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Near-Infrared Luminescence of Supramolecular Species Consisting of Osmium(II)- and/or Ruthenium(II)-Polypyridine Components

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The luminescence behavior of 10 homometallic (Os^{2+}) and heterometallic (Os^{2+}/Ru^{2+}) polynuclear metal complexes containing 2,3-dpp and/or 2,5-dpp as bridging ligands and bpy and/or biq as terminal ligands has been investigated (dpp = bis(2-pyridyl)pyrazine; bpy = 2,2′-bipyridine; biq = 2,2′-biquinoline). The nuclearity of the investigated compounds varies from 2 to 10. Each compound may be considered as a supramolecular species constituted by an assembly of distinct mononuclear components. All the examined compounds exhibit a luminescence band in the 850–1000-nm spectral region (rigid matrix, 90 K), which can be assigned to "triplet" metal-to-ligand charge-transfer levels localized on Os-containing components. Correlations among energies of the emission bands, oxidation potentials, compositions of the metal-based components, and their positions in the supramolecular array allow an unequivocal identification of the components responsible for the observed luminescence. For the Ru^{2+}/Os^{2+} mixed-metal compounds, only an Os-based luminescence is observed. Exoergonic electronic energy transfer along a row of components arranged in an "energy cascade" pattern is 100% efficient. The results obtained elucidate the role played by intercomponent energy transfer in polynuclear metal complexes and may help in designing supramolecular structures where the pattern of energy migration is synthetically controlled.

Introduction

Mononuclear Ru(II)- and Os(II)-polypyridine complexes have been studied in the past 20 years because of their outstanding photophysical and redox properties.[2-4] At present, these complexes are extensively used as building blocks to obtain photochemical molecular devices which are studied in view of possible applications such as information recording and conversion of light into chemical or electrical energy.[5-9]

Of particular interest is the so-called "antenna effect",[7] which consists of an enhanced light sensitivity obtained by increasing the overall cross section for light absorption. To achieve this result, the electronic energy generated by light absorption in an array of chromophores should be conveyed to a common component that constitutes the interface toward the use of the absorbed light energy. Polynuclear Ru(II) and Os(II) complexes of polypyridine ligands are suitable candidates to play this role because of their intense metal-to-ligand charge-transfer bands in the visible region.[2-4] An efficient photoelectrochemical cell where a trinuclear Ru(II) complex[10] plays the role of an antenna-sensitizer device has been reported.[8,11]

Luminescence is a fundamental tool in order to understand the patterns of electronic energy migration in supramolecular species. By using this tool, it has been possible to elucidate the energy migration patterns in a variety of polynuclear metal complexes.[12] We have been particularly interested[13] in systems made of Ru^{2+} and/or Os^{2+} as metal ions, 2,3-dpp and/or 2,5-dpp as bridging ligands, and bpy and/or biq as terminal ligands (dpp = (bis(2-pyridyl)pyrazine; bpy = 2,2′-bipyridine; biq = 2,2′-biquinoline; Figure 1). Several Os-containing complexes of this family, however, do not exhibit luminescence in the spectral range ($\lambda <$ 850 nm) that can be investigated with conventional spectrofluorimeters. Therefore for such complexes, which are those matching better the solar spectrum, the energy migration pattern

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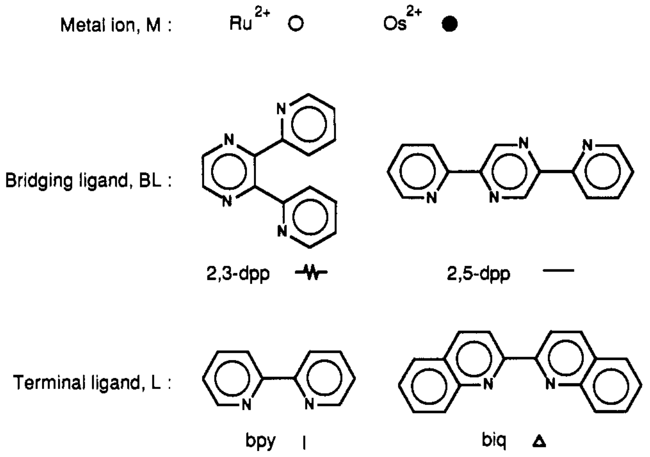


Figure 1. Components of the polynuclear compounds and symbols used.

