

# Photophysical properties of supramolecular assemblies containing polypyridine complexes and pyrene chromophores

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A supermolecule containing the complex  $[M(\text{bpy})_2(\text{bpy-O-bpy})]^{2+}$   $\{M = \text{Ru(II)}, \text{Os(II)}; \text{bpy-O-bpy} = \text{bis}[4-(2,2'\text{-bipyridinyl})\text{ether}]\}$  and a pyrene derivative (1-pyreneacetic acid) is formed in the presence of  $\text{Zn}^{2+}$  ions in acetonitrile solution. In the case of the Os(II) complex all the energy absorbed by the supramolecular system is transferred to the Os-based unit, which retains the photophysical properties of the  $[\text{Os}(\text{bpy})_2(\text{bpy-O-bpy})]^{2+}$  complex. In the Ru-based system, the excited state lifetime of the metal complex is extended to the microsecond range at room temperature, thanks to an equilibrium with the close-lying triplet excited state of the pyrene, as already found for analogous covalently linked systems. The main advantage of the supramolecular approach is essentially its high versatility, and it could find applications in many fields requiring luminescent probes possessing long lifetimes, such as clinical chemistry, chemical sensing, photocatalysis, and biophysics.

## Introduction

The synthesis and photophysical characterisation of covalently linked systems containing  $d^6$  metal diimine complexes and aromatic hydrocarbons has been the topic of several publications in recent years.<sup>1–10</sup> The interest in this area is due to different reasons. On the one hand, the characterisation of these systems gave very valuable elements for the study of energy- and electron-transfer processes. On the other hand, they led to molecular assemblies with quite interesting properties. Among them, it is worth emphasising the possibility to extend the excited state lifetimes of the metal complexes into the microsecond range. Luminescent probes possessing long excited state lifetimes can find important applications in biophysics, clinical chemistry, photocatalysis and chemical sensing.<sup>11–14</sup> In particular, long lifetimes have been found in dyads in which the triplet excited state of the metal complex {usually, complexes of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  family} lies very close in energy to that of the hydrocarbon unit (typically pyrene derivatives), so that reversible energy transfer processes between the two units are possible.

The approach of linking together the metal diimine complex and the aromatic hydrocarbon with covalent bonds is not, however, the only possibility. As a matter of fact, supramolecular chemistry can offer many different methods for

bringing the two moieties together.<sup>15</sup> The main advantage of this approach is essentially its high versatility, since many systems, possibly with the desired properties, can be built starting from a few molecular bricks which are commercially available. We report here the photophysical characterisation of a supramolecular system made up of a Ru(II)  $\{[\text{Ru}(\text{bpy})_2(\text{bpy-O-bpy})]^{2+}$ ,  $\text{bpy-O-bpy} = \text{bis}[4-(2,2'\text{-bipyridinyl})\text{ether}]\}$  (1) or an Os(II)  $\{[\text{Os}(\text{bpy})_2(\text{bpy-O-bpy})]^{2+}$  (2) complex, containing a free bpy unit as a potential bridging ligand, and a pyrene derivative (1-pyreneacetic acid, 3) with a carboxylate function as a coordinating agent. The two moieties can be brought in close contact by direct coordination to a  $\text{Zn}^{2+}$  ion. The results obtained corroborate the effectiveness of the supramolecular approach.

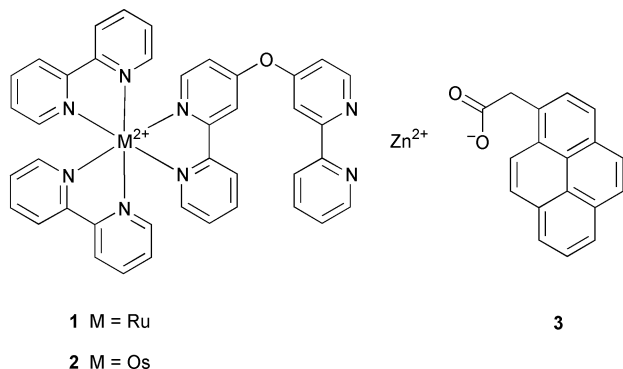
## Experimental

### Materials

The  $[\text{Ru}(\text{bpy})_2(\text{bpy-O-bpy})]^{2+}$  (1) and  $[\text{Os}(\text{bpy})_2(\text{bpy-O-bpy})]^{2+}$  (2) complexes were available from previous investigations. 1-Pyreneacetic acid (3), tributylamine and  $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  were from Aldrich and used as received. The solvent for the photophysical measurements was acetonitrile from Merck (UVASOL), used without further purification.

