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Made-to-order control of the direction of electronic energy transfer in tetranuclear luminescent metal complexes

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Abstract

We have synthesized the tetranuclear complexes $Ru[(\mu\text{-}2,3\text{-}dpp)Ru(bpy)_2]_2[(\mu\text{-}2,3\text{-}dpp)Ru(biq)_2]^{8+}$ and $Ru[(\mu\text{-}2,3\text{-}dpp)Ru(bpy)_2]_2[(\mu\text{-}2,3\text{-}dpp)Os(bpy)_2]^{8+}$ which belong to the $M[(BL)M(L)_2]_3{}^{8+}$ family (M = Ru^{2+} or Os^{2+}; BL = 2,3-dpp or 2,5-dpp; L = bpy or biq; dpp = bis(2-pyridyl)pyrazine; bpy = 2,2'-bipyridine; biq = 2,2'-biquinoline). Luminescence investigations show that in the complexes of this family the electronic energy originated upon light absorption can be channelled in any desired direction along the supramolecular structure by a suitable choice of M, L, and BL.

1. INTRODUCTION

Electronic energy transfer lies at the heart of important natural phenomena (for example, photosynthesis [1]) as well as of practical applications (for example, spectral sensitization [2]). The possibility of governing the direction of electronic energy transfer in supramolecular arrays may open the way to the design of photochemical molecular devices that can perform a variety of useful functions [3]. We are engaged in a systematic study of the photochemical, photophysical, and electrochemical properties of oligometallic compounds [4-10] that can be considered as supramolecular species since they are made of metal-containing building-blocks linked by bridging ligands. In the course of these studies, we have designed and synthesized several tetranuclear metal complexes (Fig. 1, Table 1) of general formula $M[(BL)M(L_2)]_3{}^{8+}$, where M is Ru^{2+} or Os^{2+}, L is bpy (2,2'-bipyridine) or biq (2,2'-biquinoline), and the bridging ligand BL is 2,3-dpp or 2,5-dpp (dpp = bis(2-pyridyl)pyrazine). The results obtained show that in these supramolecular systems the electronic energy originated upon light absorption can be channelled along any desired direction by a suitable choice of M, L, and BL .

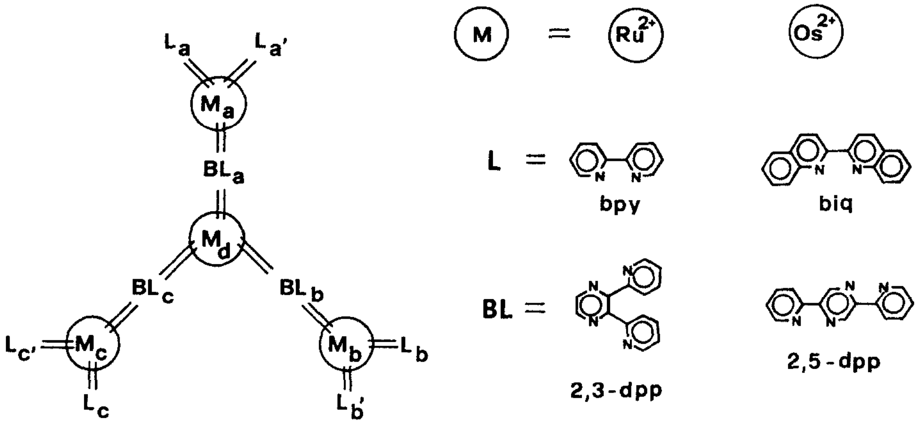

Figure 1. Schematic structure of the tetranuclear compounds 1-5. The actual composition of each complex is given in Table 1.

Since the pioneering work of Crosby [11], it is known that in Ru(II)- and Os(II)-polypyridine complexes luminescence takes place from the lowest excited level, which corresponds to a formally spin-forbidden metal-to-ligand charge transfer (^{3}MLCT) excited state. As Os(II) is easier to oxidize than Ru(II), the luminescent level of any Os(II)-polypyridine complex lies lower in energy than the luminescent level of the corresponding Ru(II) complex. It is also known that for complexes of the same metal, the energy of the luminescent level can be tuned by changing the type of polypyridine ligand [11,12]. For example, the luminescent level of a $M(bpy)_3^{2+}$ complex will always be higher in energy than the luminescent level of the corresponding $M(biq)_3^{2+}$ complex because bpy is more difficult to reduce than biq. A third, indirect way to tune the energy of the luminescent levels is that of changing the nature of