Table 1. Labels and Chemical Formulations of the Investigated Species[a]

label	formula
2A	$\mathrm{(bpy)_2Os(\mu\text{-}2,5\text{-}dpp)Os(bpy)_2^{4+}}$
2B	$\mathrm{(bpy)_2Ru(\mu\text{-}2,5\text{-}dpp)Os(bpy)_2^{4+}}$
2C	$\mathrm{(bpy)_2Ru(\mu\text{-}2,5\text{-}dpp)Ru(bpy)_2^{4+}}$ [b]
2D	$\mathrm{(bpy)_2Os(\mu\text{-}2,3\text{-}dpp)Os(bpy)_2^{4+}}$
2E	$\mathrm{(bpy)_2Ru(\mu\text{-}2,5\text{-}dpp)Os(biq)_2^{4+}}$
3A	$\mathrm{(bpy)Ru[(\mu\text{-}2,3\text{-}dpp)Os(bpy)_2]_2^{6+}}$
3B	$\mathrm{(bpy)Ru[(\mu\text{-}2,5\text{-}dpp)Os(bpy)_2]_2^{6+}}$
4A	$\mathrm{Ru[(\mu\text{-}2,5\text{-}dpp)Os(bpy)_2]_3^{8+}}$
6A	$\mathrm{[(bpy)_2Os(\mu\text{-}2,3\text{-}dpp)]_2Ru(\mu\text{-}2,3\text{-}dpp)Ru[(\mu\text{-}2,3\text{-}dpp)Os(bpy)_2]_2^{12+}}$
6B	$\mathrm{[(bpy)_2Ru(\mu\text{-}2,5\text{-}dpp)]_2Ru(\mu\text{-}2,3\text{-}dpp)Ru[(\mu\text{-}2,5\text{-}dpp)Ru(bpy)_2]_2^{12+}}$
10A	$\mathrm{Os\{(\mu\text{-}2,3\text{-}dpp)Ru[(\mu\text{-}2,3\text{-}dpp)Os(bpy)_2]_2\}_3^{20+}}$
10B	$\mathrm{Ru\{(\mu\text{-}2,3\text{-}dpp)Ru[(\mu\text{-}2,3\text{-}dpp)Os(bpy)_2]_2\}_3^{20+}}$

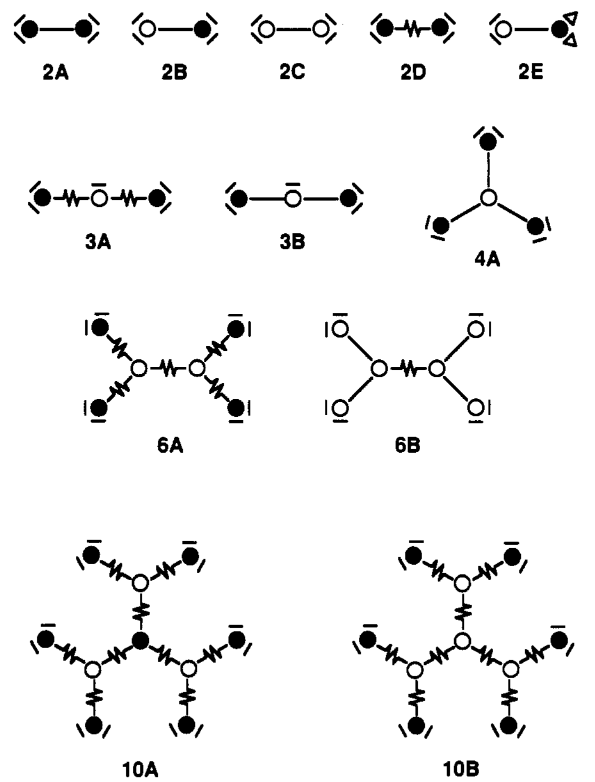
[a] For abbreviations and symbols, see Figure 1. [b] Spectroscopic properties of these species have already been published in refs 13a and 14 (**2C**) and refs 13e and 17 (**6B**). They have been reinvestigated here for comparison purposes.

could not be investigated. In this paper we report the results of a study performed on 11 polynuclear (nuclearity from 2 to 10) Os-containing complexes by means of a luminescence equipment sensitive in the near-infrared spectral region. The metals and ligands involved in the investigated complexes and the symbols used are shown in Figure 1. Chemical formulas and the numbers used as labels to indicate the various compounds are shown in Table 1. Schematic structures of the compounds are shown in Chart 1.

