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LETTER

Directional energy transfer in a luminescent tetranuclear Ru(II) polypyridine complex that contains two different types of bridging ligands

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Assembly of molecular components that exhibit suitable excited state properties can lead to photochemical molecular devices [1, 2] capable of performing light induced energy-migration and charge-separation processes [3-7]. Artificial photochemical molecular devices can be designed on the basis of building blocks that contain the necessary 'pieces of information' (i.e. suitable absorption properties, excited state energies, etc.) and bridging units that can link the building blocks to yield a suitable supramolecular structure [2]. The 2,3- and 2,5-isomers of bis(2-pyridyl)pyrazine (2,3-dpp and 2,5-dpp, Fig. 1) are interesting bridging units since they can coordinate luminescent and redox reactive ML_2 building blocks (e.g. $Ru(bpy)_2^{2+}$, where $bpy = 2,2'$ -bipyridine) [8-17].

In the last few years tri- [12, 16, 17], tetra- [9, 11, 16, 17], hexa- [18] and heptanuclear [15] complexes have been synthesized by using $Ru(bpy)_2^{2+}$ building blocks and dpp bridging ligands. In all cases, only one type of bridging ligand (i.e. either 2,3-dpp or 2,5-dpp) was used because this makes the synthetic procedure much easier. Because of this choice, equivalent $(\mu-dpp)Ru(bpy)_2^{2+}$ units are built-in at the periphery of the polynuclear species (see, for example, 2 and 3 in Fig. 1) and photoinduced energy migration

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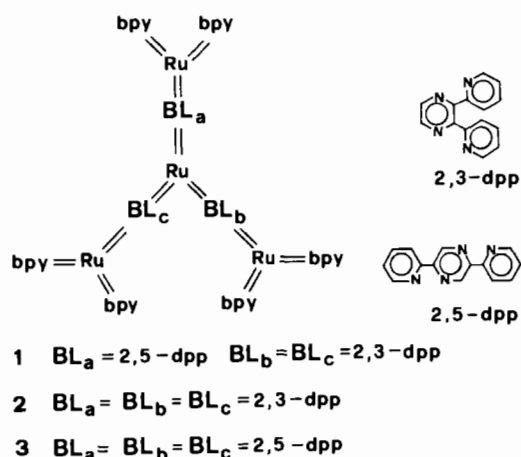


Fig. 1. Structures of the 2,3-dpp and 2,5-dpp bridging ligands and schematic representation of the tetranuclear complexes.

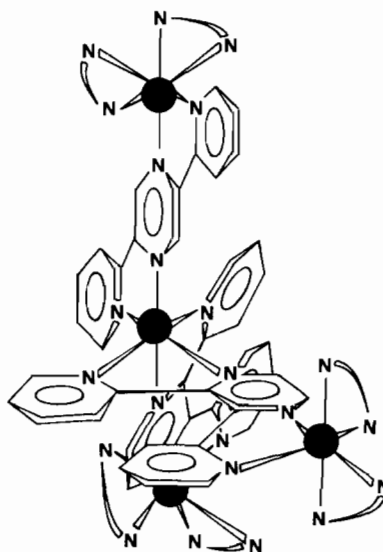


Fig. 2. Schematic view of 1. N-N stands for 2,2'-bipyridine.

takes place from the central chromophoric unit to each one of such equivalent peripheral units [9, 12, 15-17]. The equivalence of the peripheral units, however, can be removed by using different bridging ligands. In such a way it may be possible to channel energy migration towards a single peripheral chromophoric unit, a requirement that may be necessary for several types of applications (e.g. for spectral sensitization of semiconductor electrodes [19]). To explore this possibility we have designed and synthesized the complex $Ru[(\mu-2,3-dpp)Ru(bpy)_2]_2(\mu-2,5-dpp)Ru(bpy)_2]^{8+}$ (1) which contains two 2,3-dpp and one 2,5-dpp bridges (Figs. 1 and 2).

Experimental

The preparation of the bichelating ligands and of the precursor complex $[\text{Ru}(\text{bpy})_2(2,3\text{-dpp})](\text{PF}_6)_2$ as well as the details and procedures for the characterizations, absorption spectra, luminescence spectra, and luminescence lifetimes have been previously reported [16]. All reactions were carried out under argon.

Preparation of $\{\text{Ru}[(\mu\text{-}2,3\text{-dpp})\text{Ru}(\text{bpy})_2]_2\text{Cl}_2\}(\text{PF}_6)_4$ (4)

A mixture of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.011 g, 0.043 mmol), $[\text{Ru}(\text{bpy})_2(2,3\text{-dpp})](\text{PF}_6)_2$ (0.080 g, 0.086 mmol) and LiCl (0.012 g, 0.280 mmol) in 95% ethanol (15 ml) was refluxed for 7 h (after 1 h it became bladder green). The reaction mixture was then cooled to room temperature and an excess of solid NH_4PF_6 was added. The bladder green powder that formed was dissolved in acetonitrile, reprecipitated with 95% ethanol, washed with this solvent, then with diethyl ether and eventually dried *in vacuo* (0.079 g, 90% yield). *Anal.* Calc. for $\text{C}_{68}\text{H}_{52}\text{Cl}_2\text{F}_{24}\text{N}_{16}\text{P}_4\text{Ru}_3 \cdot 3\text{H}_2\text{O}$: C, 38.86; H, 2.49; N, 10.66. Found: C, 38.86; H, 2.71; N, 10.56%. $\Lambda = 316.4 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. Selected IR absorption maxima (cm^{-1}): 1607(m); 1559(w, br); 1470(s); 1450(s); 1423(s); 1393(s).

