kind of effect was observed by Tokumaru *et al.* [29] and by Möllerstedt [30] in the case of the *trans*-1-(3,3-dimethyl-but-1-enyl)pyrene and of *trans*-1-styrylpyrene, emission maxima being at 647 and 664 nm, respectively. Nevertheless, the excited-state lifetime of this ligand-centered triplet state is shorter than that of pyrene [31] (580 ms) at 77 K and also shorter than that observed for the ruthenium complexes containing a pyrene unit linked by an alkyl bridge [11,32].

FIGURE 5 Emission spectra of **Ru-b-Py** in aerated and deaerated THF solution at room temperature ($\lambda_{\text{ex}} = 480 \text{ nm}$).

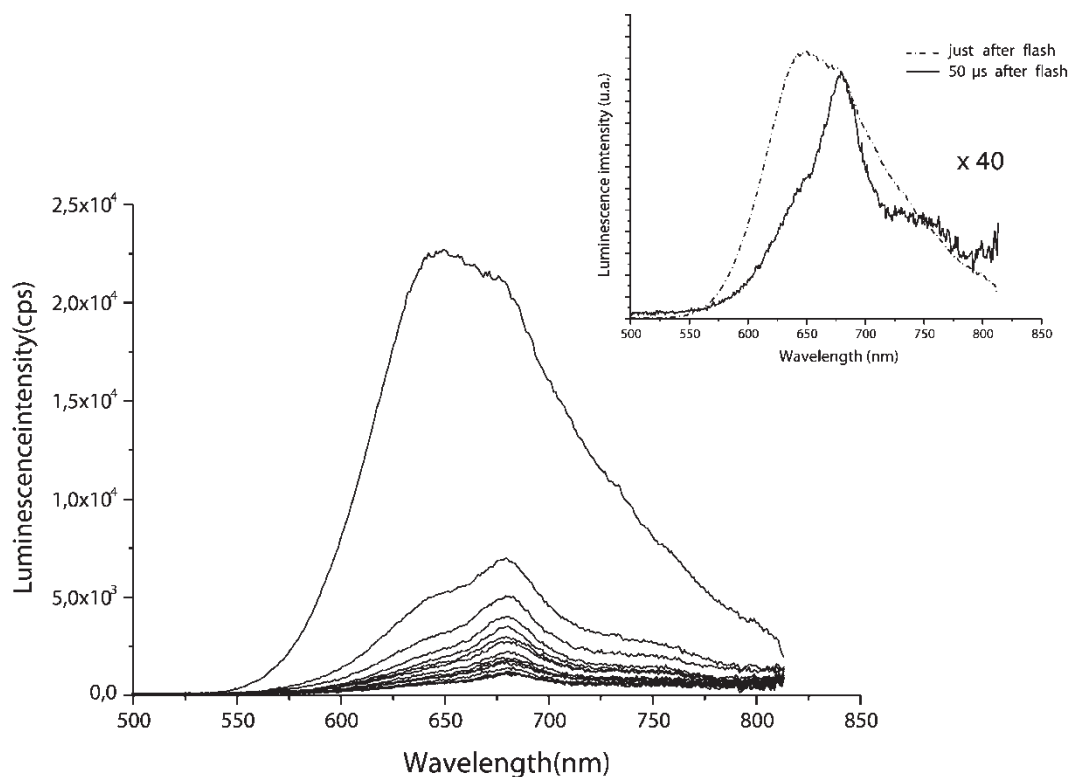


FIGURE 6 Time-resolved emission spectra of **Ru-b-Py** in deaerated butyronitrile solution at room temperature ($\lambda_{\text{ex}} = 460$ nm, 10 μs incremental time delay). The inset compares the spectra (scaled at 680 nm) at an incremental time delay of 0 and 50 μs (first and fifth spectrum) ($\times 40$).

At 77 K, the lifetime obtained at 640 nm for **Ru-b-Py** is in the same order as for **Ru-b-Ph**, ca. 36 μs . When the wavelength of observation is set at the pyrene emission band, at 675 nm, the measured lifetime (second component) is much longer (≈ 600 μs).

All the data obtained so far clearly reveal that for **Ru-b-Py**, emission is observed from two different triplet excited states, one localized on the ruthenium-based component and the other on the pyrene unit. There is no fast (ps) equilibration between the two states as can be easily seen from the emission lifetimes. Furthermore, the population of the lowest ^3LC excited state can be estimated to be less than 20%.