Experimental Section

Syntheses. The synthetic procedures needed to prepare the polynuclear compounds are based on reactions between metal-type and ligand-type precursors and have been described in detail elsewhere.[13d,e,14–17] Each precursor compound was purified by chromatography and precipitation and then characterized by elemental analysis, IR, vis, and UV spectra, conductivity values, FAB mass spectra, electrochemical potentials, and luminescence properties. The purification and characterization of the final products have also been reported.[13] The syntheses of **6A** and **6B**, which consist of two symmetric moieties, were performed by combining two components of the appropriate $\mathrm{M_a[(\mu\text{-}dpp)M_b(bpy)_2]_2Cl_2^{4+}}$ precursor with 2,3-dpp in the presence of $\mathrm{AgNO_3}$.[17]

Chart 1



Equipment. Luminescence spectra were measured in a MeOH/EtOH (4:1, v/v) glassy matrix at 90 ± 5 K. Absorption spectra were measured in the same solutions at room temperature. The concentrations of the complexes were ~2 × 10^{-4} M for the di- and trinuclear complexes, ~4 × 10^{-5} M for the tetra- and hexanuclear complexes, and ~2 × 10^{-5} M for the decanuclear species.

For the absorption spectra, we used a HP 8452A diode array spectrophotometer in the range 230–800 nm and a Cary 17 equipped with a PbS cell in the range 600–1200 nm. For the luminescence spectra, the samples were cooled in a single-walled flow tube[18] by cold nitrogen gas. The 488-nm line of a Spectra-Physics 2045 $\mathrm{Ar^+}$ laser was used for excitation. The luminescence was dispersed by a Spex 1702 single monochromator with a 600 groove/mm grating blazed at 750 nm and detected by a cooled (77 K) ADC 403L germanium photodiode in combination with an EG&G PAR 186A lock-in amplifier. A Tektronix 4052A computer or an IBM XT personal computer was used for data acquisition and storage. The reported spectra are corrected for detector and monochromator response.

Results

The complexes examined show very intense absorption bands in the visible region. The absorption spectra of **3B** and **10B** are displayed in Figure 2. Data concerning the positions of the lowest energy absorption maxima are collected in Table 2.

All the complexes are luminescent in a rigid matrix at 90 K. The luminescence spectra of **3B** and **10B** (Figure 2) and **6A** and **6B** (Figure 3) are displayed. The positions of the luminescence maxima are summarized in Table 2. It can be noticed that (i) compounds **2D**, **2E**, **3A**, **6A**, **10A**, and **10B** exhibit a broad luminescence band with a maximum in the 892–928-nm region, (ii) compounds **2A**, **2B**, **3B**, and **4A** exhibit a luminescence band with a maximum in the 960–984-nm region, (iii) compound **6B**[17] (reinvestigated for comparison purposes) exhibits a band with a maximum at 764 nm with a vibrational component at ~840 nm. Compounds **2B**, **3B**, and **4A** show some additional luminescence intensity in the 600–900-nm region, which is attributed to unidentified impurities.

