Supramolecular photochemistry. Luminescent and redox active dendritic polynuclear metal complexes

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Abstract. The synthetic strategies used to prepare di-, tri-, tetra-, hexa-, hepta-, deca-, trideca- and docosanuclear Ru(II) and/or Os(II) polypyridine-type complexes containing the 2,3-dpp and/or 2,5-dpp bridging ligands and the bpy and/or biq terminal ligands are described (dpp = *bis*(2-pyridyl)pyrazine; bpy = 2,2'-bipyridine; biq = 2,2'-biquinoline). The light absorption, luminescence, and redox properties of these polynuclear compounds can be varied by changing (i) the nuclearity, (ii) the nature of metal ions, bridging ligands and/or terminal ligands, and (iii) the position of the various components in the supramolecular structure. Because of their strong absorption in the visible spectral region and the possibility of predetermining the direction of energy migration, these compounds can be used as photochemical molecular devices (e.g., as antennas for harvesting solar energy). Because of the presence of several interacting and/or noninteracting redox centres, they are good candidates to play the role of multielectron-transfer catalysts.

Keywords. Photochemistry; photophysics; supermolecules; molecular devices.

1. Introduction

Supramolecular chemistry has shown that molecular components can be assembled to give species of nanometric dimensions (Lehn 1990; Balzani and Scandola 1991; Schneider and Durr 1991; Vögtle 1991; Whitesides *et al* 1991; Anelli *et al* 1992; Balzani and DeCola 1992). Of particular interest are tree-like structures that incorporate in their building blocks specific pieces of information, such as electronic excited states and redox levels at accessible energy values. To pursue this aim, we have designed a synthetic strategy to build up dendritic species based on luminescent and redox-active transition metal complexes, where desired metals and ligands can be placed in specific sites of the supramolecular structure. Species made of 2, 3, 4, 6, 7, 10, 13 and 22 metal-based units have already been prepared and larger species can in principle be obtained. This strategy opens the way to the synthesis of species of nanometric dimension capable of harvesting visible light and exhibiting made-to-order patterns for energy and electron migration.

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2. Building blocks and bridging ligands

In the last 20 years extensive investigations carried out on the photochemical and electrochemical properties of transition metal compounds have shown that Ru(II) and Os(II) complexes of aromatic diimines, e.g. Ru(bpy)₃²⁺ and Os(bpy)₃²⁺ (bpy = 2, 2'-bipyridine), exhibit a unique combination of chemical stability, redox properties, excited state reactivity, luminescence, and excited state lifetimes (Juris *et al* 1988; Balzani *et al* 1990; Kalyanasundaram 1991). Furthermore, their properties can be tuned within rather broad ranges by changing ligands or ligand substituents. Several hundreds of these complexes have been synthesized and characterized, and some of them have been used as sensitizers for the interconversion of light and chemical energy as well as for other purposes. Such complexes are ideal building blocks (components) to obtain supramolecular species capable of exhibiting light-induced functions.

In order to assemble such metal-containing building blocks in a supramolecular array, a variety of bridging ligands can be employed. We have concentrated our efforts on the use of the 2,3- and 2,5-bis(2-pyridyl)pyrazine (2,3- and 2,5-dpp) bridging ligands (BL) shown in figure 1.

Some important properties of the M(BL)_{3-n}(L)_n²⁺ compounds can be summarized as follows (Braunstein *et al* 1984; Brewer *et al* 1986; Campagna *et al* 1989a; Denti *et al* 1990a): (1) there are intense ligand-centred (LC) absorption bands in the UV region and moderately intense ($\epsilon_{\text{max}} \sim 1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) metal-to-ligand charge transfer (MLCT) bands in the visible region; (2) a relatively long-lived luminescence (10^{-7} – 10^{-8} s time scale at room temperature) is present in the red spectral region; (3) reversible one-electron oxidation of the metal ion takes place in the potential window +0.8/+1.7 V (vs SCE); (4) reversible one-electron reduction of each ligand takes place in the potential window –0.6/–1.1 V. Important differences relevant to our discussion are as follows: (i) Os(II) complexes are oxidized at potentials considerably less positive than Ru(II) complexes; (ii) the MLCT absorption and luminescence bands lie at lower energies for the Os(II) complexes than for the Ru(II) ones; (iii) the energy of the LUMO of the (mono-coordinated) ligands decreases in the series bpy > 2,3-dpp > 2,5-dpp > biq; as a consequence, the lowest (luminescent) ³MLCT level involves the lowest ligand of the above series which is present in the complex; (iv) the electron donor power decreases in the ligand series bpy > biq ≥ 2,3-dpp ~ 2,5-dpp.