Preparation of $\{\text{Ru}[(\mu\text{-}2,3\text{-dpp})\text{Ru}(\text{bpy})_2]_2[(\mu\text{-}2,5\text{-dpp})\text{Ru}(\text{bpy})_2]\}(\text{PF}_6)_8$ (1)

To a solution of **4** (0.037 g, 0.018 mmol) in 1:1 (vol./vol.) methanol:water (6 ml), AgNO_3 (0.006 g, 0.036 mmol) dissolved in the same solvent system (3 ml) was added. The reaction mixture was stirred at room temperature for 3 h; during this time its colour turned from bladder green to night blue, and a precipitate of AgCl appeared. A solution of $[\text{Ru}(\text{bpy})_2(2,5\text{-dpp})](\text{PF}_6)_2$ (0.019 g, 0.018 mmol) in 1:1 (vol./vol.) methanol:water (3 ml) was then added, and the reaction mixture was refluxed until TLC tests showed that all the 2,5-dpp complex had reacted (26 h). After removal of AgCl by repeated centrifugations, to the mother liquor partially evaporated *in vacuo*, an excess of solid NH_4PF_6 was added. The resulting mallow powder was filtered out, reprecipitated twice from acetonitrile solutions with 95% ethanol, washed with this solvent and with diethyl ether, and dried *in vacuo* (0.040 g, 70% yield). *Anal.* Calc. for $\text{C}_{102}\text{H}_{78}\text{F}_{48}\text{N}_{24}\text{P}_8\text{Ru}_4 \cdot 8\text{H}_2\text{O}$: C, 36.59; H, 2.47; N, 10.04. Found: C, 36.26; H, 2.45; N, 10.34%. $\Lambda = 496.4 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. Selected IR absorption maxima (cm^{-1}): 1607(m); 1561(m, br); 1468(s); 1449(s); 1421(m); 1397(m); 1369(w); 1208(w, br).

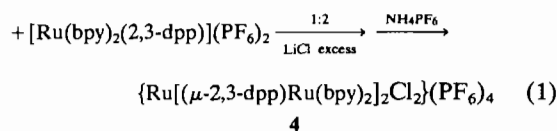
It must be pointed out that in principle complexes **1** and **4** can exist as three and four geometrical

isomers, respectively, depending on the arrangement of the ligands around the metal atoms. Furthermore, they can be mixtures of several diastereoisomeric species, owing to the chiral nature of each metal center. For these reasons, structural investigations on these species are presently prevented, as already discussed in ref. 16.

Results and discussion

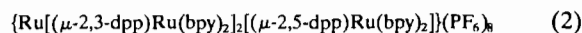
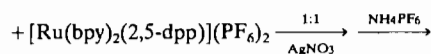
We first prepared the novel trinuclear compound $\text{Ru}[(\mu\text{-}2,3\text{-dpp})\text{Ru}(\text{bpy})_2]_2\text{Cl}_2^{4+}$ (**4**) by following the 'complexes as ligands' strategy [15, 16] shown in eqn. (1). Compound **4** is a quite interesting

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$



building block since it contains two labile Cl^- ligands and can thus be used to introduce a trimetallic fragment in species that have an unsaturated chelating site. The tetranuclear complex **1** was then obtained by the procedure indicated in eqn. (2).

$\{\text{Ru}[(\mu\text{-}2,3\text{-dpp})\text{Ru}(\text{bpy})_2]_2\text{Cl}_2\}(\text{PF}_6)_4$



The absorption spectrum of **1** (Fig. 3) is characterized by very intense bands in the visible region ($\lambda_{\text{max}} = 552 \text{ nm}$, $\epsilon = 41\,700 \text{ M}^{-1} \text{cm}^{-1}$), and is similar to, but clearly distinct from, the spectra of the homobridged compounds **2** [9, 11, 16] and **3** [17]. The emission spectrum of **1** ($\tau = 900 \text{ ns}$ in $\text{CH}_3\text{OH}/\text{C}_2\text{H}_5\text{OH}$ 4:1 (vol./vol.) rigid matrix at 77 K, and 44 ns in acetonitrile solution at 298 K) is quite similar to that of **3**, but different from that of **2** (λ_{max} (77 K): 752 (**1**), 725 (**2**), 763 (**3**) nm; λ_{max} (298 K): 812 (**1**), 782 (**2**), 810 (**3**) nm). This clearly indicates that the luminescent excited state of **1** is essentially localized in the single peripheral Ru-based chromophore which contains the 2,5-dpp bridge. Corrected excitation spectra at room temperature have shown that the luminescent level of **1** is populated with the same efficiency regardless of the excitation wavelength, as expected for an energy transfer process taking place (presumably, with unit efficiency) from all the chromophoric groups to the luminescent one. These results, taken together with those previously obtained for the compounds **2** [9, 11, 16, 17] and **3** [17] (where energy migration occurs from the

