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Review

Coupling synthetic antenna and electron donor species: A tetranuclear mixed-metal Os(II)–Ru(II) dendrimer containing six phenothiazine donor subunits at the periphery

Fausto Puntoriero[a], Francesco Nastasi[a], Marco Cavazzini[b],
Silvio Quici[b,*], Sebastiano Campagna[a,*]

[a] *Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina, Via Sperone 31, 98166 Messina, Italy*
[b] *CNR-Istituto di Scienze e Tecnologie Molecolari (ISTM), Via C. Golgi 19, 20133 Milano, Italy*

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Contents

Abstract

A new dendritic-shaped tetranuclear complex, $[Os\{(\mu\text{-},3\text{-dpp})Ru(bpy\text{-}PTZ)_2\}_3]^{8+}$ (**1**), containing an $\{Os(\mu\text{-}2,3\text{-dpp})_3\}^{2+}$ chromophore as the core and three $\{(\mu\text{-}2,3\text{-dpp})Ru(bpy\text{-}PTZ)_2\}^{2+}$ polypyridine building blocks as peripheral subunits, has been prepared (2,3-dpp = 2,3-bis(2′-pyridyl)pyrazine; bpy-PTZ = 10-(2,2′-bipyridin-4-yl)methyl)phenothiazine). Compound **1** can be viewed as an integrated light-harvesting antenna–reaction center species, in that the $\{Os\{(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2\}_3\}^{8+}$ subunit is an efficient antenna system, coupled to well-known electron donor subunits, the phenothiazine (PTZ) moieties. The absorption spectrum, redox behavior, and luminescence behavior (both at room temperature in fluid solution and at 77 K in rigid matrix) of **1** have been investigated and compared with the properties of the parent $[Os\{(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2\}_3]^{8+}$ complex (**2**). The absorption spectrum and redox behavior confirm that **1** behaves as a supramolecular, multicomponent species, in that each subunit (including the phenothiazine donor groups) is only slightly perturbed by the others. Analogously to what happens in the model complex **2**, the light absorbed by the peripheral Ru(II) chromophores is transferred to the Os(II) core: however, the luminescence of the Os(II) core is efficiently quenched in **1** via moderately exoergonic reductive electron transfer by the peripheral phenothiazine donors, in spite of the presence of the intermediate Ru(II) centers. The quenching process becomes inefficient at 77 K.

Keywords: Luminescence; Ru(II) polypyridine complexes; Os(II) polypyridine complexes; Energy transfer; Electron transfer

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* Corresponding authors.
E-mail addresses: silvio.quici@istm.cnr.it (S. Quici), campagna@unime.it (S. Campagna).

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1. Introduction

Metallodendrimers are extensively investigated for several reasons: one such reason is that they can behave as efficient artificial light-harvesting antenna systems [1]. Indeed, the dendritic structure allows one to build up multicomponent species having a large number of metal centers (i.e., chromophores, when suitable building blocks are selected) in relatively few synthetic steps. Moreover, substantial control of the topography of the final assembly can be obtained, and this can translate into control of the functional assembly in terms of space, energy, and time, so fitting several prerequisites for synthetic antennae [2].

Taking advantage of the above-described circumstances, we [3] and others [4] prepared several dendrimers based on Ru(II) and Os(II) polypyridine complexes and exploited the energy transfer processes occurring in these systems [5].

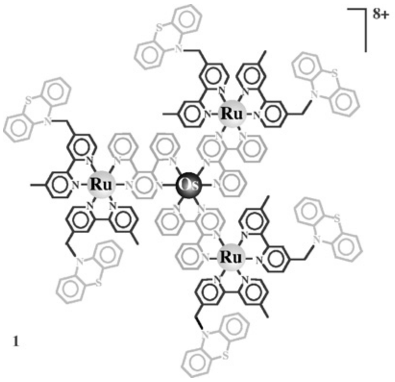
In recent times, research on artificial photosynthesis has evolved towards the investigation of antenna–reaction centers integrated systems, in which light-harvesting antenna species are coupled with electron donor or acceptor subunits [6–8]. In the present paper we briefly discuss recent developments in the area of integrated antenna–charge separation systems (and related species) and report the preparation and the absorption spectrum, redox behavior, and luminescence properties of a new coupled antenna–reaction center species **1**, namely a tetranuclear mixed-metal dendrimer containing an $\{Os(\mu\text{-}2,3\text{-dpp})_3\}^{2+}$ chromophore as the core and three $\{(\mu\text{-}2,3\text{-dpp})Ru(bpy\text{-}PTZ)_2\}^{2+}$ polypyridine building blocks as peripheral subunits (2,3-dpp = 2,3-bis(2′-pyridyl)pyrazine; bpy-PTZ = 10-(2,2′-bipyridin-4-yl)methyl)phenothiazine). Such a species contains six phenothiazine (PTZ) donor groups which are potential quenchers via reductive electron transfer of the metal-to-ligand charge transfer (MLCT) emission of the Os-based core. Comparison of the properties of the title compound with those of the model compound $[Os\{(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2\}_3]^{8+}$ (**2**) [9], that is the antenna subunit, is also made. The structural formulae of **1** and **2** are shown in Fig. 1.

