

Hexanuclear polypyridine complexes containing different metals, bridging ligands and/or terminal ligands. Absorption spectra, electrochemical oxidation, luminescence properties and intercomponent energy transfer

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Abstract

Four novel hexanuclear complexes of general formula $[(L)_2M(\mu-BL)]_2M(\mu-BL)M[(\mu-BL)M(L)_2]_2^{12+}$, where the metal ions M are Ru^{2+} and/or Os^{2+} , the bridging ligands BL are 2,3-dpp and/or 2,5-dpp, and the terminal ligands L are bpy and/or biq, have been investigated (dpp = bis(2-pyridyl)pyrazine; bpy = 2,2'-bipyridine; biq = 2,2'-biquinoline). These polymetallic complexes can be considered as supramolecular species made of six distinct metal-containing units. They display very intense ligand centered absorption bands in the UV region (ϵ_{max} in the order of $2.5 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) and broad and intense bands in the visible region (ϵ_{max} in the order of $5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). On electrochemical oxidation, the metal centers are oxidized at the same or different potentials depending on the nature of the metal ions (Ru^{2+} or Os^{2+}) and on their positions (inner or outer) in the supramolecular structure. For all the novel compounds, luminescence can be observed in the red or near-IR spectral region. The luminescence properties, which are characteristic of specific metal-containing units, show that exoergic electronic energy transfer between adjacent units is 100% efficient, whereas it is much lower when higher energy units are interposed. Various energy migration patterns can be obtained by placing different units in suitable sites of the supramolecular array.

Introduction

Assembly of molecular components that exhibit suitable excited state and redox properties can lead to photochemical molecular devices capable of performing light-induced energy-migration and charge-separation processes [1, 2]. Artificial photochemical molecular devices can be designed on the basis of (i) metal-containing building blocks that exhibit suitable ground and excited state properties, and (ii) bridging ligands capable of linking the building blocks to form appropriate supramolecular structures [2, 3].

$Ru(II)$ [4, 5] and $Os(II)$ [5, 6] complexes of polypyridine-type ligands are suitable building blocks for the design of supramolecular systems capable of performing light-induced functions. In the last few years we have extensively used these building blocks to obtain

compounds of nuclearity between 2 and 13 [7–13]. In principle, for a compound of a given nuclearity the light absorption, luminescence, redox properties and the intercomponent energy transfer pattern can be varied by changing (i) the type of metal ion, (ii) the type of bridging ligand, (iii) the type of terminal ligand, and (iv) the position of the various components in the supramolecular structure. We have decided to explore in detail these effects by designing, synthesizing and investigating eight different hexanuclear compounds. As shown in Fig. 1, the components used are the Ru^{2+} and Os^{2+} metal ions, the 2,3-dpp and 2,5-dpp bridging ligands, and the bpy and biq terminal ligands (dpp = bis(2-pyridyl)pyrazine; bpy = 2,2'-bipyridine; biq = 2,2'-biquinoline). The structures of the hexanuclear compounds are schematized in Fig. 2. The properties of compounds 1–4, each one of which is made of two equivalent trimetallic moieties, have been previously reported [9]. In this paper we report the prop-

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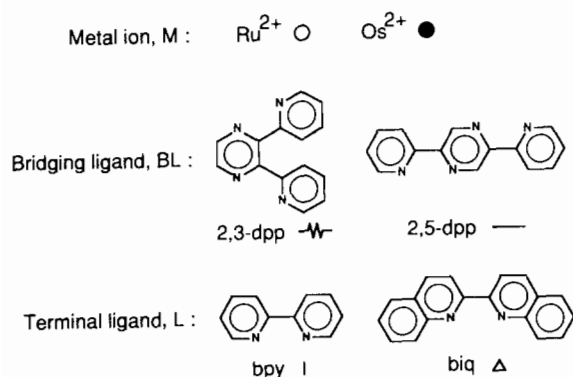


Fig. 1. Components of the hexanuclear compounds and symbols used.