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

3. Synthetic strategies

Mononuclear transition metal complexes are synthesized by combining metal ion (M) and free ligands (L), as shown below:

In the last few years we have been developing a procedure to synthesize oligonuclear metal complexes of desired nuclearity and chemical structure (Campagna *et al* 1989b, 1991, 1992; Denti *et al* 1990–1993; Serroni *et al* 1991–1992). Such a procedure is based on the use of *complexes* (building blocks) in the place of the metal (M) and/or ligands (L) in the synthetic reaction (1). The place of M can be taken by mono- or oligonuclear complexes that possess easily replaceable ligands, and the place of L can be taken by mono- or oligonuclear complexes which contain free chelating sites ("complexes as metals" and "complexes as ligands" strategy).

Some of the building blocks used in our syntheses are sketched in scheme 1. The synthetic routes followed to obtain complexes of nuclearity from 10 to 22 are illustrated in table 1. In each equation, the first reactant plays the role of a metal and the second one plays the role of a ligand. A list of the complexes prepared in our laboratory is also reported in the same table. More details on the synthetic procedures (and on the characterization of the compounds) can be found in the original papers. The final step to obtain the docosanuclear compound is shown in scheme 2.

Schematic views of the decanuclear and tridecanuclear complexes containing 2,3-dpp as a bridging ligand are shown in figures 2 and 3.

As shown in table 1, the synthetic strategy used is versatile and selective, since the sites occupied by different metals and ligands in the structure of the polynuclear compounds can be synthetically predetermined by the appropriate choice of the building blocks. Recently we have also elaborated a strategy to grow oligonuclear metal complexes in an arborol-like structure according to a divergent approach (scheme 3) (Serroni *et al* 1992).

Scheme 1.

Table 1. Synthetic routes used for the synthesis of deca-, trideca-, and docosanuclear complexes. Original references a, b etc are given in parentheses.*Decanuclear compounds*

10A	(a, b)	$M_a = M_b = M_c = \text{Ru}$	$\text{BL} = 2,3\text{-dpp}$	$L = \text{bpy}$
10B	(a)	$M_a = M_b = M_c = \text{Ru}$	$\text{BL} = 2,3\text{-dpp}$	$L = \text{biq}$
10C	(a)	$M_a = M_b = \text{Ru}, M_c = \text{Os}$	$\text{BL} = 2,3\text{-dpp}$	$L = \text{bpy}$
10D	(a)	$M_a = M_b = \text{Ru}, M_c = \text{Os}$	$\text{BL} = 2,3\text{-dpp}$	$L = \text{biq}$
10E	(a)	$M_a = \text{Ru}, M_b = M_c = \text{Os}$	$\text{BL} = 2,3\text{-dpp}$	$L = \text{bpy}$
10F	(a)	$M_a = M_c = \text{Ru}, M_b = \text{Os}$	$\text{BL} = 2,3\text{-dpp}$	$L = \text{bpy}$

Tridecanuclear compounds

13A	(c)	$M = \text{Ru}$	$\text{BL} = 2,3\text{-dpp}$	$L = \text{bpy}$
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Docosanuclear compounds

22A	(d)	$M = \text{Ru}$	$\text{BL} = 2,3\text{-dpp}$	$L = \text{bpy}$
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References: (a) – Denti *et al* (1992a); (b) – Serroni *et al* (1991); (c) Campagna *et al* (1992); (d) – Serroni *et al* (1992).

Scheme 2.

Figure 2. Schematic view of a decanuclear complex.

4. General properties

The compounds described in this paper are well-characterized supramolecular species made of a well-defined number of metal-containing components. They carry an overall positive charge that is twice the number of the metal atoms. Neglecting the PF_6^- counter ions, the docosanuclear compound **22A** (6 in scheme 2) is made of 1090 atoms, has a molecular weight of 10890 daltons, and an estimated size of about 5 nm. Besides the 22 metal atoms, it contains 24 terminal bpy ligands and 21, 2,3-dpp bridging ligands (Serroni *et al* 1992). Differences arising from the possible presence of isomeric species are not expected to be sizeable in the electrochemical and spectroscopic properties discussed below.