2. Integrated artificial light-harvesting antenna/charge separation systems and related species

One of the most important natural process – from which life of Earth is derived – is photosynthesis. This process is based on several *actions* performed by various pigments, highly organized in a, hierarchical supramolecular fashion [10]. Such actions are: (i) absorption of solar light and its delivery to a specific subunit; (ii) photo-induced charge separation; (iii) multielectron and/or hole collection; (iv) production of high-energy content chemical species (fuels) by the use of the chemical energy stored by charge separation. Actions (i)–(iv) occur sequentially, and the resulting *function* is photochemical conversion of solar energy into chemical energy. The corresponding systems operating (i)–(iv) are: light-harvesting antennae, reaction centers for charge separation, charge pool species, and multielectron transfer catalysts. Research on *artificial* antennae [2,11] and reaction centers [12] is well developed, although there is still a large space and an effective need for significant improvements, while only a few examples of efficient photo-induced multicharge collection systems [13] are known, and even less developed is the field of photo-induced multielectron transfer catalysts [14]. However, to achieve an effective artificial photosynthesis, all the above-mentioned systems must work together, so integrated multicomponent species are needed.

One of the first examples of integrated systems was the trinuclear species $[\{(bpy)_2Ru(\mu\text{-BL})\}_2IrCl_2]^{5+}$ (bpy = 2,2′-bipyridine), reported by Brewer and coworkers [13a]. This species employed π systems of polyazine bridging ligands (BL) to collect electrons and coupled two Ru(II) chromophores (devoted to collect visible light, that is the antenna part) to an Ir(III) core, a potential reaction center (see Chart 1, compound **A**). The two Ru(II) light absorbers were electronically isolated and could each undergo MLCT to the bridging ligands. The complex had the capacity to photochemically collect multiple electrons on the π systems of BLs bound to a central metal, and therefore is better regarded as an integrated antenna–reaction center–charge pool system. The ability of Ir(III) to undergo a two-electron reduction process (the Ir(III)/Ir(I) process) via chloride loss and change of conformation was proposed to possibly play a role in the electron collection mechanism.

A noticeable series of integrated antenna–reaction center systems have been developed in collaboration by the teams of Gust, the Moores, and Lindsey [6,8b,15]. This pool of researchers employed multiporphyrin dendritic systems in connection with fullerene moieties (for an example, see Chart 1, **B**). The multiporphyrin assemblies played the role of the



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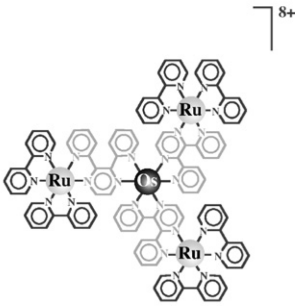

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Fig. 1. Structural formulae of the new species **1** and of the model compound **2**.