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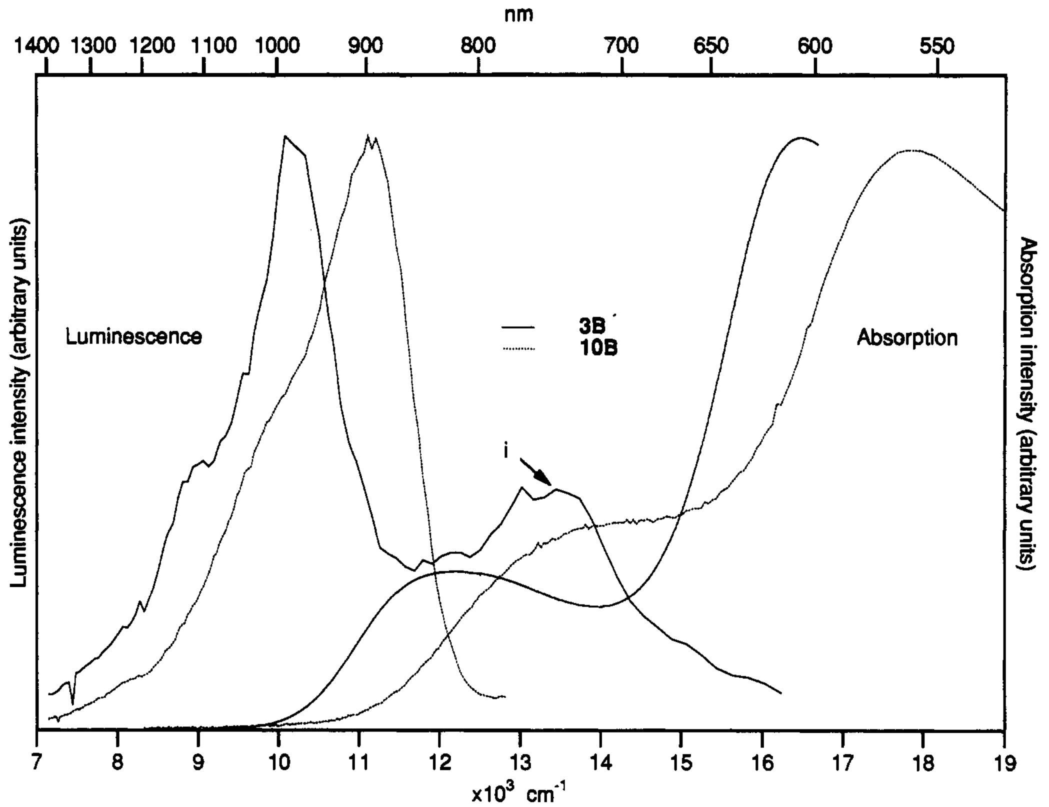

Figure 2. Absorption spectra (at room temperature) and emission spectra (at 90 K) of **3B** and **10B** in MeOH/EtOH (4:1, v/v). i is an impurity band.

Table 2. Absorption and Emission Maxima of the Investigated Species

species	absorption[a] λ, nm (ϵ, M^{-1} cm^{-1})	emission[b] λ, nm (ν, cm^{-1})
2A	616 (27 000),[c] 799 (9750), 891 (12 400)	984 (10 200)
2B	601 (19 200), 810 (4850)	968 (10 300)
2C	585 (15 900)[c]	771 (13 000)
2D	555 (21 800),[c] 742 (6390)	928 (10 800)
2E	620 (17 900), 757 (5890), 820 (5870)	900 (11 100)
3A	559 (36 300), 663 (sh), 738 (sh), 808 (sh)	896 (11 200)
3B	606 (33 800), 819 (9170)	980 (10 200)
4A	618 (24 600)[c]	960 (10 400)
6A	560 (81 500),[d] 717 (19 600)	912 (11 000)
6B	577 (54 100)[d]	764 (13 100)
10A	563 (140 500),[e] 720 (sh)	900 (11 100)
10B	560 (132 500),[e] 720 (sh)	892 (11 200)

[a] Lowest energy absorption features in acetonitrile solution at room temperature. [b] Emission maxima in an EtOH/MeOH (1:4, v/v) glassy matrix at 90 K. [c] Reference 13a. [d] Reference 13e. [e] Reference 13d.

In all cases the luminescence bands show a shoulder in the low-energy side suggesting the presence of an unresolved vibrational structure. The bandwidth varies between 850 and 2100 cm^{-1}. The intensities of the luminescence bands are comparable, except that of **6B**, which is estimated to be 20 times higher.

Discussion

General Considerations. The schematic structures shown in Chart 1 are useful to indicate the chemical composition of the various species and to discuss the interactions between the various building blocks (*vide infra*). It should be noticed that the two coordinating nitrogen atoms of each chelating site of the bridging ligands (Figure 1) are not equivalent. As a consequence, different geometrical isomers can exist, in principle, for the metal centers coordinated to two or three bridging ligands.[14] Each complex can also be a mixture of several diastereomeric species, owing to the chiral nature of each mononuclear building block. The presence of isomers could cause band broadening. The half-widths of the recorded bands, however, are comparable to the half-width of the $Os(bpy)_3^{2+}$ luminescence band, suggesting that different isomers, if present, exhibit very similar luminescence bands.