Table 1
Composition of the tetranuclear compounds (structure shown in Fig. 1)

compound	M	BL	L
1	Ru^2	2,3-dpp	bpy
2	$M_a=M_b=M_c$:Ru^{2+} M_d:Os^{2+}	2,3-dpp	bpy
3	M_a:Os^{2+} $M_b=M_c=M_d$:Ru	2,3-dpp	bpy
4	Ru^{2+}	BL_a:2,5-dpp $BL_b=BL_c$:2,3-dpp	bpy
5	Ru^{2+}	2,3-dpp	$L_a=L_a'$:biq $L_b=L_b'=$ $=L_c=L_c'$:bpy

the ancillary ligands (i.e., of the ligands that are not involved in the lowest energy MLCT transition). For example, when an X ligand of a ML_nX_m complex is replaced by a Y ligand which is a better electron donor that X, the ^{3}MLCT level will move to lower energy because of the increased electron density (and the consequent decrease in the ionization potential) of the metal. By using these concepts, we have designed a series of tetranuclear complexes (Fig. 1, Table 1) where the direction of electronic energy transfer can be synthetically controlled.

2. EXPERIMENTAL SECTION

2.1. Materials and methods

Details and procedures for IR spectra, conductivity measurements, absporption spectra, luminescence spectra, and luminescence lifetimes have been previously reported [6]. The preparations of compounds **1** [4,13], **2** [4], **4** [9], of the trinuclear complex substrate $\{Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_2Cl_2\}(PF_6)_4$ [10], and of the complex-ligands $[Os(bpy)_2(2,3\text{-dpp})](PF_6)_2$ [8] and $[Ru(biq)_2(2,5\text{-dpp})](PF_6)_2$ [6] have also been reported. The reactions and manipulations involving biq derivatives have been performed in light-protected vessels.

2.2. Syntheses of the new complexes

$\{Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_2[(\mu\text{-}2,3\text{-dpp})Os(bpy)_2]\}(PF_6)_8$ **(3).** To a solution of $\{Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_2Cl_2\}(PF_6)_4$ (0.0700 g, 0.0342 mmol) in 1:1 methanol/water (3 ml), solid $AgNO_3$ (0.0116 g, 0.0682 mmol) was added. After 3 h stirring at room temperature under argon, a precipitate of AgCl appeared. To the Paris blue mixture obtained a solution of $[Os(bpy)_2(2,3\text{-dpp})](PF_6)_2$ (0.0351 g, 0.0342 mmol) in ethylene glycol (3 ml) was added. The mixture was refluxed for 24 h, then cooled to room temperature. AgCl was separated by repeated centrifugations and to the mother liquor an excess solid NH_4PF_6 was added. The cyclamen powder that formed was filtered off, dissolved in acetonitrile and purified by gel filtration on Sephadex G-10 (acetonitrile eluant). From the eluate the product was recovered by addition of 95% ethanol and partial rotary evaporation at reduced pressure. It was repeatedly washed with 95% ethanol, then with diethyl ether and eventualy dried in vacuo (0.080 g, 71% yield). Anal. Calcd. for $C_{102}H_{78}F_{48}N_{24}OsP_8Ru_3\cdot 8H_2O$: C,35.65, H,2.76, N,9.78.

Found: C,35.66, H,2.58, N,9.87. Selected IR absorption maxima (cm^{-1}): 1606 (m), 1559 (w, br), 1469 (s), 1449 (s), 1423 (s), 1395 (s).

$\{Ru[(\mu\text{-}2,3\text{-}dpp)Ru(bpy)_2]_2[(\mu\text{-}2,3\text{-}dpp)Ru(biq)_2]\}(PF_6)_8$ (5). The procedure used was the same as that described above. The yield was 60%. Anal Caldc. for $C_{118}H_{86}F_{48}N_{24}P_8Ru_4 \cdot 8H_2O$: C,39.94, H,2.90, N,9.47. Found: C,39.74, H,2.63, N,9.71. Selected IR absorption maxima (cm^{-1}): 1599 (m, br), 1559 (vw, br), 1508 (m), 1465 (s), 1445 (s), 1428 (s), 1392 (s).