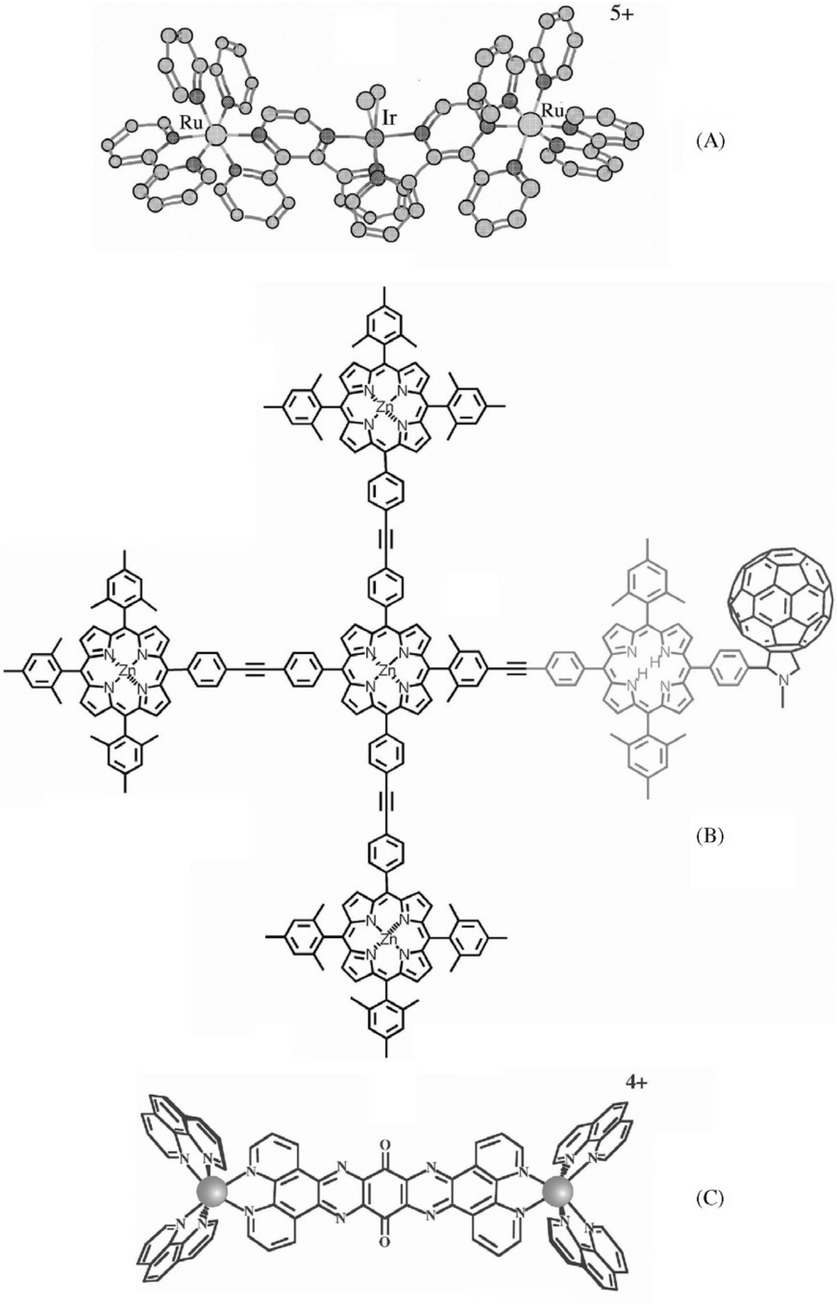
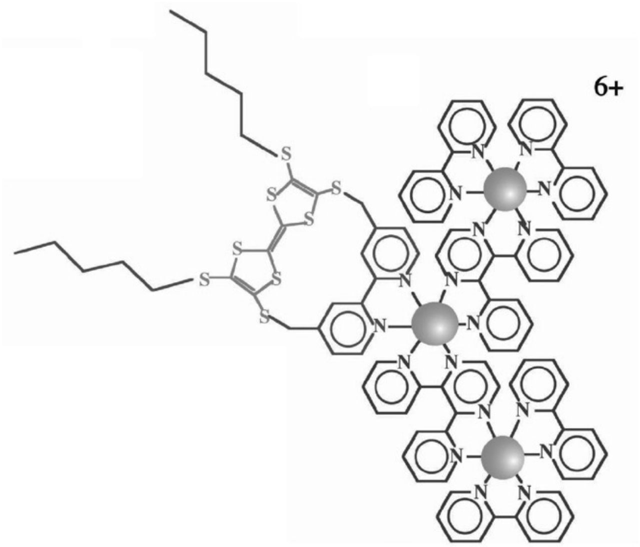


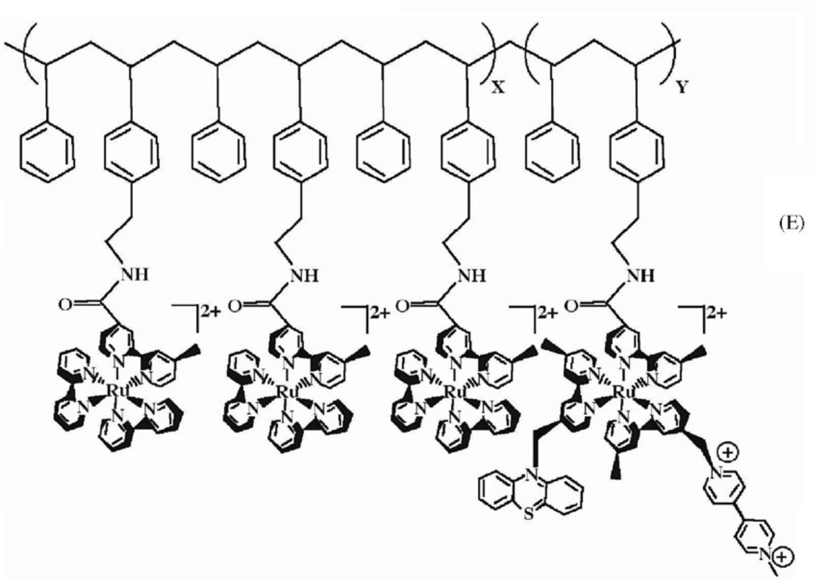
Chart 1.

antenna, and the fullerene moieties acted as the acceptor of the photo-induced electron transfer process. The lowest-energy porphyrin (usually, a free-base porphyrin) of the multiporphyrin dendritic systems had the role of the energy trap of the assemblies and of the excited donor of the electron transfer process, analogously to the “special pair” of a natural photosynthetic apparatus.