It is well-known that, in mononuclear Os(II)- and Ru(II)-polypyridine complexes, light excitation causes the population of the lowest ^{3}MLCT level with 100% efficiency.[19] This level undergoes radiative and radiationless decay on the microsecond/nanosecond time scale (depending on solvent and temperature), with a relatively small luminescence quantum yield (usually, the quantum yield is larger for Ru(II) than for Os(II) complexes).[2–4] Since Os(II) is much easier to oxidize than Ru(II),[2–4,20] the energy of the luminescent ^{3}MLCT level is lower for the Os(II) complexes.

As shown by the data collected in Table 2, the polynuclear compounds studied in this work exhibit broad and intense absorption bands in the visible spectral region. Comparison with the spectra of other members of this family[13,14,16,17,21] shows that the laser excitation wavelength (488 nm) corresponds to a spectral region where there is strong overlap of Ru → bpy and Os → bpy (λ_{max} ~ 430 nm), Ru → 2,3-dpp (λ_{max} ~ 530 nm), Os → 2,3-dpp (λ_{max} ~ 560 nm), Ru → 2,5-dpp (λ_{max} ~ 585 nm), and also Os → biq and Os → 2,5-dpp (λ_{max} ~ 610 nm) charge-transfer bands. Therefore, laser excitation populates ^{1}MLCT excited states in the various components with approximately equal probability. Singlet–singlet energy transfer could then take place, with population of the lowest energy ^{1}MLCT level, followed by intersystem crossing to the ^{3}MLCT level of that component. However, we believe that singlet–singlet energy transfer can hardly

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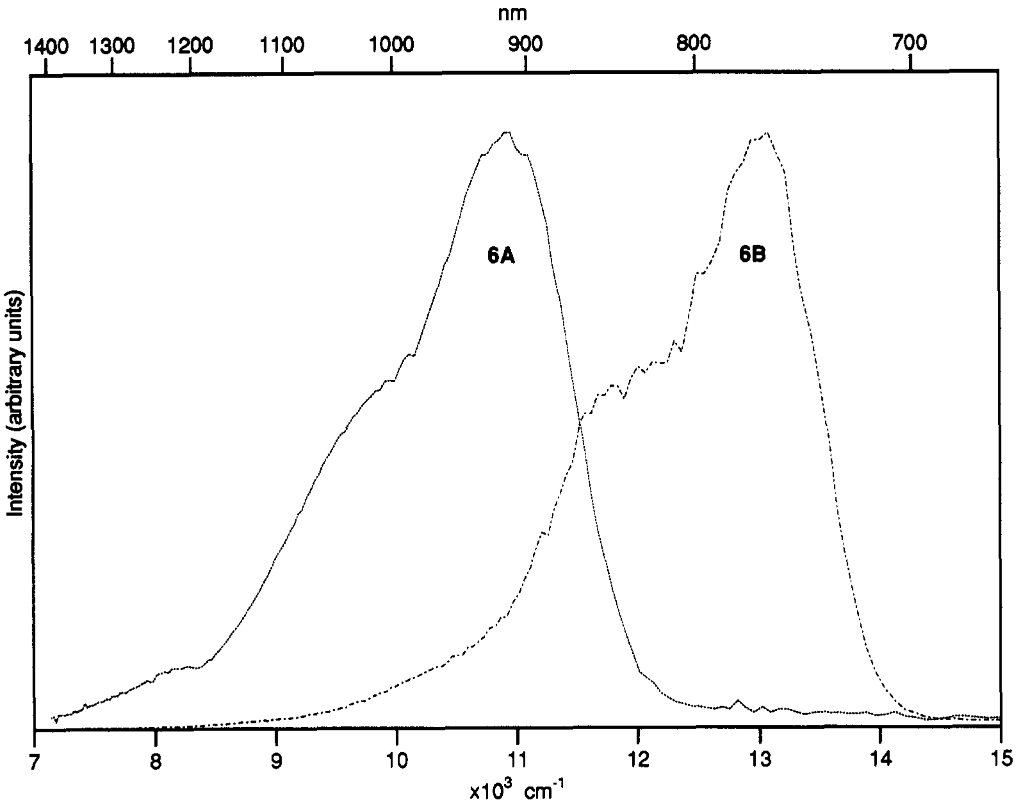

Figure 3. Luminescence spectra of **6A** and **6B** at 90 K in MeOH/EtOH (4:1, v/v).

compete with the subpicosecond[22] singlet–triplet relaxation within each component. Therefore, the most likely result of light excitation is the population with unitary efficiency of the lowest energy ^{3}MLCT level of the component where light absorption has taken place.