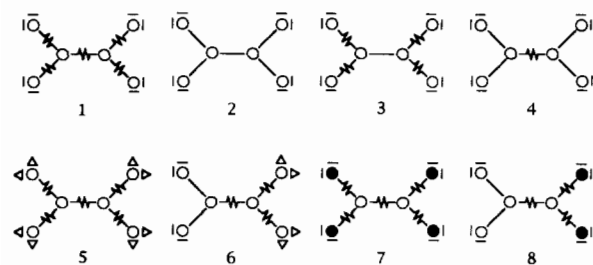
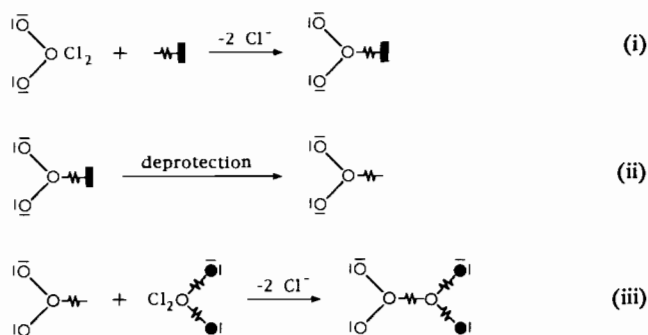


Fig. 2. Schematic representations of the hexanuclear compound (for symbols see Fig. 1).

erties of the novel compounds 5–8 and we present a comparative discussion of all the hexanuclear compounds examined. The novel compounds are interesting for several reasons: (a) 6 and 8 are made of different trinuclear moieties; (b) 7 and 8 contain different metal ions; (c) 6 and 8 contain different bridging ligands; (d) 6 contains different terminal ligands. Furthermore, if we consider the whole 1–8 series of compounds, we can see that (e) 4 and 5 are the parent species of 6, and (f) 4 and 7 are the parent species of 8. Comparison of the various properties within the entire family of compounds is thus expected to give important pieces of information on the factors that affect the spectroscopic, electrochemical and energy-transfer behavior.

Materials and methods

The synthesis of the hexanuclear complexes 5 and 7, which contain two equivalent trinuclear moieties, has been performed by combining two units of the appropriate $M[(\mu\text{-BL})M(L)_2]_2\text{Cl}_2(\text{PF}_6)_4$ precursor with a BL ligand, as previously described for compounds 1–4 [9]. The preparation of compounds 6 and 8, which contain non-equivalent trinuclear moieties, has been carried out by a protection/deprotection procedure within the ‘complexes-as-ligands/complexes-as-metals’ synthetic strategy [14]. As illustrated in Scheme 1 for



Scheme 1.

compound 8, this procedure involves the following steps: (i) reaction of a trinuclear $M[(\mu\text{-BL})M(L)_2]_2\text{Cl}_2^{4+}$ ‘complex–metal’ precursor with a protected BL ligand to obtain a ‘protected’ $M[(\mu\text{-BL})M(L)_2]_2(\text{BL-CH}_3)^{7+}$ species; (ii) deprotection of the above product to obtain the $M[(\mu\text{-BL})M(L)_2]_2(\text{BL})^{6+}$ ‘complex–ligand’; (iii) reaction of the ‘complex–ligand’ with an appropriate $M[(\mu\text{-BL})M(L)_2]_2\text{Cl}_2^{4+}$ ‘complex–metal’. Details on the protection/deprotection procedures [15], the preparation of the $M[(\mu\text{-BL})M(L)_2]_2\text{Cl}_2^{4+}$ building blocks [9, 12], and the characterization of the various compounds [12, 15] are reported elsewhere.

All the room temperature experiments were carried out in acetonitrile solutions. For the luminescence experiments at 77 K, a MeOH/EtOH 4:1 (vol./vol.) matrix was used. The equipment and procedures used to obtain absorption spectra, emission and excitation spectra, excited state lifetimes, and oxidation potentials have been described elsewhere [7]. The procedure for the calibration of the number of electrons corresponding to the various oxidation waves has also been described in detail [12]. Experimental errors in the reported data are as follows: absorption maxima, 2 nm; emission maxima, 4 nm; excited state lifetime, 10%; oxidation potentials, 20 mV. As far as the molar absorption coefficients are concerned, the uncertainty in their absolute values is $\leq 10\%$ because of the highly diluted solutions used (10^{-5} – 10^{-4} M).