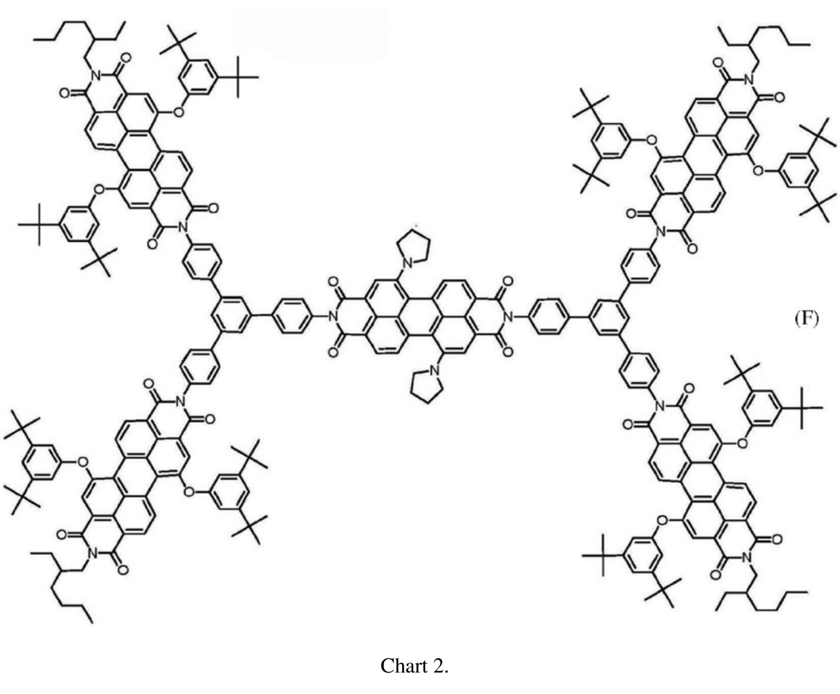
Integrated antenna–charge pool systems based on dinuclear Ru(II) complexes were also reported [13c,16]. These species contained bridging ligands – schematically, a phenanthroline-pyrazinebenzenepyrazine-phenanthroline (called tatpp) and a phenanthroline-pyrazine-quinone-pyrazine-phenanthroline (tatpq) ligand – having in their molecular frame easily reduced sites (for an example, see Chart 1, **C**). Such a circumstance allowed the dinuclear Ru(II) species to collect two or four electrons photochemically, by taking advantage of the low energy acceptor orbitals localized on the BL. The mechanism was optical excitation of the MLCT state in which the acceptor orbital was a phen-type (phen = 1,10-phenanthroline) orbital of the BL, followed by energy transfer to a lower-lying excited state located on the central moiety of the BL, largely uncoupled with the metal centers. Photolysis (in the presence of a sacrificial agent and in de-oxygenated solution) of $[(phen)_2Ru(tatpq)Ru(phen)_2]^{4+}$, one of the species studied, led to four electrons (and four protons, generated by the sacrificial agent) stored in the central moiety of the bridge. In the studied



(D)



(E)



(F)

Chart 2.

systems, the two peripheral Ru(phen)$_3$-type components acted as light harvesting antenna subunits and the BL as multielectron collectors.

The coupling between Ru(II) chemistry and dendrimers led to the preparation of a dendron-type, trinuclear Ru(II) species bearing an electron donor group made of a tetrathiafulvalene-substituted species [7]. Quite interestingly, in this species (Chart 2, compound **D**) charge separation takes place in spite of the fact that the electron donor group is not directly connected to the energy trap subunit of the trichromophoric antenna system. Most likely, it is the non-negligible coupling among the metal chromophores which allows for long-distance electron transfer. Unfortunately, charge recombination is quite fast and the charge separated state does not accumulate.

Integrated antenna–reaction center systems relatively different from all the examples mentioned above, have been prepared by Meyer and coworkers [8a,17]. In these cases, a soluble polymer backbone is used as the scaffold, to which a large number of Ru(II) polypyridine complexes are linked to play the role of the light-harvesting units. Anthraquinone and phenothiazine polymer-linked subunits are used as electron acceptor and donor groups (both are good electron transfer quenchers of the Ru-based chromophores), respectively. Excitation energy migrates among the various Ru(II) chromophores to reach a metal-based subunit close to the electron transfer quenchers. Charge separation is then obtained. Various modifications of this basic molecular design were also reported [17], including systems in which the anthraquinone and phenothiazine subunits are directly linked to a polymer-appended Ru(II) chromophore (for an example, see Chart 2, **E**).

An intriguing system integrating antenna and charge separation functions has been reported by Wasielewski and coworkers [18]. The light-harvesting antenna structure was here represented by perylenediimmide chromophores (see Chart 2, **F**), whose self-assembly to elicit a reaction center subunit (by symmetry breaking occurring in the assembled system) is capable to carry out charge separation.

Whereas the basic concepts powering the integrated systems are common, it is clear from the above examples that the design approaches can be quite various [19]. In the following sections of this paper we extend the combination of dendrimer chemistry and Ru(II) polypyridine complexes by developing a new integrated light-harvesting antenna/charge separation molecular device, with the aim of contributing to the design of efficient integrated multicomponent, supramolecular systems for photochemical solar energy conversion processes.

3. The title species: results and discussion

Compound **1** has been synthesized by using the "complexes as ligands/complexes as metals" synthetic strategy [20]. The "complex metal" precursor Ru(bpy-PTZ)$_2$Cl$_2$ was prepared by classical methods [21] from RuCl$_3$ (a commercial reagent) and bpy-PTZ [22], and then reacted with the "complex ligand" Os(2,3-dpp)$_3^{2+}$ [9] species. Such a reaction gave **1** in good yield, after chromatographic purification (see Section 4).