### Spectroscopic measurements

Absorption spectra were recorded with a Perkin-Elmer lambda 16 spectrophotometer. Uncorrected emission and corrected excitation spectra were obtained with a Perkin-Elmer LS-50 spectrofluorimeter equipped with a Hamamatsu R3896 phototube. Luminescence lifetimes (uncertainty  $\pm 7\%$ ) in the range 1 ns–20  $\mu\text{s}$  were obtained with an Edinburgh single-photon counting apparatus, in which the flash lamp was filled with  $\text{D}_2$ . Phosphorescence lifetimes in the millisecond range were obtained with a Perkin-Elmer LS-50 spectrofluorimeter. Luminescence quantum yields (uncertainty  $\pm 15\%$ ) were

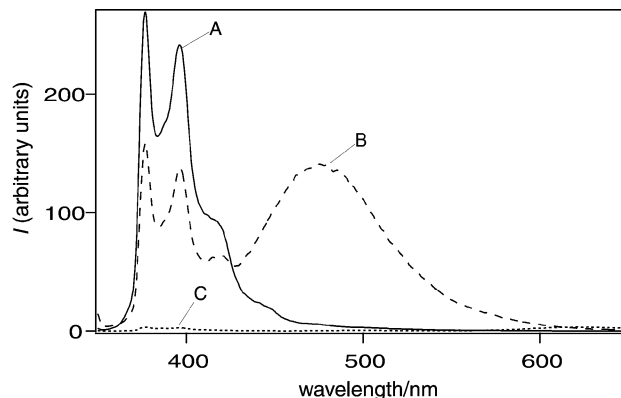


determined using  $[\text{Ru}(\text{bpy})_3]^{2+}$  ( $\Phi = 0.028$  in aerated water<sup>18</sup>) as a standard. In order to allow comparison of emission intensities, corrections for instrumental response, inner filter effects<sup>19</sup> and phototube sensitivity were performed. A correction for differences in the refractive index was introduced when necessary.

## Results and discussion

The photophysical properties of **1** and **2** in acetonitrile are very similar to those of the parent  $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $[\text{Os}(\text{bpy})_3]^{2+}$  complexes<sup>20,21</sup> (Table 1). As already discussed for **1**,<sup>16</sup> the electronic communication through the bridging ligand bpy-O-bpy is small enough so as to not modify substantially the properties of the connected units. The electronic interaction is however not negligible, since it has been found to be sufficiently large to allow efficient energy transfer through the bridge, a necessary condition for the buildup of multicentre antenna systems. The presence of a small electronic interaction is also shown by the effect on the photophysical properties of **1** and **2** upon addition of  $\text{Zn}^{2+}$  ions. In particular, for the Ru complex a 7 nm redshift of the luminescence band can be observed, accompanied by an increase of the excited state lifetime (Table 1). A small (3 nm) redshift has also been observed for the Os complex. These findings can be explained in terms of a lower electronic density on the bridging ligand, caused by the coordination with the  $\text{Zn}^{2+}$  ion. This effect decreases the energy of the metal-to-ligand charge transfer transition involving the bpy-O-bpy unit, causing the observed shift of the luminescence band, as already observed in other cases.<sup>22,23</sup>

Compound **3** shows in the  $10^{-6}$ – $10^{-4}$  M concentration range the characteristic fluorescence of the pyrene monomer, with only a small redshift due to the substitution in the 1-position with the alkyl chain.<sup>24</sup> At 77 K, a phosphorescence band with  $\lambda_{\text{max}} = 606$  nm can also be observed, with a lifetime of 170 ms. Addition of a stoichiometric amount of tributylamine deprotonates the carboxylic group but does not cause any change in the absorption and fluorescence spectra, because of the long distance between the pyrene moiety and the acidic function.<sup>24</sup> As already reported, however, addition of  $\text{Zn}^{2+}$  ions up to a stoichiometric ratio of 1:2 (metal:pyrene) leads to strong changes in the absorption and fluorescence spectra.<sup>24</sup> In particular, a broadening of the pyrene absorption bands, a decrease in the intensity of the fluorescence band ( $\lambda_{\text{max}} = 378$  nm,  $\tau = 16$  ns) due to the pyrene monomer and the appearance of a new, large, and very intense band centred at 476 nm ( $\tau = 15$  ns) can be observed (compare curves A and B in Fig. 1). These findings are attributed to the formation of a complex with 1:2 (metal:pyrene) stoichiometry, in which the two pyrene units, lying very close to each other, can interact to form a dimer even in the ground