Results and discussion

While the synthesis of hexanuclear species that contains two equivalent trinuclear moieties is simple [9], the synthesis of compounds 6 and 8, which are made of two different trinuclear moieties (Fig. 2), requires a protection/deprotection procedure illustrated in Scheme 1.

The representation of the complexes given in Fig. 2 are useful to indicate the composition of the various species and to discuss the interactions among the various

building blocks, but they do not represent the real structures of the compounds. An attempt to represent one of the possible configurations of **3** is shown in Fig. 3. It should also be pointed out that the two coordinating nitrogen atoms of each chelating site of the bridging ligands are not equivalent (Fig. 1). As a consequence, different geometrical isomers can exist, in principle, for the metal centers coordinated to two or three bridging ligands. Other stereochemical complications arise from the fact that 2,3-dpp (and perhaps also 2,5-dpp) is not planar. It should also be noticed that each complex can be a mixture of several diastereoisomeric species owing to the chiral nature of the mononuclear units. For these reasons, structural investigations on these systems are difficult. Differences arising from the possible presence of isomeric species are not expected to be sizeable in the electrochemical and spectroscopic properties discussed below (see, for example, ref. 16).

As shown in the representation of Fig. 2, the hexanuclear compounds can be viewed as made by two (identical or different) trinuclear moieties linked by a bridging ligand. From this point of view, which will be very useful to discuss similarities and differences in the behaviour of the various compounds, the couples of compounds **4** and **5**, and **4** and **7** can be thought as the parent compounds of **6** and **8**, respectively. Similarly, **4**, **6** and **8** can be thought as the same trinuclear $\text{Ru}[(\mu\text{-}2,5\text{-dpp})\text{Ru}(\text{bpy})_2]_2(\text{2,3-dpp})^{6+}$ species which is linked to three different moieties. The same approach can be used to compare the properties of **5** and **6**, and of **7** and **8**.

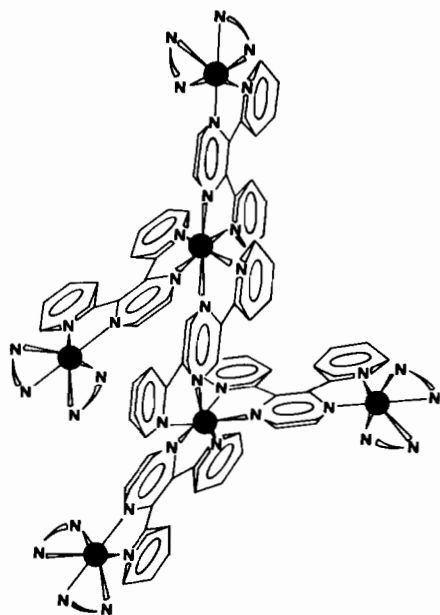


Fig. 3. Schematic view of compound **3**.

Absorption spectra

The electronic absorption spectra of compounds **5**–**8** in acetonitrile solution at 298 K are displayed in Figs. 4 and 5, and the position of the maxima and molar absorption coefficients of the lowest energy $^1\text{MLCT}$ bands are reported in Table 1. A satisfactory assignment of the various bands can be done by comparing these spectra with those of compounds **1**–**4** [9] and of other compounds of the same family [7, 10, 12]. The very intense bands in the UV region can be assigned to ligand-centered transitions. The bands with maxima at 243 and 285 nm, which can be clearly seen in compounds **7** and **8** and are absent in compound **5**, are due to transitions localized on the bpy ligands. The bands with maxima at 267 and 380 nm (compounds **5** and **6**) are assigned to the biq ligands. The intense and broad