Table 1
Redox data of the complexes, in deaerated acetonitrile

Compound	Oxidations	Reduction
1	+0.82 [6]; +1.34; +1.73 [3]	−0.57; −0.68; −0.78
2	+1.25; +1.55 [3]	−0.55; −0.65; − 0.77

$E_{1/2}$ values vs. SCE are reported; the number in brackets refers to the number of exchanged electrons. All the processes are reversible.

3.1. Redox behavior

3.1.1. Oxidation

The oxidation pattern of **1** shows three reversible processes (see Table 1; Fig. 2). On the basis of the oxidation processes of the model species **2** (Table 1), a detailed assignment can be made. The one occurring at less positive potentials (+0.82 V versus SCE), not shown by **1** but occurring at a potential close to that assigned to phenothiazine oxidation in other PTZ-containing species [23], can be straightforwardly attributed to the one-electron oxidation of the six phenothiazine moieties. The second and third processes (Table 1) are assigned to the oxidation of the Os(II) core and to the one-electron oxidation of the three Ru(II) subunits, respectively. The metal-centered oxidation processes take place at potentials more positive than the corresponding processes of **2**, most likely as a consequence of interaction with the already oxidized PTZ subunits. In agreement with such an attribution, the Ru(II)-centered oxidations are more displaced to positive values than the Os(II)-centered oxidation on passing from **1** to **2** (ΔV between the corresponding processes of **2** and **1** is 180 mV for the Ru(II) centers and 90 mV for the Os(II) ones, see Table 1), reflecting the distance between the redox-active phenothiazine and metal-centered sites.

3.1.2. Reduction

The reduction pattern of **1** is very close to that of the model species **2** (Table 1): it is characterized by three partially overlapping one-electron reversible processes, assigned to the first reduction of each of the three dpp bridging ligands. At potentials more negative than −0.80 V, the second reduction steps of

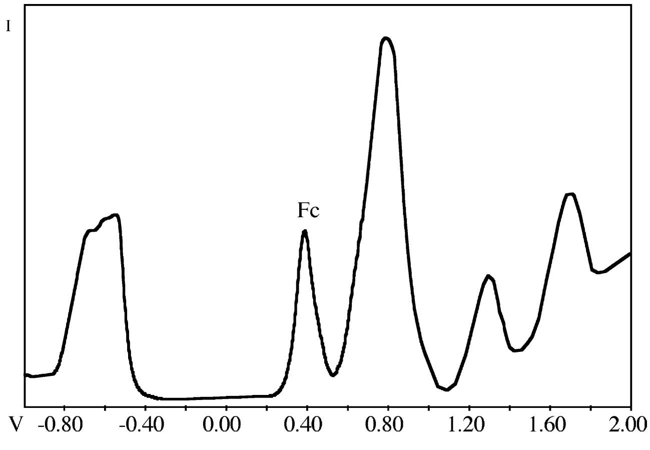


Fig. 2. Differential pulse voltammogram of **1** in acetonitrile.

Table 2
Spectroscopic and luminescence data of **1** and model complex **2** in deaerated acetonitrile fluid solution (298 K) or butyronitrile matrix (77 K)

Compound	Absorption, 298 K		Luminescence, 298 K		Luminescence, 77 K	
	λ_{max} (nm)	ε (M−1 cm−1)	λ_{max} (nm)	τ (ns)	λ_{max} (nm)	τ (ns)
1	290 442 550	181000 40000 40500	–	–	802	440
2	428 549	27000 40000	875	18	802	410

each bridging ligand are expected, as well as the reduction of the peripheral bpy ligands, on the basis of the properties of similar complexes [20b,24,25]: in fact, **1** exhibits other reduction processes, but they cannot be discussed in detail owing to absorption of the species at the electrode.

3.2. Absorption spectrum

The absorption spectrum of **1** (Table 2; Fig. 3) is roughly similar to that of the model species **2**: in particular, the absorption band at about 285 nm is assigned to spin-allowed π–π* transitions (ligand-centered, LC) involving the bpy ligands, and the broad absorption between 300 and 360 nm is assigned to spin-allowed π–π* transitions involving the dpp bridging ligands. In the visible region, the absorption peaking at about 440 nm of **1** can be mainly attributed to the spin-allowed Ru → bpy-PTZ charge-transfer (CT) transition and the broad band peaking at 550 nm is assigned to the spin-allowed Ru → μ-dppe Os → μ-dpp CT transitions, with the Os(II)-based transitions occurring at lower energy. Finally, the absorption tail at wavelength longer than 600 nm receives contribution from spin-forbidden CT transitions [26].