As one can understand from the schematic views shown in figures 2 and 3, species with high nuclearity exhibit a three-dimensional branching structure of the type shown by otherwise completely different compounds based on polyamidoamines or other organic components (for some recent papers see Shahlai and Hart 1990, Gopidas *et al* 1991, Hawker *et al* 1991, Newkome *et al* 1991 and Nagasaki *et al* 1992; see

Figure 3. Schematic view of a tridecanuclear complex.

Tomalia *et al* 1990, for a comprehensive review). Therefore endo- and exoreceptor properties can be expected, which will be the object of future investigations.

We would like to stress that our complexes differ from most of the organic-type arborols or dendrimers prepared so far owing to two fundamental reasons: (i) each component exhibits valuable intrinsic properties such as absorption of visible (solar) radiation, luminescence, and redox levels at accessible potentials; (ii) by a suitable choice of the building blocks, different components can be placed in specific sites of the supramolecular array, as one can understand from figure 4 where the syntheses of 6 different decanuclear complexes, using different precursors, are schematized. In

Scheme 3.

Figure 4. Scheme showing the synthetic control of the composition of decanuclear compounds.

Table 2. Spectroscopic and electrochemical properties of selected polynuclear compounds.^a

Compounds		Absorption		Emission		Electro-chemistry
		$\lambda_{\max}^b$ (nm)	ϵ (M ⁻¹ cm ⁻¹)	$\lambda_{\max}$ (nm)	τ (ns)	$E_{1/2}^{\text{ox}}$ [V] ^c vs SCE
10A	Ru{(μ -2,3-dpp)Ru[(μ -2,3-dpp)Ru(bpy) ₂] ₂ } ₃ ²⁰⁺	541	125000	809	55	+1.46 [6]
10B	Ru{(μ -2,3-dpp)Ru[(μ -2,3-dpp)Ru(biq) ₂] ₂ } ₃ ²⁰⁺	555	109000	789	130	+1.62 [6]
10C	Os{(μ -2,3-dpp)Ru[(μ -2,3-dpp)Ru(bpy) ₂] ₂ } ₃ ²⁰⁺	550	117000	808	65	+1.17 [1]
				860	d	+1.50 [6]
10F	Os{(μ -2,3-dpp)Ru[(μ -2,3-dpp)Os(bpy) ₂] ₂ } ₃ ²⁰⁺	563	140500	900 ^e	d	+1.05 [6]
						+1.39 [1]
13A	Ru{(μ -2,3-dpp)Ru(bpy)(μ -2,3-dpp)Ru[(μ -2,3-dpp)Ru(bpy) ₂] ₂ } ₃ ²⁶⁺	544	133000	800	62	+1.50 [9] ^f
22A	Ru{(μ -2,3-dpp)Ru[(μ -2,3-dpp)Ru{(μ -2,3-dpp)Ru(bpy) ₂] ₂ } ₂ } ₃ ⁴⁴⁺	542	202400	802	d	+1.52 [12]

(a) Experiments in acetonitrile solution at room temperature, unless otherwise noted. Luminescence lifetimes are aerated values, unless otherwise stated. (b) Lowest energy ¹MLCT band. (c) The numbers within brackets indicate the number of electrons exchanged. (d) Not measured. (e) At 90 K in MeOH/EtOH 4:1 (v/v) glassy matrix. (f) This wave exhibits a large separation between cathodic and anodic peaks ($\Delta E = 180$ mV). This suggests that there is a superposition of two closely spaced oxidation processes; the first one has been attributed to one-electron oxidation of six independent redox sites, and the second one to one-electron oxidation of three independent redox sites.

other words, our arborols are species with a high “information” content and can therefore be exploited to perform valuable functions (*vide infra*).

The absorption, emission, and redox properties of some selected compounds are shown in table 2.