TABLE III Emission lifetimes of the three complexes in deaerated solutions, at room temperature, together with the excitation and observation (detection) wavelengths

	Solvent	τ (μs)	$\lambda_{\text{ex}}/\lambda_{\text{obs}}$ (nm)
Ru-b-OH	THF	3.1	480/640*
	BCN	2.5	480/620*
	ACN	2.7	480/640*
Ru-b-Ph	BCN	3.2	360/600 to 700
	THF	5.4 and 17	450/620 to 750 [†]
Ru-b-Py	BCN	4.0 and 40	460/650 to 750 ^{†,‡}
	ACN	3.0 and 20	460/620 to 750 [†]

*Single line emission measurements. [†]Determined with OMA IV equipment. [‡]Determined with a streak camera.

In order to investigate further the nature of emissive-excited state, and to obtain a complete picture of the processes occurring in the excited molecules, the transient absorption spectra of the complexes were recorded at room temperature.

Transient Absorption Spectroscopy

Figure 8 shows the transient differential absorption spectra for **Ru-b-Py** in THF solution for excitation at 460 nm and of the **b-Py** system (excitation at 355 nm). In Fig. 8, also the transient absorption spectrum of the **Ru-b-Ph** reference system is depicted.

The **Ru-b-Py** spectrum presents a bleaching between 350 and 500 nm with a minimum at 425 nm and a shoulder at 470 nm. This is due to depopulation of the ground state. As in the time-resolved emission, we can observe a spectral change in the transient absorption traces, indicating the change in populations of the two states, which is mostly reflected in the apparent shape of the ground-state bleaching. In fact, the shape of the band between 420 and 480 changes with time, and in the higher-energy part of the band, the formation of a positive absorption can be detected, since the spectrum loses intensity in this region. The lack of a positive absorption band at about 415 nm is mainly due to the overlap with the ground-state bleaching

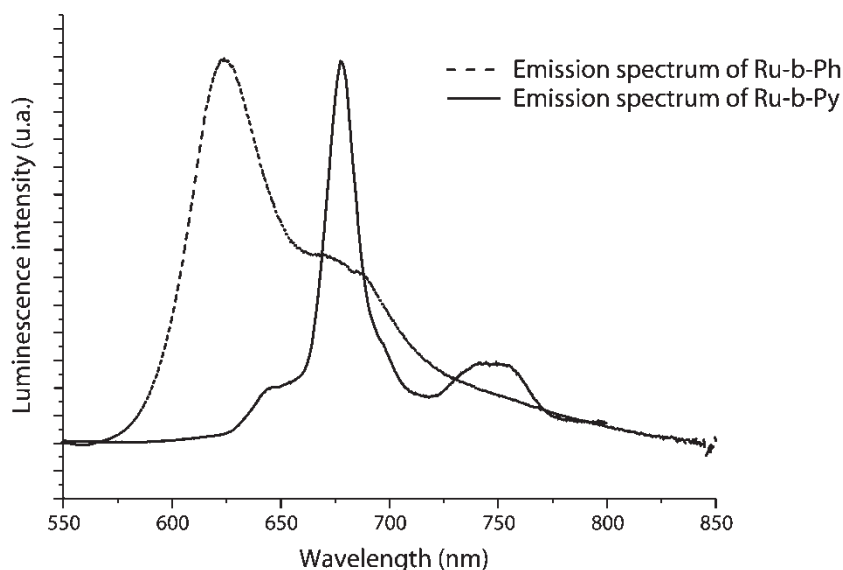


FIGURE 7 Emission spectra of **Ru-b-Ph** and **Ru-b-Py** obtained in THF at 77 K, with a 10 μ s delay.

(1 MLCT and 1 LC). Taking into account the emission results, we have to conclude that the spectral change is caused by pyrene triplet formation. Whereas the transient absorption spectra of both the **Ru-b-Py** system and the **Ru-b-Ph** system give a relatively broad band between 500 and 850 nm, comparison with the transient absorption spectrum of **b-Py** (Fig. 8) clearly shows that the spectral shape of the **Ru-b-Py** transient must be attributed to the pyrene triplet. Furthermore, the signals show a biexponential decay, with lifetimes of 30 and 200 μ s. The latter lifetime is also observed for the thoroughly degassed **b-Py** reference system at room temperature. The transient absorption of 3 Py is known to have a maximum around 415 nm, but also shows absorption bands around 520 and 480 nm [11,31,33].

For the **Ru-b-Ph** system, the broad transient absorption band between 550 and 850 nm can be attributed to the absorption of the radical anion of the substituted bipyridyl unit. Transient absorption spectra of the other ruthenium complexes show similar features and a monoexponential decay, similar to the reported lifetimes, over the whole spectrum.

Clearly, the emission lifetime of the ruthenium chromophore is not strongly quenched, indicating that the formation of the pyrene triplet state from the Ru is slower than its intrinsic decay. Still, the pyrene triplet state is populated with ca. 20% efficiency, and as its intrinsic decay is very slow, the Ru chromophore is repopulated, displaying a delayed luminescence lifetime of ca. 40 μ s. Whereas the intrinsic decay of the pyrene triplet has not yet been observed in the emission study, it can be easily detected using transient absorption spectroscopy.