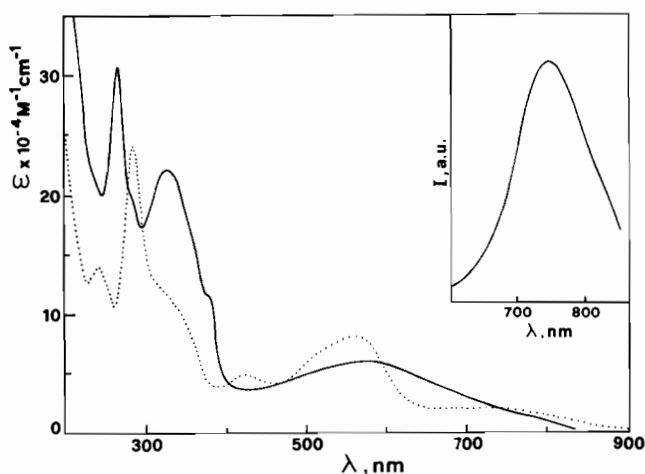


Fig. 4. Absorption spectra of **5** (—) and **7** (····) in acetonitrile solution at room temperature. The inset shows the luminescence band of **5** at room temperature. Compound **7** shows an emission band at ~ 900 nm (90 K).

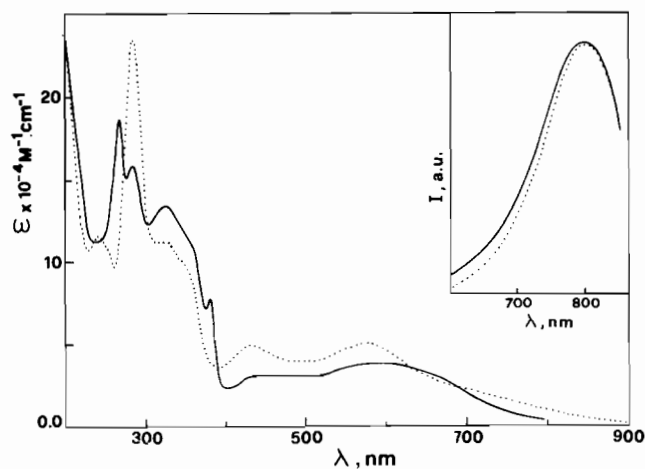


Fig. 5. Absorption and luminescence (inset) spectra of **6** (—) and **8** (····) in acetonitrile solution at room temperature. Compound **8** shows another emission band at ~ 900 nm (90 K). In the case of **6**, $\lambda_{\text{exc}} = 440$ nm. For more details, see text.

TABLE 1. Spectroscopic, photophysical and electrochemical data of the hexanuclear compounds^a

Complex	Absorption ^b 298 K λ_{\max} (nm) ($\epsilon \times 10^3$)	Luminescence ^c				Electrochemistry 298 K E_{ox} (V) (n) ^d
		298 K		77 K		
		λ_{\max} (nm)	τ (ns)	λ_{\max} (nm)	τ (μ s)	
1	540 (59.0)	770	53	716	1.33	+1.44 (4)
2	582 (52.0)	810	40	756	0.83	+1.38 (4)
3	540 (62.2)	768	55	716	1.30	+1.41 (4)
4	577 (54.1)	812	44	764	0.83	+1.36 (4)
5	571 (60.2)	760	80	716	1.56	$\sim +1.8$ (~ 4) ^e
6	588 (39.0)	790 ^f	41	750 ^f	1.27	+1.50 (2); +1.66 (2)
7	560 (81.5)			(~ 900) ^g		+1.06 (4)
8	576 (50.3)	802	39	752; (~ 900) ^g	0.82	+1.05 (2); +1.45 (2)

^aAcetonitrile solutions, unless otherwise noted; for compounds 1–4, see also ref. 9. ^bLowest energy spin-allowed band. ^cEmission maxima (uncorrected) and luminescence lifetimes in aerated acetonitrile solution (298 K) or 4:1 MeOH/EtOH matrix (77 K). ^d $E_{1/2}$ values vs. SCE; the number of exchanged electrons is given in brackets. ^eAdsorption of the complex on the electrode makes these data relatively uncertain. ^f $\lambda_{\text{exc}} = 440$ nm. ^gPreliminary results at 90 K, ref. 20.