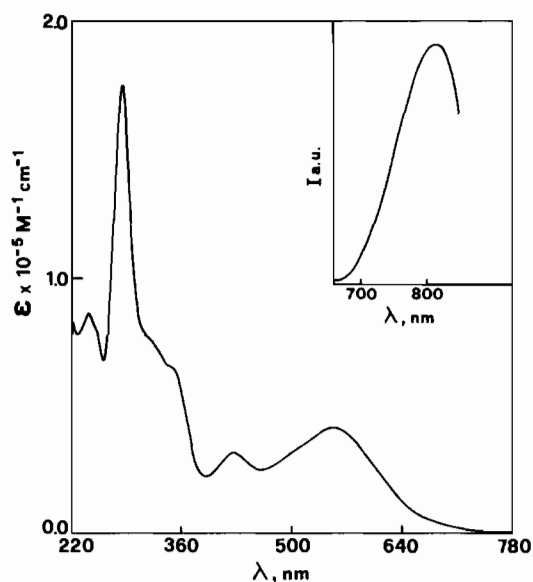


Fig. 3. Absorption and (inset) uncorrected luminescence spectra of **1** in acetonitrile solution at 298 K.

central chromophore to all the peripheral ones) and for the heterotetrametallic compound $\text{Os}[(\mu\text{-}2,3\text{-dpp})\text{Ru}(\text{bpy})_2]_3^{8+}$ [11, 17] (where energy migration occurs from the peripheral chromophores to the central one), show that in polynuclear metal complexes it is possible to control the direction of electronic energy transfer by a suitable choice of the components.

Acknowledgements

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References

- 1 V. Balzani, L. Moggi and F. Scandola, in V. Balzani (ed.), *Supramolecular Photochemistry*, Reidel, Dordrecht, The Netherlands, 1987, p. 1.
- 2 V. Balzani and F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood, Chichester, U.K., 1991, Ch. 12.
- 3 J. S. Connolly and J. R. Bolton, in M. A. Fox and M. Chanon (eds.), *Photoinduced Electron Transfer*, Part D, Elsevier, New York, 1988, p. 303.
- 4 M. R. Wasielewski, in M. A. Fox and M. Chanon (eds.), *Photoinduced Electron Transfer*, Part A, Elsevier, New York, 1988, p. 161.
- 5 D. Gust and T. A. Moore, *Science*, **244** (1989) 35.
- 6 T. J. Meyer, *Acc. Chem. Res.*, **22** (1989) 163.
- 7 J. R. Norris, Jr. and D. Meisel (eds.), *Photochemical Energy Conversion*, Elsevier, New York, 1989.
- 8 Y. Fuchs, S. Lofters, T. Dieter, W. Shi, R. Morgan, T. C. Streckas, H. D. Gafney and A. D. Baker, *J. Am. Chem. Soc.*, **109** (1987) 269.
- 9 W. R. Murphy, K. J. Brewer, G. Gettliffe and J. D. Petersen, *Inorg. Chem.*, **28** (1989) 81.
- 10 K. Kalyanasundaram and Md. K. Nazeeruddin, *Inorg. Chem.*, **29** (1990) 1888.
- 11 S. Campagna, G. Denti, L. Sabatino, S. Serroni, M. Ciano and V. Balzani, *J. Chem. Soc., Chem. Commun.*, (1989) 1500.
- 12 S. Campagna, G. Denti, L. Sabatino, S. Serroni, M. Ciano and V. Balzani, *Gazz. Chim. Ital.*, **119** (1989) 415.
- 13 R. M. Berger, *Inorg. Chem.*, **29** (1990) 1920.
- 14 J. B. Cooper, D. B. MacQueen, J. D. Petersen and D. W. Wertz, *Inorg. Chem.*, **29** (1990) 3701.
- 15 G. Denti, S. Campagna, L. Sabatino, S. Serroni, M. Ciano and V. Balzani, *Inorg. Chim. Acta*, **176** (1990) 175.
- 16 G. Denti, S. Campagna, L. Sabatino, S. Serroni, M. Ciano and V. Balzani, *Inorg. Chem.*, **29** (1990) 4750.
- 17 G. Denti, S. Campagna, L. Sabatino, S. Serroni, M. Ciano and V. Balzani, in E. Pelizzetti and M. Schiavello (eds.), *Photochemical Conversion and Storage of Solar Energy*, Kluwer, Dordrecht, 1991, p. 27.
- 18 G. Denti, S. Campagna, S. Serroni, M. Ciano and V. Balzani, submitted for publication.
- 19 R. Amadelli, R. Argazzi, C. A. Bignozzi and F. Scandola, *J. Am. Chem. Soc.*, **112** (1990) 7099.