We can therefore assess the energetic scheme reported in Fig. 9. Excitation at 370 nm, where the two chromophores absorb, leads to the population of the 1 LC and 1 MLCT state. The excited state centered on the pyrene relaxes either by energy transfer to the excited state 1 MLCT or by intersystem crossing (ISC) to the 3 LC, due to the presence of the ruthenium unit (heavy atom effect). Excitation at 480 nm leads to preferential population of the 1 MLCT state, which is deactivated to the 3 MLCT state by intersystem crossing and can either emit or interconvert into the 3 LC state.

Hissler *et al.* [18] reported picosecond resolved transient absorption spectra of acetylene-pyrene linked directly or via Pt(II) to Ru(bpy) $_3$ where the triplet of acetylpyrene at 410 nm was clearly observed. For the direct linkage, a much broader transient spectrum was observed. An influence of the bridge on the photophysical properties of the triplet state of the complexes was observed.

CONCLUSIONS

From the spectroscopic data presented for the **Ru-p-Py** complex and the free ligand **p-Py**, we can infer that the two chromophores are strongly coupled and that the triplet states of the two chromophores influence each other. The presence of the heavy atom Ru(II) enhances the intersystem crossing in the pyrene-containing ligand, as it displays room-temperature phosphorescence, which is quite uncommon for such systems. The triplet state of the pyrene in turn acts as a reservoir and thereby enhances the lifetime of the ruthenium moiety, and very long-lived species can be obtained. Thus, an intricate interplay of the two excited states, which

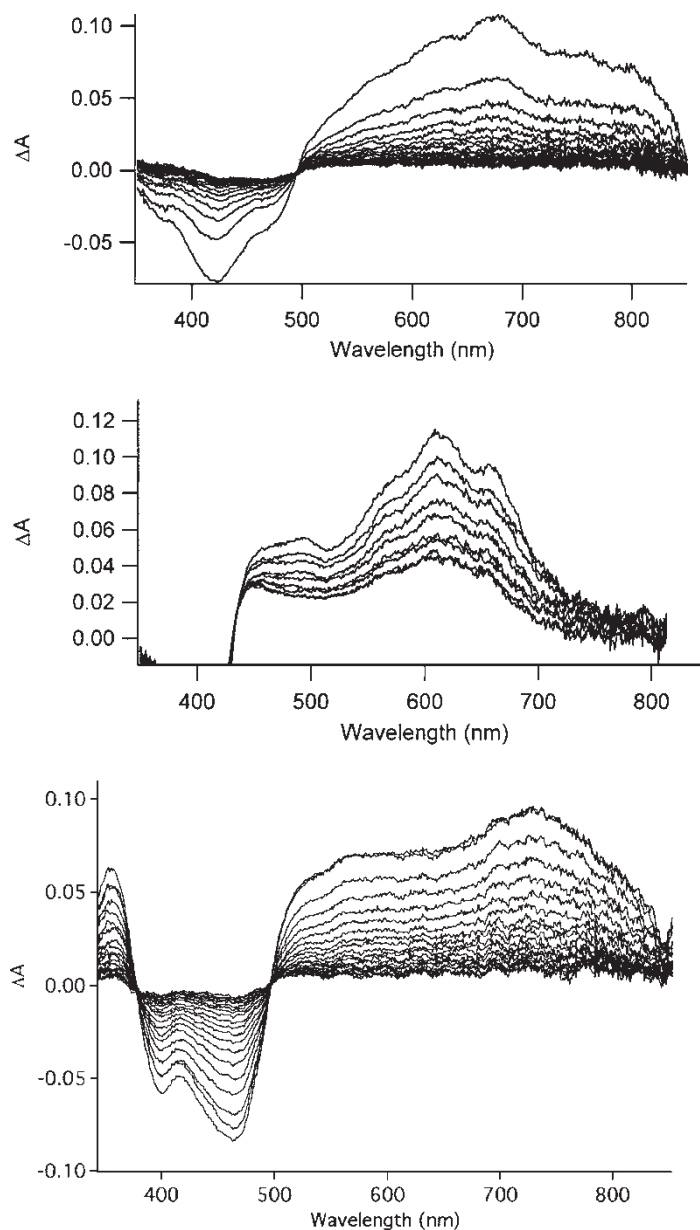


FIGURE 8 Top: Transient absorption spectrum of **Ru-b-Py** in deaerated THF ($\lambda_{\text{ex}} = 450$ nm, 25 μs incremental time delay). Middle: the transient absorption spectrum of **b-Py**. Bottom: transient absorption spectrum of **Ru-b-Ph** in deaerated butyronitrile ($\lambda_{\text{ex}} = 450$ nm, 500 ns incremental time delay).