3. RESULTS

The absorption spectra of **3** and **5** are shown in Fig. 2. Compounds **3** is not luminescent, whereas compound **5** exhibits a luminescent band both in rigid matrix at 77 K and in fluid solution at room temperature (Fig. 2, inset). Its luminescence data are collected in Table 2, where the data of the previously investigated compounds **1**, **2**, and **4** are also summarized. For each luminescent compound, corrected excitation spectra show that the luminescent level is populated with the same efficiency regardless of the excitation wavelength.

4. DISCUSSION

Oligonuclear compounds like those examined in this work (Fig. 1) can be considered as supramolecular systems, i.e. as an ensemble of metal-containing building blocks each exhibiting its own ground and excited state properties [14-16]. The interaction between the various building blocks, however, is strong enough to cause a very efficient electronic energy transfer towards the building block(s) where the lowest energy excited state is localized. Such a lowest excited state is usually luminescent, and from the luminescent properties of the system it is in fact possible to establish which is (are) the building blocks where electronic energy has been channelled.

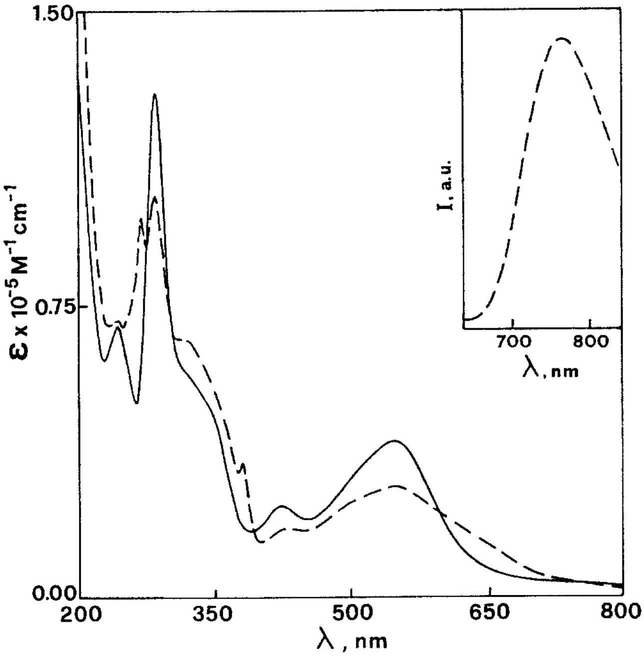

Figure 2. Absorption spectra of compounds 3 (full line) and 5 (dashed line) in acetonitrile solution at room temperature. The inset shows the luminescence band of 5 under the same conditions.

For the tetranuclear compounds discussed in this paper (Fig. 1, Table 1), energy migration can take place according to the four different patterns that are schematized in Fig. 3.

Case (i) obtains when there are three equivalent building blocks at the periphery, whose lowest excited state is lower in energy than the lowest excited state of the central building block. This happens in compound **1** [4,13]: since bpy is a better electron donor than 2,3-dpp [6], the peripheral Ru^{2+} ions have a higher electron density than the central Ru^{2+} ions, and thus the Ru^{2+}--->(μ-2,3-dpp) CT transition occurs at lower energy for the peripheral Ru^{2+} ions.

Case (ii) of Fig. 3 refers to systems in which the lowest excited state involves the central building block. To obtain a system of this type, we have designed and synthesized [4] compound **2**, where the central building block is Os-based

Table 2
Luminescence data

compound	77K[a] λ_{max}[c] nm	77K[a] τ µs	300 K[b] λ_{max}[c] nm	300 K[b] τ ns	behaviour[d]
1[e]	721	1.4	778	50	(i)
2[f]	798	0.4	830	18	(ii)
3	no luminescence for λ< 900 nm				(iii)
4[g]	752	0.9	812	43	(iii)
5	720	1.5	768	110	(iv)

[a] MeOH/ETOH 4:1 (v/v); [b] aerated acetonitrile: [c] uncorrected spectra; [d] see also Fig. 3; [e] see also refs. 4 and 13; [f] see also ref. 4; [g] ref. 9.

whereas the peripheral ones are Ru-based. The luminescence of **2** occurs at much lower energy than that of **1** (Table 2), showing that the emitting excited state involves the central, Os-based unit.