5. Absorption spectra

Since the interaction between the various metal-containing units is weak (*vide infra*) the absorption spectra of the oligonuclear complexes are, as one can expect, a combination of the absorption spectra of the single metal-containing components. When many components are present, the absorption spectra show very intense bands all over the UV and visible spectral region. For example, the spectra of the decanuclear compounds **10B** and **10C** (figure 5) (Denti *et al* 1992a) show absorption bands with ϵ up to 600,000 M⁻¹cm⁻¹ in the UV region and up to 140,000 M⁻¹cm⁻¹ in the visible region. The bands with maxima at 262 and 380 nm can be assigned to $\pi \rightarrow \pi^*$ transitions of the biq ligands, the band at 282 nm to $\pi \rightarrow \pi^*$ transitions of the bpy ligands, and the broad absorption in the 300–350 nm region to $\pi \rightarrow \pi^*$ transitions of the biq and 2,3-dpp ligands. The broad bands observed in the visible region receive contributions from several types of metal-to-ligand charge-transfer (MLCT) transitions. The energies of these transitions depend on the nature of the donor metal ion, the acceptor ligand and the ancillary ligands.

Figure 5. Absorption spectra of the decanuclear compounds **10B** and **10C** in acetonitrile solution at room temperature.

6. Electrochemical properties

The mononuclear compounds of the $M(BL)_{3-n}(L)_n^{2+}$ series exhibit reversible redox-processes. On reduction, each L ligand is reduced twice and each BL ligand is reduced four times in the potential window $-0.5/-3.1$ V (Roffia *et al* 1993). The reduction potential of each ligand depends on its electronic properties and, to a smaller extent, on the nature of the metal and of the other ligands coordinated to the metal. It follows that on reduction of a polynuclear complex which contains several ligands (e.g., 21 ligands are present in the decanuclear complexes), an extremely complicated pattern with many overlapping peaks is observed. On oxidation of mononuclear complexes in the potential window $< +1.6$ V, only one peak is observed in the differential pulse voltammograms, which concerns the metal ion. The oxidation potential depends strongly on the nature of the metal ion (Os(II) is oxidized at less positive potentials compared to Ru(II)) and, less dramatically, on the nature of the coordinated ligands. Because of the electronic properties of the isolated components (and of the stabilization of the LUMO of 2,3-dpp and 2,5-dpp on coordination to a second metal centre), it can be expected that for the metal-containing building blocks which are present in the synthesized polynuclear compounds the oxidation potential of the metal (and the energy of the lowest (luminescent) excited state) increases in the series $Os(bpy)_2(\mu-2,5-dpp)^{2+} \leq Os(bpy)_2(\mu-2,3-dpp)^{2+} < Os(biq)_2(\mu-2,5-dpp)^{2+} \leq Os(biq)_2(\mu-2,3-dpp)^{2+} < Os(\mu-2,5-dpp)_3^{2+} < Os(\mu-2,3-dpp)_3^{2+} < Ru(bpy)_2(\mu-2,5-dpp)^{2+} \leq Ru(bpy)_2(\mu-2,3-dpp)^{2+} < Ru(biq)_2(\mu-2,5-dpp)^{2+} \leq Ru(biq)_2(\mu-2,3-dpp)^{2+} < Ru(bpy)(\mu-2,5-dpp)_2^{2+} \leq Ru(bpy)(\mu-2,3-dpp)_2^{2+} < Ru(\mu-2,3-dpp)_3^{2+}$.

It can also be expected (and it is confirmed by the experimental data, table 2) that in the polynuclear complexes the metal-metal interaction is non-negligible for metals coordinated to the same bridging ligand, whereas it is very weak for metals that do not share the same bridging ligand. Thus, equivalent units that are not directly

connected are oxidized at the same potential. This allows us to control the number of electrons lost at certain potentials by placing in the supramolecular species the desired number of suitable, equivalent, and noninteracting units. For example, in compound **10C** (figure 4), the differential pulse voltammogram (figure 6) shows an oxidation peak at +1.17 V, which is assigned to one-electron oxidation of the central Os^{2+} metal ion, and another peak at +1.50 V, which has the same bandwidth but six times higher intensity, that can be assigned to the independent one-electron oxidation of the six peripheral noninteracting Ru^{2+} ions. Oxidation of the three intermediate Ru^{2+} ions is further shifted towards more positive potentials and cannot be observed in the potential window examined. For **10E**, oxidation involves first the six peripheral Os^{2+} ions (which contain the stronger electron donor bpy ligand in their coordination sphere), and then the central one (figure 6).