In a system made of "isolated" components, the lowest ^{3}MLCT level of each component would undergo its own radiative (luminescence) and radiationless decay to the ground state on the 10^{-6}–10^{-7}-s time scale (at 90 K), as do the mononuclear complexes.[2-4] Weak interaction between components, however, may cause transfer of electronic energy according to well-known mechanisms.[23-25] The interaction between metal ions connected by the same bridging ligand is small but certainly not negligible.[13] As a consequence, exoergonic energy transfer between contiguous components is expected to be faster than the intracomponent decay to the ground state, with a consequent quenching of the luminescence of the energy-donor component. Energy-transfer processes between remote components, however, may be slow. Finally, the possibility of an electron-transfer-quenching mechanism should also be taken into consideration.

Luminescence Behavior. As mentioned above, the energy of the lowest (luminescent) ^{3}MLCT level of each mononuclear component of a polynuclear compound is primarily determined by the nature of metal and ligands and only slightly affected by the contiguous components. For example, in polynuclear Ru(II) complexes the $\mathrm{Ru(bpy)_2(\mu\text{-}2,3\text{-}dpp)^{2+}}$ component emits at ~720 nm, the $\mathrm{Ru(bpy)_2(\mu\text{-}2,5\text{-}dpp)^{2+}}$ component at ~770 nm, and so on.[14] With these guidelines, we will now try to assign the luminescence bands observed in this work to specific metal-containing components.

Complex **2D** consists of two equivalent $\mathrm{Os(bpy)_2(\mu\text{-}2,3\text{-}dpp)^{2+}}$ components, which must therefore be responsible for the observed luminescence band with λ_{max} = 928 nm. Similarly, the luminescence band observed for **2A** with λ_{max} = 984 nm can be assigned to the $\mathrm{Os(bpy)_2(\mu\text{-}2,5\text{-}dpp)^{2+}}$ component. Compound **2B** consists of a $\mathrm{Os(bpy)_2(\mu\text{-}2,5\text{-}dpp)^{2+}}$ and a $\mathrm{Ru(bpy)_2(\mu\text{-}2,5\text{-}dpp)^{2+}}$ component, which would be expected to emit at approximately the same wavelengths as the two parent compounds **2A** (984 nm) and **2C** (771 nm). However, **2B** shows only one intrinsic emission band at 968 nm, which can be assigned to the Os-based component. Clearly, the ^{3}MLCT excited state of the Ru-based component is quenched by the contiguous Os-based one (vide infra). Similarly, the only luminescence band observed for **2E** (λ_{max} = 900 nm) can be assigned to the Os-based component (the Ru-based one would be expected to emit at 771 nm; see above). Incidentally, we wish to note that the higher emission energy of the $\mathrm{Os(biq)_2(\mu\text{-}2,5\text{-}dpp)^{2+}}$ component compared to that of the $\mathrm{Os(bpy)_2(\mu\text{-}2,5\text{-}dpp)^{2+}}$ one is due to the lower electron-donor power of the biq ligand compared to bpy.[13a,14]

Compounds **3A**, **6A**, **10A**, and **10B** each display a luminescent band very close to that displayed by compound **2D**. Such bands can thus be attributed to the $\mathrm{Os(bpy)_2(\mu\text{-}2,3\text{-}dpp)^{2+}}$ components that are present in these species. The small shifts compared with the band of **2D** are due to the perturbing effects of the different moieties linked to the luminescent $\mathrm{Os(bpy)_2(\mu\text{-}2,3\text{-}dpp)^{2+}}$ component.

Compounds **3B** and **4A** each display a luminescent band not far from those displayed by **2A** and **2B**. Such bands can thus be attributed to the $\mathrm{Os(bpy)_2(\mu\text{-}2,5\text{-}dpp)^{2+}}$ components, whose ^{3}MLCT level is only slightly perturbed by the contiguous moieties. Since other intrinsic luminescent bands are not present in these compounds, we conclude that the excited states of the other metal-containing components are completely quenched by the presence of $\mathrm{Os(bpy)_2(\mu\text{-}2,5\text{-}dpp)^{2+}}$ (*vide infra*).