**Fig. 1** Fluorescence spectra ( $\lambda_{\text{exc}} = 340$  nm) at room temperature of acetonitrile solutions containing  $2.5 \times 10^{-5}$  M each of tributylamine and (A) **3**, (B) **3** and  $\text{Zn}(\text{ClO}_4)_2$ , (C) **1**,  $\text{Zn}(\text{ClO}_4)_2$  and **3**.

state. The observed changes are so strong that this very simple system has been suggested as a possible chemosensor for the detection of divalent metal ions.<sup>24</sup>

Upon addition of equimolar amounts of tributylamine,  $\text{Zn}^{2+}$  ions, **3**, and **1** or **2**, to an acetonitrile solution, we could observe photophysical properties that were very different from those typical of the isolated chromophores, even in the presence of  $\text{Zn}^{2+}$  ions (Table 1). As far as the absorption spectrum is concerned, that shown by the solution containing all the above-mentioned compounds is very similar to what is expected from the algebraic summation of the different chromophores. It is, however, worth noting that the band of the pyrene chromophore is slightly redshifted, without presenting the broadened form characteristic of the dimeric pyrene.

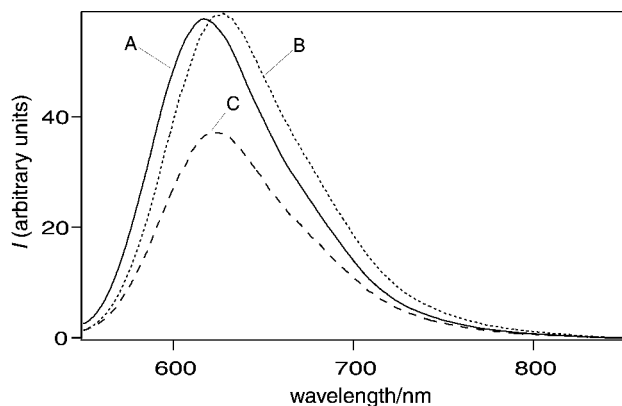
On the other hand, in the system **1**- $\text{Zn}^{2+}$ -**3**, the fluorescence typical of the pyrene monomer is almost completely quenched (the residual intensity being less than 2%), without any intensity increase in the 440–540 nm region, where the band attributable to the dimeric form of the pyrene can be typically observed (see curve C in Fig. 1). Upon excitation of the MLCT band of the Ru complex at 450 nm, where only the latter species absorbs, a luminescence band peaking at 624 nm can be observed. This band is very similar, although 37% less intense, to that observed when **1** and  $\text{Zn}^{2+}$  ions are mixed together (compare curves B and C in Fig. 2). Excitation spectra performed at  $\lambda_{\text{em}} = 620$  nm (where, at room temperature, only the luminescence band of the Ru complex is present) clearly show the presence of the absorption band of the pyrene chromophore.

In the system **1**- $\text{Zn}^{2+}$ -**3**, the analysis of the excited state decay profile was also very interesting. When the analysis was performed at 377 nm, on looking at the signal of the pyrene

**Table 1** Photophysical data in air-equilibrated acetonitrile solution at room temperature

System	Absorption $\lambda_{\text{max}}/\text{nm}$ ( $\epsilon/\text{M}^{-1} \text{cm}^{-1}$ )	Luminescence		
		$\lambda_{\text{max}}/\text{nm}$	$\tau/\text{ns}$	<i>I</i> (%)
<b>1</b>	453(10 300)	620	149	100
<b>2</b>	480(11 100)	727	31	100
<b>3</b>	340(40 000)	377	17	100
<b>1</b> - $\text{Zn}^{2+}$	453(10 300)	627	175	100 <sup>a</sup>
<b>2</b> - $\text{Zn}^{2+}$	480(11 100)	730	31	78 <sup>a</sup>
<b>3</b> - $\text{Zn}^{2+}$	342(28 100)	377	16	61 <sup>a</sup>
		476	15	
<b>1</b> - $\text{Zn}^{2+}$ - <b>3</b>	343(37 200)	377 <sup>b</sup>	15 <sup>b</sup>	1.5 <sup>a,b</sup>
	453(10 300)	624 <sup>c</sup>	12, 180, 380 <sup>c</sup>	63 <sup>a,c</sup>
<b>2</b> - $\text{Zn}^{2+}$ - <b>3</b>	343(38 600)	377 <sup>b</sup>	16 <sup>b</sup>	3 <sup>a,b</sup>
	480(11 100)	730 <sup>c</sup>	30 <sup>c</sup>	78 <sup>a,c</sup>

<sup>a</sup> Relative intensity with respect to the free component taken as 100%. <sup>b</sup> Pyrene-centred fluorescence. <sup>c</sup>  $\text{M}(\text{bpy})_3^{2+}$ -centred luminescence.