In conclusion, the electrochemical data offer a fingerprint of the chemical and topological structure of the oligonuclear compounds. Furthermore, made-to-order synthetic control of the number of electrons exchanged at a certain potential can be achieved.

Figure 6. Oxidation patterns for some decanuclear complexes. Fc indicates the oxidation peak of ferrocene, used as an internal standard.

7. Luminescence

Light excitation in the visible absorption bands populates $^1\text{MLCT}$ excited states in the various components. Investigations carried out on $\text{Ru}(\text{bpy})_3^{2+}$ with fast techniques indicate that the originally populated $^1\text{MLCT}$ excited states undergo relaxation to the lowest energy $^3\text{MLCT}$ level in the subpicosecond time scale (Carrol and Bruss 1987; Bradley *et al* 1989; Yabe *et al* 1989; Cooley *et al* 1990). If this behaviour, as it seems likely, is of general validity for the various components of the polynuclear compounds, the actual result of light excitation is the population with unitary efficiency of the lowest energy $^3\text{MLCT}$ level of the component where light absorption has taken place. If each component were isolated, as it happens in mononuclear complexes, competition between radiative (luminescence) and radiationless decay to the ground state would account for the deactivation of the $^3\text{MLCT}$ level, with an overall rate constant, measured from the luminescence decay, in the range 10^6 – 10^8 s^{-1} . All the members of the mononuclear $\text{M}(\text{BL})_{3-n}(\text{L})_n^{2+}$ family, in fact, display a characteristic luminescence both in rigid matrix at 77 K and in fluid solution at room temperature. When the components are linked together in a supramolecular array, electronic energy can be transferred from an excited component to an unexcited one even if the electronic interaction is weak. In most of the polynuclear compounds examined, only a luminescence band corresponding to the lowest energy $^3\text{MLCT}$ level is observed (table 2), indicating that energy transfer from upper-lying to lower-lying levels does occur (*vide infra*).

8. Antenna effect

The natural photosynthetic systems show that for solar energy conversion purposes supramolecular arrays are needed which absorb as much visible light as possible and are capable of channelling the resulting excitation energy towards a specific site of the array (*antenna devices*). The polynuclear metal complexes described in this paper are excellent light absorbers in the entire visible region. Furthermore, efficient energy transfer can take place between their components, as shown by the presence of only one luminescence band for compounds which contain more than one type of chromophoric units. The occurrence of energy transfer can be established by the quenching of the luminescence of the donor unit and the sensitization of the luminescence of the acceptor unit, and its efficiency can be estimated by comparing the absorption and excitation spectra. The energy levels involved in energy transfer are the lowest $^3\text{MLCT}$ excited state of each component. Because of these properties of the components and of the stabilization of the LUMO of 2,3-dpp and 2,5-dpp on coordination to a second metal centre, it can be expected that for the metal-containing building blocks which are present in the polynuclear compounds the energy of the lowest (luminescent) excited state increases (as does the oxidation potential, *vide supra*) in the series $\text{Os}(\text{bpy})_2(\mu\text{-}2,5\text{-dpp})^{2+} \leq \text{Os}(\text{bpy})_2(\mu\text{-}2,3\text{-dpp})^{2+} < \text{Os}(\text{biq})_2(\mu\text{-}2,5\text{-dpp})^{2+} \leq \text{Os}(\text{biq})_2(\mu\text{-}2,3\text{-dpp})^{2+} < \text{Os}(\mu\text{-}2,5\text{-dpp})_3^{2+} < \text{Os}(\mu\text{-}2,3\text{-dpp})_3^{2+} < \text{Ru}(\text{bpy})_2(\mu\text{-}2,5\text{-dpp})^{2+} \leq \text{Ru}(\text{bpy})_2(\mu\text{-}2,3\text{-dpp})^{2+} < \text{Ru}(\text{biq})_2(\mu\text{-}2,5\text{-dpp})^{2+} \leq \text{Ru}(\text{biq})_2(\mu\text{-}2,3\text{-dpp})^{2+} < \text{Ru}(\text{bpy})(\mu\text{-}2,5\text{-dpp})_2^{2+} \leq \text{Ru}(\text{bpy})(\mu\text{-}2,3\text{-dpp})_2^{2+} < \text{Ru}(\mu\text{-}2,3\text{-dpp})_3^{2+}$.