However, in the visible region some interesting differences between the absorption spectra of **1** and **2** clearly emerge: in fact, the region between 400 and 500 nm is quite different for **1** and **2** (Table 2; Fig. 3)—a larger absorption is found for **1** compared to **2**. To further highlight the differences in absorption spectra, the spin-allowed Ru → bpy CT transition of **2** maximizes at 428 nm and, owing to the presence of the electron donor phenothiazine substituent(s) on the bpy peripheral ligands of **1**, one could expect that such a band maximum was possibly blue-shifted in **1**, not red-shifted as experimentally found. The experimental observations therefore suggest that another transition takes place in **1** and contributes to the 400–500 nm absorption features. Such a transition cannot be a π–π* or an n–π* transition centered in the PTZ subunit(s), since these transitions occur in the UV region [23,27]. A possible explanation appears to be a charge-transfer transition involving the PTZ group as the donor and some subunit of the antenna component as the acceptor. The first candidate would be a PTZ-to-bpy CT transition: however, such a transition should be common to the large number of Ru(II)–polypyridine complexes containing bpy-PTZ or similar ligands [23], but it has never been reported. However, since **1** contains several bpy-PTZ ligands, the absorbance of the PTZ-to-bpy CT band could become significant, so the fact that such a transition has never been mentioned in previously studied systems cannot exclude that it is relevant here. It could also be possible that the absorption feature in the 400–500 nm region of **1** is due to a PTZ-to-(μ-dpp) CT transition. A similar transition, leading to a quite strong absorption in the same spectral region, has been reported for the closely related compound $[\mathrm{Os}\{(\mu\text{-}2,3\text{-dpp})\mathrm{Ru}(\text{bpy-pyrene})_2\}_3]^{8+}$ (**3**, bpy-pyrene = 4-(methyl)-4′-[2-(1-pyrenyl)ethyl]-2,2′-bipyridine; see Fig. 4) [28]. In this latter species, a pyrene-to-(μ-dpp) CT band substantially dominates the 400–550 nm region (for **3**, ε at 440 nm is close to 85,000 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ and considering the absorption of the model

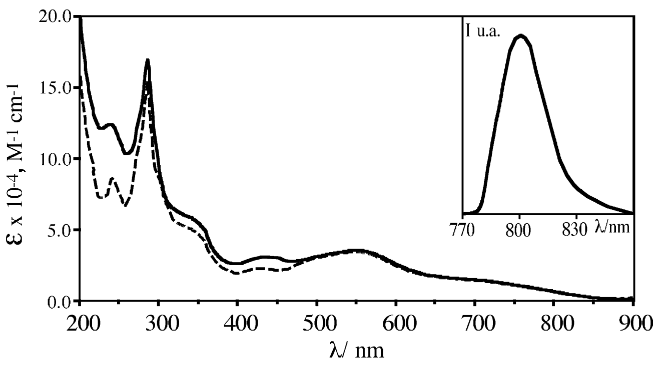


Fig. 3. Absorption spectra of **1** (solid line) and **2** (dashed line) in acetonitrile at room temperature. Inset: emission spectrum of **1** in butyronitrile rigid matrix at 77 K.

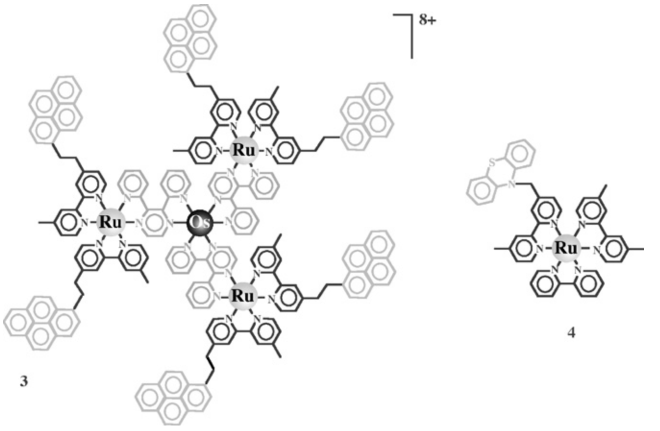


Fig. 4. Structural formulae of compounds **3** and **4**, used for the discussion.

species **2** at the same wavelength, most of such a huge molar absorption was attributed to the pyrene-to-(μ-dpp) CT band). In **3** the ethylene chains connecting bpy and pyrenyl subunits are flexible enough to allow proximity and therefore direct strong interactions between the pyrenyl subunits and μ-2,3-dpp bridges, whereas this seems to be more difficult for PTZ in **1**, due to the shorter methyl connector. Moreover, because of the different donor abilities of pyrene [29] and PTZ groups, the PTZ-to-(μ-dpp) CT band should lie to substantially lower energies. This also agrees with the energy level of the calculated product of the electron transfer quenching of the excited Os(II)-core chromophore, which would be such a PTZ-to-(μ-dpp) CT state (see later). In conclusion, we propose that the increased absorption feature in the 400–500 nm region of **1** compared to **2** is due to the occurring of sizeable PTZ-to-bpy CT transitions.

Taken together, redox data and electronic absorption spectroscopy indicate that **1** is an effective supermolecule, in that the individual subunits keep their own properties (redox potentials, absorption bands) in the multicomponent array.