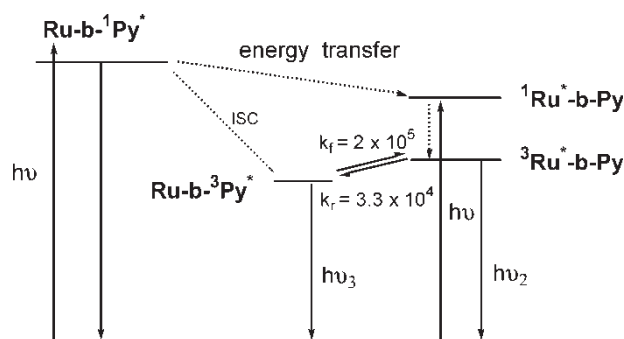


FIGURE 9 Representation of the energy levels and processes that take place in **Ru-b-Py** upon excitation, together with localization of the excitation, spin state and the rates at room temperature.

display a strong but chromophorically distinct oxygen sensitivity, is observed. The decay of luminescence is always biexponential at room temperature, and we observe, in time-resolved emission and in transient absorption, an evolution of the shape of the spectrum.

The excited state with the longer lifetime is specifically due to the presence of the pyrene chromophore. Furthermore, detailed time-resolved studies reveal for the **Ru-b-Py** complex a relatively slow, forward triplet equilibration rate, in the order of $2 \times 10^5 \text{ s}^{-1}$ (5 μs), and a back energy transfer rate ($3.3 \times 10^4 \text{ s}^{-1}$) that is still faster than the intrinsic decay time of the pyrene. In the case of model complexes **Ru-b-Ph** and **Ru-b-OH**, the emission

spectra are quite simple, and luminescence decays are monoexponential. However, the high degree of conjugation of the substituted bpy causes an increase in the excited state lifetime compared with the Ru(bpy)₃²⁺ complex.

MATERIALS AND METHODS

A preliminary account describing the synthesis of the ligand **b-Py** has been reported previously. The full description of the synthesis of the ligands will be described elsewhere.

The preparation of the ruthenium complexes was performed according to a classical procedure. The ligands were reacted with one molar equivalent of the Ru(bpy)₂Cl₂ precursor in refluxing ethanol (freshly distilled) under a nitrogen atmosphere for 20 h. To the cooled reaction mixture was added an aqueous solution of KPF₆ (excess). After centrifugation, the solid was dried *in vacuo* and subjected to chromatography.

Ru-b-Py

The solid was chromatographed using two consecutive, deactivated alumina columns, eluting with dichloromethane containing increasing amounts of methanol (from 0.5 to 1% v/v). Orange powder, yield 62%. Mass spectrometry (FAB +): Low-resolution MS: 1294.9 (M⁺ - 1PF₆⁻), 1150.6 (M⁺ - 2PF₆⁻); HR-MS: Calculated for C₇₂H₆₈N₆O₂RuPF₆: 1295.409674. Found: 1295.408906.

Ru-b-OH

Chromatography on a silica gel column, eluting with water/NaCl/AN/MeOH mixture. Red solid, yield 49%. Low-resolution MS: 1153.6 (M⁺ - 1PF₆⁻), 1008.5 (M⁺ - 2PF₆⁻). HR-MS: Calculated for C₅₉H₆₆N₆O₃Ru: 1008.421902. Found: 1008.423988.

Ru-b-Ph

Chromatography on Sephadex CM C-25 (Fluka), eluting with water/MeOH/acetone 65/20/15 v/v). Red solid. Yield 8% (non-optimized). Low resolution MS: 1026 (M⁺ - 2PF₆⁻). HR-MS: Calculated for C₆₂H₆₄N₆O₂Ru: 1026.4191159. Found: 1026.413423.

Photophysical Measurements

UV-Vis absorption spectra were determined with a Hewlett Packard 8453 diode array spectrophotometer. Emission spectra were recorded on a SPEX Fluorolog I (1681) instrument equipped with an R928 photomultiplier (Products for

Research) or a Spex Fluorolog I-212 equipped with a phosphorescence mode unit.

Spectrally and time-resolved emission was determined with a Hamamatsu C-5680 streak-camera equipped with a M 5677 sweep unit or with a gated Optical Multichannel Analyzer (OMA IV) from EG&G instruments. The latter was also used for transient absorption spectroscopy. As excitation and white probe sources, a tuneable Coherent Infinity laser (1 ns pulses FWHM) and an EG&G Xe flash lamp (X 504) were used. Single-line emission measurements were performed using an Oriel 77250 monochromator and photomultiplier tube coupled to a Tektronix oscilloscope.

Owing to the extremely long excited-state lifetimes and their oxygen sensitivity, the use of the freeze-pump-thaw method was essential for deaerating, and at least three cycles were used. Bubbling with argon for 30 min was clearly not sufficient.

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