**Fig. 2** Luminescence spectra ( $\lambda_{\text{exc}} = 450$  nm) at room temperature of acetonitrile solutions containing  $2.5 \times 10^{-5}$  M each of tributylamine and (A) **1**, (B) **1** and  $\text{Zn}(\text{ClO}_4)_2$ , (C) **1**,  $\text{Zn}(\text{ClO}_4)_2$  and **3**.

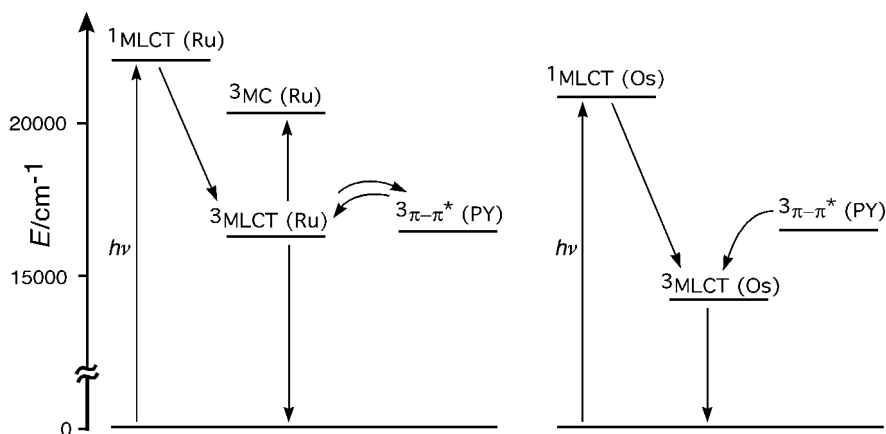
monomer, we obtained a single exponential decay with a resulting lifetime (15 ns) very similar to that observed for **3** alone. A triple excited state decay was on the contrary observed on looking at the Ru-centred luminescence: a quite short component (12 ns) and a longer one (380 ns) accompanied that typical of the Ru complex in the presence of Zn ions (180 ns). When complex **2** was present, a single exponential decay (30 ns) was instead observed, similar to that of the free chromophore **2** under the same conditions.

In principle, in the solution obtained on mixing equimolar amounts of tributylamine,  $\text{Zn}^{2+}$  ions, **3** and **1** or **2**, different species could be present: the metal complex and the pyrene derivative alone, their complexes with  $\text{Zn}^{2+}$  ions having 1 : 1 and 1 : 2 (metal : ligand) stoichiometries, and a system in which the  $\text{Zn}^{2+}$  ion is surrounded by one pyrene moiety and one Ru or Os complex. The results obtained clearly show that **3** is present in the free form and as its complex with  $\text{Zn}^{2+}$  [with both 1 : 1 and 1 : 2 (metal : ligand) stoichiometries] in very small quantities, since their typical, otherwise intense fluorescence (at 377 and 476 nm for the monomeric and dimeric form, respectively) is almost absent in the luminescence spectra. More precisely, the residual fluorescence at 377 nm, since the lifetime is the same as that found for **3** alone, should be attributed to the presence of less than 2% of the free component. An even lower percentage (<1%) can be in turn assigned to the complex formed with two molecules of **3** and one  $\text{Zn}^{2+}$  ion. As a consequence, the species containing pyrene should be present, with a percentage higher than 95%, in the ternary system containing also the metal complex **1** or **2**. In this system, energy transfer occurs with high efficiency and high rate constants ( $k_q > 10^{11} \text{ s}^{-1}$ ) from the singlet excited state of the pyrene to the lowest MLCT triplet state of

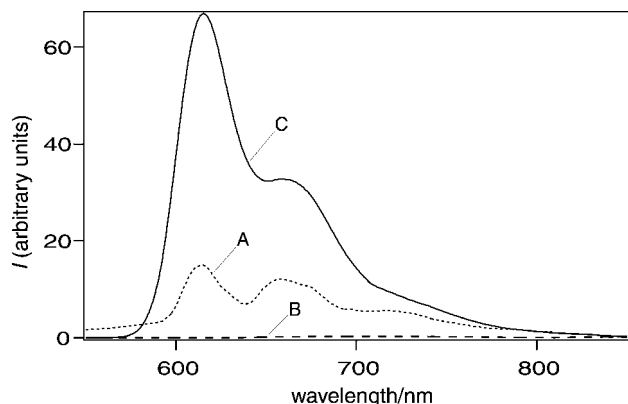
the Ru or Os complex, as can be seen from the excitation spectra performed at  $\lambda_{\text{em}} = 620$  and 730 nm (for the Ru and Os complex, respectively), where the contribution of the absorption bands of the hydrocarbon moiety is evident. The efficiency of such an energy transfer process is comparable with those obtained in covalently linked systems.<sup>1–10</sup>