Intercomponent Energy Transfer. As discussed above, the most

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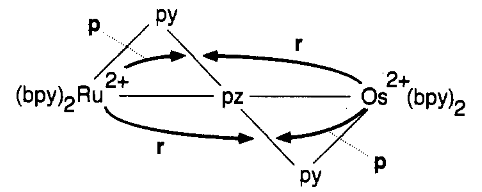

Figure 4. Representation of proximate (p) and remote (r) charge-transfer excitation in the binuclear $(bpy)_2Ru(\mu\text{-}2,5\text{-}dpp)Os(bpy)_2{}^{4+}$ species (**2B**). py and pz represent the pyridine and pyrazine rings of the dpp bridging ligand. For more details, see text.

likely result of light excitation with the 488-nm laser line is the population of the lowest ^{3}MLCT excited state of each of the various components of the oligonuclear compounds with about the same probability. Each component is potentially luminescent, but the results show that only one intrinsic luminescent band is observed even for the compounds which contain components of different nature.

The observed emission band can be assigned in all cases to the component(s) with the lowest energy ^{3}MLCT level. This indicates that in the oligonuclear compounds intercomponent quenching has to occur. An obvious quenching mechanism is electronic energy transfer from upper lying to lower lying ^{3}MLCT levels of the various components. This process has indeed been shown to occur with unitary efficiency for a variety of oligonuclear Ru(II) and Ru(II)/Os(II) compounds,[5–7,12a,d,e,i,13] including $Os[(\mu\text{-}2,3\text{-}dpp)Ru(bpy)_2]_3{}^{8+}$.[26] For such compounds the lowest ^{3}MLCT level of the species is high enough in energy to undergo luminescence in the region covered by conventional spectrofluorimeters ($\lambda < 850$ nm), so that the occurrence of intercomponent energy transfer was demonstrated by comparison between the absorption and excitation spectra. With the equipment at our disposal excitation spectra could not be recorded. Therefore we cannot prove that the quenching of the luminescence of the component(s) with high-energy ^{3}MLCT levels is accompanied by the sensitization of the luminescence of the component(s) with the lowest ^{3}MLCT level. Sensitization, however, seems unavoidable for the following reasons.

For compound **2B** (taken as a prototype of two different, contiguous components), the maximum of the Os-based ^{3}MLCT luminescence lies at ~10 200 cm^{-1} as in the parent compound **2A**. From the luminescence of the other parent compound **2C** it can be estimated that the maximum of the Ru-based ^{3}MLCT luminescence **2B** lies at about 13 000 cm^{-1}. For both metal-based components, the ligand involved in the CT excited state is the bridging 2,5-dpp ligand. As schematized in Figure 4, one can consider two MLCT excited states for each metal center, namely a "proximate" and a "remote" one,[27] depending on which of the two pyridine rings of the bridging ligand is involved, besides the pyrazine ring, in the charge-transfer process. Since the electronic affinity of the bridging ligand (as measured by the first reduction potential of $(bpy)_2M(\mu\text{-}2,5\text{-}dpp)M(bpy)_2{}^{4+}$, when M = Ru^{2+} and/or Os^{2+})[13a] is the same regardless of the coordinated metal, for each component the remote MLCT level must lie above the proximate one because of a smaller Coulombic stabilization. The resulting energy level diagram is schematized in Figure 5. As discussed above, upon laser excitation radiationless decay within each component populates the lowest (proximate) excited level of that component. The quenching of the proximate Ru-based MLCT level can then occur through various routes. One possibility is a Förster-type energy-transfer mechanism,[28] since the spin–orbit coupling induced by the heavy atom confers a nonnegligible singlet character on the formally triplet lowest MLCT level of the Ru-based component. Alternately, energy transfer may occur by a Dexter-type (electron exchange) mechanism,[29] schematized by path a + b in Figure 5. Deactivation of the excited $Ru(bpy)_2(\mu\text{-}2,5\text{-}dpp)^{2+}$ component could also occur via an intercomponent electron-transfer process (which is still an energy-transfer process if we consider the entire species as a single molecule)[5–7,14,27] leading to the remote Os-based CT excited state (path a, Figure 5). This process will most likely be followed by a fast rearrangement of the charge on the bridging ligand (path b, Figure 5) leading again to the proximate (luminescent) Os-based level. Thus, an intercomponent electron-transfer-quenching mechanism would have the same final result (sensitization of the lowest energy luminescent level) as an intercomponent energy transfer. There is no obvious experimental way to discriminate between the two processes.