3.3. Luminescence properties and excited state decays

To discuss the excited-state properties of a multicomponent species like **1**, it is convenient to recall the properties of the isolated components, the light-harvesting antenna component $\{Os\{(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2\}_3\}^{8+}$ (which corresponds to the model species **2**, in its turn a multicomponent system), and the donor PTZ group(s).

Complex **2** is the most intensively investigated species, from the photophysical viewpoint, of the large family of dpp-bridged polynuclear Ru(II) and Os(II) complexes [1a,3a–c,9,20,24–26]. In this compound, all the light energy collected by the various chromophores is quantitatively channeled to the Os(II) core, which emits from its lowest-lying excited state, namely a ^{3}MLCT level [1a,9,26]. The very high efficiency of the energy transfer from Ru(II)-based CT levels to the Os(II)-based CT levels is due to a significant electronic interaction between the subunits. Indeed, in this species excitation of the singlet Ru-to-bridge CT manifold leads to population of the Os-to-bridge CT states (singlet–singlet energy transfer) with a lifetime of 60 fs, comparable or faster than intersystem crossing within the Ru(II) subunit(s) [26]. Ultrafast triplet–triplet energy transfer also takes place, with a lifetime of 600 fs [26]. The triplet Os → μ-dpp CT state, the final excited state of the decay processes from the upper-lying excited states of **2**, then emits with a relatively long lifetime (Table 2). Given the extremely high rate constants of the energy transfer processes, any other dissipation energy decay route within the Ru(II) chromophores is negligible.

The PTZ group is a very good electron donor subunit, and has frequently been used in metal polypyridine complexes to obtain photo-induced charge separation [23]. Relatively high rate constants for reductive electron transfer quenching of MLCT states of polypyridine metal complexes have been calculated [23], but in all the cases never faster than 10^{12} s^{-1}, which is slower (see above) than the *slowest* (triplet–triplet) energy transfer rate from the peripheral Ru-based excited chromophores to the central Os-based excited core. Therefore, if photo-induced electron transfer can take place in **1**, it is assumed to involve the central Os(II) core.

The 77 K luminescence and redox data allow us to calculate the excited-state reduction potential $^*E_{\text{red}}$ of the Os(II) core of **1**, namely +0.98 V. Therefore, the driving force ΔG for the reductive photo-induced electron transfer from PTZ to the excited Os-based chromophore is −0.16 eV [30], so indicating that the quenching process is moderately exoergonic. On looking at the structural formula of **1** (Fig. 1), the donor and acceptor are separated by a $\{(\mu\text{-dpp})Ru(bpy)\}^{2+}$ moiety, which plays the role of the spacer. However, it has already been demonstrated that in such type of dendritic species high-energy spacers based on metal complexes allow for very fast electron transfer [7,31,32]. As a matter of fact, the emission of the Os(II) core is totally quenched in **1** at room temperature in fluid solution, so indicating that the photo-induced electron transfer is quite efficient and the rate constant of the process has to be $>5 \times 10^8$ s^{-1}, from the emission lifetime of **2**. When the driving force is taken into account, such a rate constant value compares well with the forward electron transfer from PTZ to an excited Ru(II) chromophore reported for the tris-heteroleptic mononuclear compound **4** (see Fig. 4) [23h]. For this latter species, for which the driving force is only 0.07 eV, the rate constant of the process is 2.5×10^7 s^{-1} [23h]. Obviously, the separation between donor and acceptor partners is much larger in **1**, but apparently this does not limit the rate of the electron transfer too much, so confirming the good tunnelling properties of high-energy metal-based components in metallodendrimers of this class. Fig. 5 depicts the proposed energy level scheme and decays and Fig. 6 shows the energy and electron transfer processes occurring in the title complex.

The Os(II) core emission is restored in **1** at 77 K in rigid matrix (Fig. 3, inset; Table 2). This further confirms our attribution of luminescence quenching at room temperature to photo-induced electron transfer, as moderately exoergonic electron transfer processes are usually inefficient at low temperature because of the presence of nuclear barriers [33].

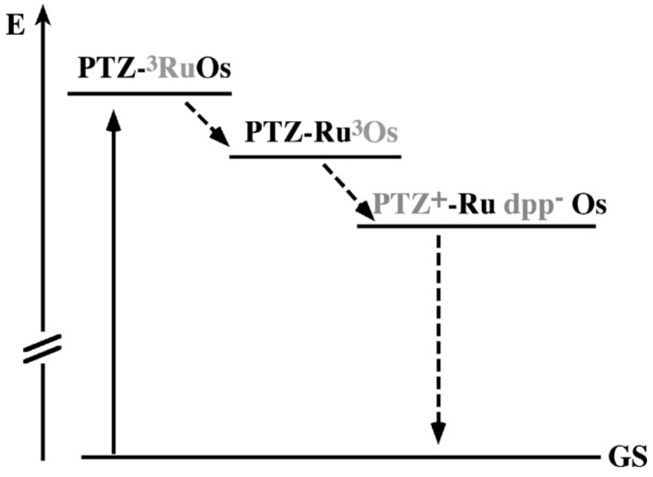


Fig. 5. Schematic energy level diagram and decays of **1**. Only the lowest-lying excited states are shown.