The presence of a triple exponential decay for the luminescence of the Ru complex can also be easily understood. When direct excitation of the Ru moiety is performed, if it lies close to the pyrene moiety, its luminescence can be quenched because of an energy transfer process to the close lying triplet excited state of the pyrene. This additional channel for the decay of the triplet MLCT state centred on the Ru moiety is responsible for the shorter component found in the analysis of the decay profile. It is worth noting that the rate constant for this energy transfer process ( $k_q = 6.1 \times 10^7 \text{ s}^{-1}$ ) is lower than those found in covalently linked systems,<sup>1,3,6,7,9</sup> most probably because of the larger distance between the donor and acceptor, the lower electronic conjugation between them, and of a less favourable energy gradient. In addition to this, however, since the energy gap between the two triplet states is small (ca.  $200 \text{ cm}^{-1}$ , calculated from the highest energy feature of their phosphorescence band at 77 K), a back energy transfer from pyrene to the Ru chromophore is possible (Fig. 3), as already shown for all the covalently linked systems studied so far. As in those cases, since the radiative rate constant of the Ru complex is much greater than the pyrene radiative decay rate, almost all the energy is emitted through the  $[\text{Ru}(\text{bpy})_3]^{2+}$ -type moiety.<sup>25</sup> The reversibility of this energy transfer process is then the reason for the longer component in the decay profile. This is also true at 77 K, where again the only luminescence band that can be observed is that of the Ru chromophore (Fig. 4) featuring a lifetime in the millisecond range (3 ms), although at this temperature the phosphorescence of the free pyrene could be observed. At room temperature the presence of molecular oxygen, on the contrary, quenches both the triplet states and drastically reduces, as expected, the lifetime of the longer component. The presence in the mixture of a decay component similar to that for **1** complexing the  $\text{Zn}^{2+}$  ions is, on the contrary, due to the small fraction (<5%) of **1** that is complexed by  $\text{Zn}^{2+}$ , but then does not form a ternary system with **3**.

When complex **2** is present, again the prevalent species is the ternary system, as expected because the coordinating properties of **1** and **2** are similar, since they are related to the nature of the bridging ligand. This behaviour explains the almost complete quenching of the pyrene fluorescence. In the case of **2** however, the triplet state of pyrene is much higher in energy with respect to the triplet MLCT state of the Os complex, so that all the energy is transferred to this latter unit. Once populated, directly or *via* fast energy transfer from the



**Fig. 3** Schematic representation of the energy level diagram of the ternary systems **1**- $\text{Zn}^{2+}$ -**3** (left) and **2**- $\text{Zn}^{2+}$ -**3** (right).



**Fig. 4** Phosphorescence spectra ( $\lambda_{\text{exc}} = 450$  nm,  $t_d = 1$  ms) at 77 K of acetonitrile solutions containing  $2.5 \times 10^{-5}$  M each of tributylamine and (A) **3**, (B) **1** and  $\text{Zn}(\text{ClO}_4)_2$ , (C) **1**,  $\text{Zn}(\text{ClO}_4)_2$  and **3**.

pyrene excited states, its photophysical behaviour is presumed to be very similar to that of **2** alone, since no additional pathway for the decay of this state is now available, nor can equilibria be set up with the pyrene-centred triplet state, since in this case the energy gap is much larger with respect to the system containing the Ru centre (Fig. 3).

## Conclusions

In this work we have presented a supramolecular approach for the formation of assemblies containing a polypyridine metal (Ru or Os) complex and a pyrene derivative. In particular, when equimolar amounts of **3**, tributylamine, zinc perchlorate, and **1** or **2** were mixed together in an acetonitrile solution, among the species that could possibly form, the ternary one with one pyrene moiety and one polypyridine complex around a  $\text{Zn}^{2+}$  ion is by far (>95%) the most prevalent. As already reported for covalently linked systems, we have found that, when the Ru complex **1** was present in the assembly, its excited state lifetime is extended into the micro-second range. This could be important for practical applications in fields of great importance for social and economical reasons, such as biophysics, clinical chemistry, photocatalysis and chemical sensing. Compared to the systems obtained through covalent bonds, the supramolecular assemblies presented here can be much more versatile, since the hydrocarbon unit can be chosen among the almost infinite series of compounds having a carboxylate function. In this way, a dyad having photophysical properties suitable for the desired application can be obtained with a fast screening process without requiring long and time consuming synthesis.

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