absorptions in the 310–350 nm region are mainly due to transitions localized on 2,5-dpp and biq. The 2,3-dpp ligand absorbs in the same spectral region, but with lower intensity. The absorption bands in the visible region are due to metal-to-ligand charge transfer transitions. As one can see, these bands are broad and overlap heavily. However, one can identify a metal-to-bpy charge transfer band at 424 (7) and 435 (8) nm, a metal-to-(μ -2,3-dpp) charge transfer band around 560 nm (7), and overlapping charge transfer bands involving the biq and 2,5-dpp ligands in the 550–700 nm region. For the two Os-containing compounds (particularly, for 7), there is a broad absorption around 750 nm due to spin-forbidden metal-to-ligand charge transfer transitions.

As mentioned above, compound 6 is made of two different trinuclear moieties, which are found in the symmetric compounds 4 and 5. In the same way, 8 can be thought as deriving from the moieties found in 4 and 7. Comparison between the spectrum of 8 with the semisum of the spectra of 4 and 7 shows that the ligand-centered bands are practically identical, whereas relatively small differences can be noticed in the charge-transfer region above 500 nm. This indicates that there is some electronic interaction between the two different trinuclear moieties of 8. In the case of 6, the differences from the semisum of the spectra of the parent compounds 4 and 5 are more noticeable, suggesting that the electronic interaction between the two trinuclear moieties of 6 is larger. We will see later that the same conclusions can be drawn from the electrochemical and luminescence data.

Electrochemical oxidation

It is well known that electrochemical oxidation of mono- and polynuclear Ru(II) and Os(II) polypyridine

complexes concerns the metal ions [4–6]. Previous investigations carried out on complexes of this family [12, 17] have shown that: (i) Os²⁺ is oxidized at potentials considerably less positive than Ru²⁺, (ii) the electron donor power decreases in the ligand series bpy > biq \geq 2,3-dpp \approx 2,5-dpp; (iii) the metal–metal interaction is noticeable for metals coordinated to the same bridging ligand and decreases sharply on increasing number of the interposed components. All the novel compounds 5–8 undergo reversible oxidation processes whose potentials are collected in Table 1, together with the data previously obtained for compounds 1–4. One can see that all the ‘symmetrical’ compounds (1, 2, 3, 4, 5 and 7) exhibit a four-electron oxidation wave that can be attributed to oxidation, at nearly the same potential, of the four equivalent peripheral metal ions (Table 1, Fig. 6). The oxidation waves of the two inner metal ions are expected to occur at higher potential [9]; furthermore they are displaced to more positive values owing to the presence of the already oxidized peripheral units, and thus cannot be observed in the potential window examined. One can notice that the oxidation potential of the peripheral units increases, as expected, in the series Os(bpy)₂(μ -2,3-dpp)²⁺ < Ru(bpy)₂(μ -2,5-dpp)²⁺ < Ru(bpy)₂(μ -2,3-dpp)²⁺ < Ru(biq)₂(μ -2,3-dpp)²⁺. For compounds 6 and 8 the oxidation pattern is quite different: two waves of equal height, both corresponding to a two-electron oxidation process, are observed. For compound 8 (Fig. 6, Table 1) the first oxidation wave occurs at nearly the same potential as the four-electron wave of compound 7. This shows that, as expected, the two Os-containing units are the first to be oxidized. The second wave concerns the oxidation of the two Ru(bpy)₂(μ -2,5-dpp)²⁺ units. Since such units lie far away from the previously oxidized Os-containing units, their oxidation