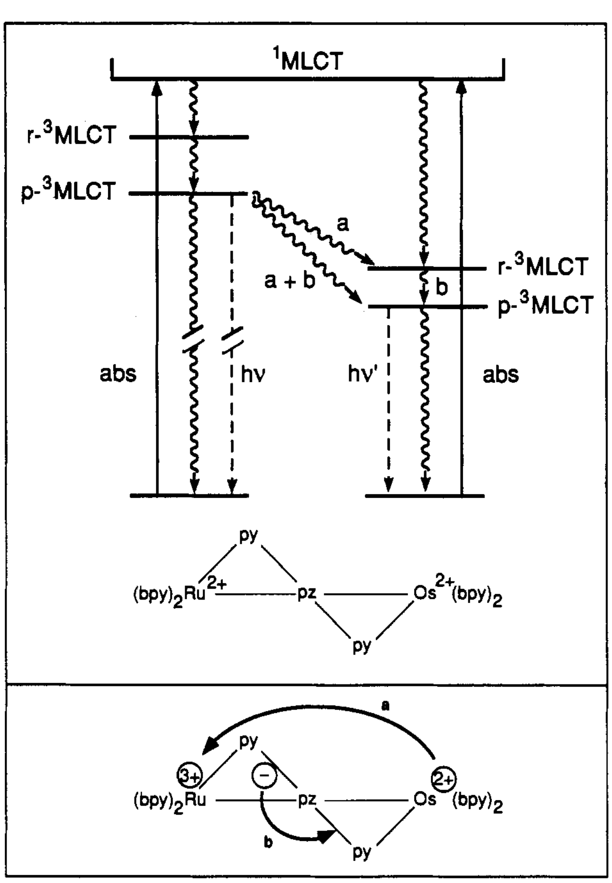

Figure 5. Schematic diagram of the lowest-energy excited states of **2B**. p and r indicate proximate and remote MLCT levels, respectively.

The above discussion based on Figure 5 can be applied to any couple of contiguous components and can account not only for the behavior of compounds **2B** and **2E** but also for the behavior of compounds **3A**, **4A**, **6A**, and **10B**, where the components are arranged in a vectorial "energy cascade" pattern. For example, in **10B** the excited central Ru-based component is expected to be quenched by the intermediate Ru-based components which, in their turn, are expected to be quenched by the peripheral Os-based ones, in agreement with the luminescence results (Figure 2).

In compound **10A** the components are not arranged in an energy-transfer cascade pattern. The lowest excited state of the system is that of the peripheral Os-based components, but the energy of the lowest excited state of the intermediate Ru-based component is higher that the energy of the lowest excited state of the central Os-based one. The energy-transfer process from the central to the peripheral units could thus be slow because of

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the separation distance, thereby allowing the radiative decay of the central unit to occur. In such a case, two luminescence bands could be expected, one due to the peripheral Os-based units (~11 100 cm^{-1}, as in **10B**) and one due to the central unit (~11 400 cm^{-1}, as in the previously investigated[26] Os[(μ-2,3-dpp)Ru(bpy)$_2$]$_3$$^{8+}$ species). The latter band, however, should be at least 6 times weaker than the former (since each component of **10A** absorbs approximately the same fraction of exciting light), and therefore it would hardly be seen. Thus, the presence of only one luminescence band (12 000 cm^{-1}) in the spectrum of **10A** is not informative regarding the occurrence of a center-to-periphery energy-transfer process.

Conclusions

In this paper we have shown that polynuclear Os(II)–polypyridine compounds exhibit luminescence in the near-infrared spectral region and that in compounds containing Os^{2+}-based and Ru^{2+}-based components the electronic excitation energy migrates toward the former components, because they exhibit the lowest energy excited states. Exoergonic energy transfer between adjacent components (i.e., between components which share a bridging ligand) is 100% efficient, leading to vectorial energy migration along rows of components arranged in an "energy cascade" pattern. Because of this possibility to control the direction of electronic energy transfer and because of the large molar absorption coefficients exhibited over the entire visible spectrum, polynuclear Os-based compounds appear suitable as antenna-sensitizer devices for solar energy conversion[7,11] and for other applications based on photoinduced energy- and electron-transfer processes.

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