By using the above guidelines, it is possible to design polynuclear complexes where the component(s) with the lowest energy excited state(s) is (are) located in the desired

position(s) of the supramolecular structure. This allows a synthetic control of the direction(s) of energy migration after light absorption.

For the decanuclear compounds 10A–10F, the directions along which energy transfer processes are exoergonic are schematically indicated by arrows in figure 7 (Denti *et al* 1992a). 10A displays a luminescence band at 809 nm that can be assigned straightaway to the peripheral (bpy)₂Ru → BL excited states. The lack of luminescence at shorter wavelengths and the constancy of the luminescence quantum yield on changing the excitation wavelength indicate that the chromophoric groups based on the central and intermediate Ru²⁺ ions undergo an efficient deactivation to the peripheral Ru-based units as expected because energy transfer is exoergonic in the direction from centre to periphery. 10B exhibits exactly the same behaviour as 10A. For compounds 10C and 10D, a broad luminescence band is observed at room temperature, with a shoulder on its low energy tail. The maxima of the luminescence bands almost coincide with those of the bands exhibited by 10A and 10B, respectively. The predominant emission can thus be assigned to the peripheral units. Subtraction (after normalization) of the luminescence band of 10A from that of 10C and of the band of 10B from that of 10D yields a band with maximum at ~860 nm, as expected for the luminescence of a central Os unit. We conclude that, at room temperature, 10C and 10D emit from both the central and the peripheral units. Such behaviour is consistent with the fact that in 10C and 10D the lowest excited state of the intermediate Ru-based units lies at higher energy (~2000 cm⁻¹) than the lowest excited state of the peripheral units. Thus for 10C and 10D the two-step energy-transfer process from the peripheral units to the central one (where the lowest energy excited state of the supramolecular array is located) must be very slow since its first step is endoergonic by ~2000 cm⁻¹. Direct (through space) energy transfer from the peripheral to the central units is exoergonic but should be slow because of the large separating distance. A quantitative evaluation of the energy transfer efficiency from the peripheral to the central unit is difficult to make from luminescence quantum yield data because of the strong overlap between the absorption bands of the various units.

For 10E and 10F the lowest excited states are localized on the peripheral (bpy)₂Os → BL units which are expected to emit around 900 nm. With infrared-sensitive equipment (Juris *et al* 1993) luminescence bands at 900 and 892 nm can in fact be observed for 10E and 10F, respectively. The lack of any Ru-based luminescence for 10F indicates a 100% efficient centre-to-periphery channelling of the excitation energy, as expected because of the energy gradient (figure 7). For 10E, deactivation of the central Os-based unit by the peripheral ones should not occur because the first step of this process is endoergonic. The lack of observable luminescence from such a central unit may simply be due to the fact that most of the light, at any excitation wavelength, is absorbed by the much more numerous peripheral and intermediate units.

9. Conclusion

A synthetic strategy has been developed to obtain supramolecular dendritic structures of nanometric dimensions made of metal complex units capable of a high information content (light absorption, luminescence, redox activity). Specific metal and/or ligands

Figure 7. Energy migration patterns for some decanuclear compounds. Empty and full circles indicate Ru^{2+} and Os^{2+} , respectively. In the peripheral positions, circles and squares indicate $\text{M}(\text{bpy})_2$ and $\text{M}(\text{biq})_2$ components, respectively. The arrows indicate the exoergonic energy transfer steps.

can be placed in predetermined sites of the supramolecular array by an appropriate choice of the building blocks. It is thus possible to design species where several important functions can be synthetically controlled. In particular, made-to-order control of the number of electrons lost at a certain potential and of the direction of electronic energy transfer can be achieved.

Because of their strong absorption in the visible spectral region and the possibility of predetermining the direction of energy migration, these compounds can be used as photochemical molecular devices (e.g., as antennas for harvesting solar energy) (Balzani *et al* 1987; Balzani and DeCola 1992, chap. 7). Because of the presence of several interacting and/or noninteracting redox centres, they are good candidates to play the role of multielectron-transfer catalysts.

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