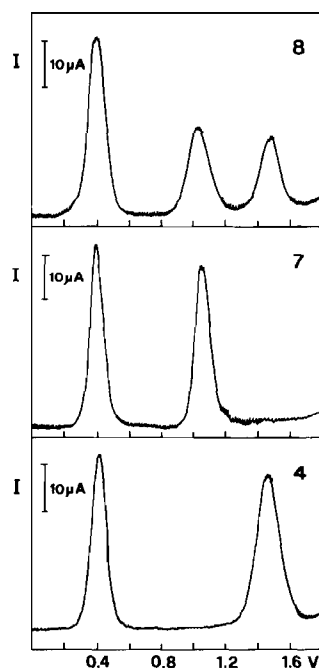


Fig. 6. Differential pulse voltammograms of compounds 4, 7 and 8 in acetonitrile solution. The peak at +0.40 V is ferrocene used as a reference.

potential is close to that of the equivalent peripheral units of 4. The small difference is likely due to a weak electronic perturbation caused by the oxidized Os-containing trinuclear moiety. A couple of two-electron waves is also present in the case of 6. This result is consistent with the expectation, drawn from the potentials of the parent compounds 4 and 5, that oxidation of the two $\text{Ru}(\text{bpy})_2(\mu\text{-}2,5\text{-dpp})^{2+}$ units is followed by oxidation of the two $\text{Ru}(\text{biq})_2(\mu\text{-}2,3\text{-dpp})^{2+}$ units. From the data gathered in Table 1 one can see that oxidation of the two $\text{Ru}(\text{bpy})_2(\mu\text{-}2,5\text{-dpp})^{2+}$ units of 6 occurs at a more positive potential compared to the oxidation potential of the four units of the parent compound 4, whereas the reverse is true for the oxidation potential of the two $\text{Ru}(\text{biq})_2(\mu\text{-}2,3\text{-dpp})^{2+}$ units compared to that of the four units of the parent compound 5. This behaviour can be accounted for as follows. The oxidation potentials of 4 and 5 indicate that the $\text{Ru}[(\mu\text{-}2,5\text{-dpp})\text{Ru}(\text{bpy})_2]_2^{6+}$ trinuclear moiety is a better electron donor than the $\text{Ru}[(\mu\text{-}2,3\text{-dpp})\text{Ru}(\text{biq})_2]_2^{6+}$ one. Thus, in the mixed compound 6 some electron donation from the former to the latter moiety takes place with a consequent increase in the oxidation potentials of the $\text{Ru}(\text{bpy})_2(\mu\text{-}2,5\text{-dpp})^{2+}$ units and a decrease in the oxidation potential of the $\text{Ru}(\text{biq})_2(\mu\text{-}2,3\text{-dpp})^{2+}$ ones.

Luminescence and intercomponent energy transfer

It is well known that Ru(II) and Os(II) polypyridine compounds exhibit luminescence from the lowest triplet

metal-to-ligand charge-transfer excited state [4–6]. The luminescence bands of 5, 6 and 8 are shown in Figs. 4 and 5. Compound 7 does not show any luminescence when observed with a conventional equipment ($\lambda < 850$ nm). From spectroscopic/electrochemical correlations [4–6, 12, 17–19], luminescence arising from the peripheral Os-based units would be expected to occur above 850 nm. Preliminary experiments carried out with an IR sensitive equipment have shown that both 7 and 8 exhibit a luminescence band at ~ 900 nm (90 K) [20].

From previous work [7, 8, 12, 17, 18, 21] it is well known that exoergic energy transfer between two directly connected units is so fast to cause 100% efficient luminescence quenching of the higher energy unit and sensitization of the lower energy one. For the symmetric compounds 5 and 7, the luminescence behaviour is very simple: emission originates from the lowest excited state, which is the metal-to-bridging ligand charge transfer level of the peripheral units. The observed excited state lifetimes (Table 1) are in the expected range for such a type of emission.