To channel energy towards a single peripheral unit (Fig. 3, case (iii)) we have designed compounds **3** and **4**. In compound **3** (Fig. 1, Table 1), there are three Ru^{2+}-based and one Os^{2+}-based building blocks. That containing Os^{2+} is located in a peripheral site. Electronic energy is therefore expected to migrate towards this site. The Os^{2+}--->(µ-2,3-dpp) CT level of the peripheral $Os(bpy)_2$(µ-2,3-dpp)$^{2+}$ building block is expected to lie below 10000 cm^{-1} [8,17]. The lack of

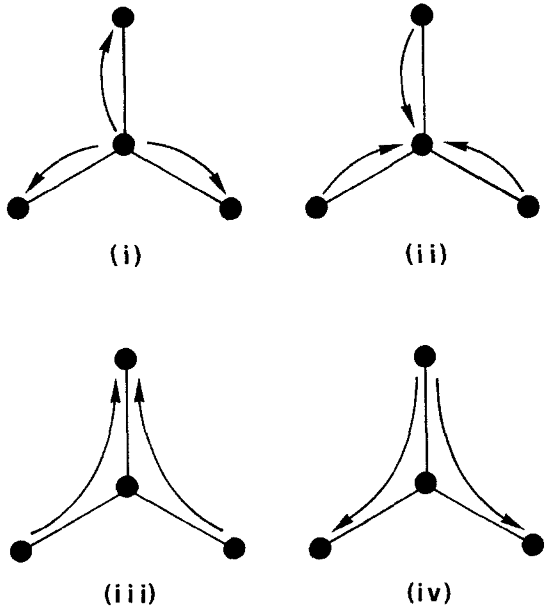

Figure 3. Schematic representation of the four directions of electronic energy transfer. For more details, see text.

luminescence from compound **3** in the spectral region $\lambda < 900$ nm (which is the limit of our equipment) confirms that energy migration takes place to the Os-containing site. In compound **4** [9], an energetic "asymmetry" in the supramolecular structure has been created by using different bridging ligands (Table 1). Since 2,5-dpp is easier to reduce than 2,3-dpp [6,9], the Ru ---> BL CT excited state of the $Ru(bpy)_2(\mu\text{-}2,5\text{-}dpp)^{2+}$ building block is lower in energy than the Ru ---> BL CT excited state of the $Ru(bpy)_2(\mu\text{-}2,3\text{-}dpp)^{2+}$ ones. Electronic energy is thus expected to be channelled towards the former building block. The observed luminescence (Table 2) is indeed that expected for a $Ru(bpy)_2(\mu\text{-}2,5\text{-}dpp)^{2+}$ unit, as shown by comparison with the luminescence of the homobridged $Ru[\mu\text{-}2,5\text{-}dpp)Ru(bpy)_2]_3{}^{8+}$ species [6].

Pattern (iv) for energy migration (Fig. 3) requires the presence of two equivalent peripheral building blocks whose lowest excited state is lower in energy than the lowest excited states of the central and of the third peripheral building blocks. To obtain this energy migration pattern we have designed compound **5**, where an energetic "asymmetry" has been created by using different terminal ligands L (Fig. 1, Table 1). This strategy is based on the fact that bpy is a better electron donor than biq, so that the metal ions of the $Ru(bpy)_2(BL)^{2+}$ building blocks have a higher electron density than the metal ion of the $Ru(biq)_2(BL)^{2+}$ building block. It follows that the lowest Ru ---> BL CT excited state of the former building blocks is lower in energy than the lowest Ru ---> BL CT excited state of the latter. Energy migration is therefore channelled on the two bpy-containing building blocks. The luminescence data obtained for **5** are indeed those expected for $Ru(bpy)_2(\mu\text{-}2,3\text{-}dpp)^{2+}$ units, as shown from a comparison with the data obtained for $[Ru(\mu\text{-}2,3\text{-}dpp)Ru(bpy)_2]_3{}^{8+}$ and other systems of the same family [6].

5. CONCLUSION

Both in natural and artificial photochemical molecular devices it is quite important to channel the absorbed light energy towards a specific component which performs (or triggers) a useful function (for example, charge separation in the photosynthetic reaction center [18]). We have shown that, taking transition metal complexes as building blocks, it is possible to design and synthesize artificial supramolecular systems where *the direction of energy migration can be predetermined*. The design of such systems requires the knowledge of the spectroscopic and excited state properties of the building blocks and appropriate synthetic techniques (such as the "complexes as ligands" strategy [7]) to place the various building blocks in specific sites of the supramolecular array.

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