The luminescence behaviour of the non-symmetric compound 6 and 8 is more complicated. The lowest excited state in compound 8 is located on the $\text{Os}(\text{bpy})_2(\mu\text{-}2,3\text{-dpp})^{2+}$ units. Besides the luminescence band of these units at ~ 900 nm [20], an emission band at shorter wavelength (802 nm at room temperature, 752 nm at 77 K) is also observed (Table 1, Fig. 5). Such an emission is characteristic of the $\text{Ru}(\text{bpy})_2(\mu\text{-}2,5\text{-dpp})^{2+}$ units, as shown by the luminescence properties of 2 and 4. A quantitative comparison with the luminescence efficiency of a 50% mixture of 4 and 7 (Fig. 7) shows that the luminescence efficiency of the $\text{Ru}(\text{bpy})_2(\mu\text{-}2,5\text{-dpp})^{2+}$ units in 8 is 30% of that exhibited in 4 (excitation was performed at 285 nm, which corresponds to bpy ligand-centered bands). No luminescence from the central Ru-based units, which would be expected to occur at 690 nm [12], is observed. These results can be easily interpreted on the basis of the known energy ordering of the lowest excited state of the various units: $\text{Ru}(\mu\text{-}2,3\text{-dpp})_3^{2+} \geq \text{Ru}(\mu\text{-}2,5\text{-dpp})_2(\mu\text{-}2,3\text{-dpp})^{2+} > \text{Ru}(\text{bpy})_2(\mu\text{-}2,5\text{-dpp})^{2+} > \text{Os}(\text{bpy})_2(\mu\text{-}2,3\text{-dpp})^{2+}$. Energy transfer from the central units to the peripheral ones is 100% efficient because the process is exoergic and the donor-acceptor units are directly connected. However, energy transfer from the higher energy $\text{Ru}(\text{bpy})_2(\mu\text{-}2,5\text{-dpp})^{2+}$ units to the lower energy $\text{Os}(\text{bpy})_2(\mu\text{-}2,3\text{-dpp})^{2+}$ ones exhibits a low efficiency since the two units are separated by two higher energy units. The situation is somewhat similar for compound 6, where the energy position and half-width of the luminescence band is found to depend on the excitation wavelength, suggesting that both the lower energy $\text{Ru}(\text{bpy})_2(\mu\text{-}2,5\text{-dpp})^{2+}$ and the upper

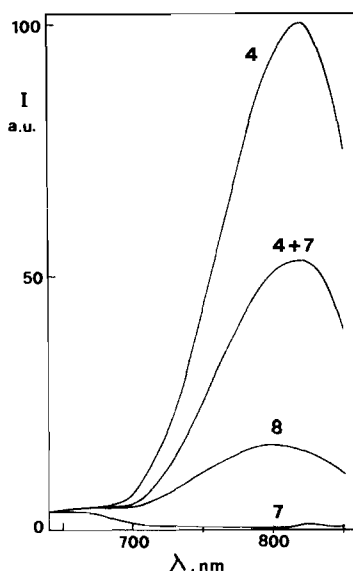


Fig. 7. Relative luminescence intensities ($\lambda_{\text{exc}}=285$ nm) of 3.4×10^{-6} M solutions of 4, 7 and 8, and of a 1.7×10^{-6} M solution of 4 and 7.

energy $\text{Ru}(\text{biq})_2(\mu\text{-}2,3\text{-dpp})^{2+}$ units are luminescent. This, of course, implies a low efficiency for energy transfer from the latter to the former units. For this complex, unfortunately, quantitative evaluation of the intensities of the two emission bands is prevented by the electronic interaction between the two trinuclear moieties.

Conclusions

The series of hexanuclear compounds 1–8 is very interesting not only because of the intrinsic spectroscopic, excited state and redox properties of each single compound, but also because of the correlations observed for the various properties on moving along the series. The main results emerged from this investigation are as follows: (i) each metal-containing unit brings its own properties into the hexanuclear species; (ii) electronic perturbation between different units may cause sizeable changes in the spectroscopic and redox properties; (iii) predetermined oxidation patterns can be obtained by placing suitable units in appropriate sites of the supramolecular structure; (iv) the efficiency of exoergic energy migration between two remote units is lower than 100% when higher energy units are interposed.

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