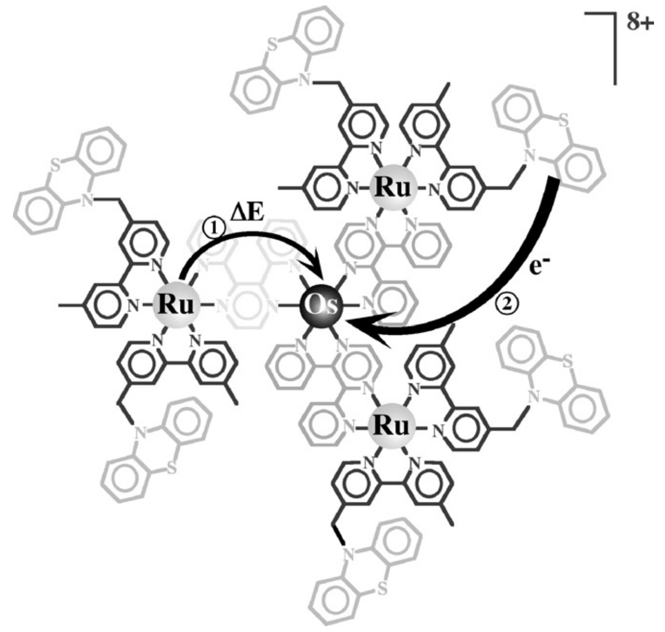


Fig. 6. Schematic representation of the photo-induced energy and electron transfer processes occurring in **1**. For details, see text.

4. Experimental

4.1. Synthesis

4.1.1. cis-[$Cl_2Ru(bpy\text{-}PTZ)_2$]

A solution of $RuCl_3 \cdot 3H_2O$ (100 mg, 0.382 mmol), bpy-PTZ [12] (291.47 mg, 0.764 mmol), and LiCl (32.40 mg, 0.764 mmol) in 3.5 ml of DMF was refluxed for 8 h. The solution cooled to room temperature was added to 15.0 ml of acetone and cooled at 0 °C for 12 h. The violet precipitate formed was isolated by filtration and washed several times with H_2O. The final product was a violet solid (yield: 65%).

4.1.2. [$Os\{(\mu\text{-}2,3\text{-}dpp)Ru(bpy\text{-}PTZ)_2\}_3](PF_6)_8$ (**1**)

A mixture of *cis*-[$Cl_2Ru(bpy\text{-}PTZ)_2$]$\cdot 2H_2O$ (117.81 mg, 0.126 mmol) and $AgNO_3$ (42.80 mg, 0.252 mmol) in 10 ml of ethanol was refluxed for 16 h. The solution was added slowly to a solution of [$Os(2,3\text{-}dpp)_3](PF_6)_2$ (50 mg, 0.042 mmol) in 5 ml of ethanol and refluxed for 2 days. The cooled solution was treated with an excess of solid NH_4PF_6, the violet precipitate formed was isolated by filtration and purified by column chromatography on neutral aluminium oxide (Ø: 2.5 cm; length: 20 cm; aluminium oxide activity: 1), eluting with a 3:1 (v/v) CH_3CN/toluene mixture. The second band obtained (violet) was rotary evaporated and the residue dissolved in a small amount of CH_3CN and precipitated by addition of diethyl ether. The final product was a violet solid (yield: 70%).

4.2. Equipment and procedures

Electrochemical measurements were carried out in argon-purged acetonitrile at room temperature with a PAR 273 multipurpose equipment interfaced to a PC. The working electrode was a glassy carbon (8 mm^2, Amel) electrode. The counter electrode was a Pt wire, and the reference electrode was an SCE separated with a fine glass frit. The concentration of the complexes was about 5×10^{-4} M. Tetrabutylammonium hexafluorophosphate was used as supporting electrolyte and its concentration was 0.05 M. Cyclic voltammograms were obtained at scan rates of 20, 50, 200, and 500 mV/s. For reversible processes, half-wave potentials (versus SCE) were calculated as the average of the cathodic and anodic peaks. The criteria for reversibility were the separation of 60 mV between cathodic and anodic peaks, the close to unity ratio of the intensities of the cathodic and anodic currents, and the constancy of the peak potential on changing scan rate. The number of exchanged electrons was measured with differential pulse voltammetry (DPV) experiments performed with a scan rate of 20 mV/s, a pulse height of 75 mV, and a duration of 40 ms, and by taking advantage of the presence of ferrocene used as the internal reference. Absorption spectra were recorded with a JASCO 560 spectrophotometer. Luminescence spectra were performed with a Spex-Jobin Yvon Fluoromax-2 spectrofluorimeter equipped with a Hamamatsu R3896 photomultiplier, and were corrected for photomultiplier response using a program purchased with the fluorimeter. Emission lifetimes were measured with an Edinburgh OB-900 single-photon counting spectrometer equipped with a Hamamatsu PLP-2 laser diode (pulse width at 408 nm, 59 ps).

Experimental uncertainties are as follows: absorption maxima, ±2 nm; molar absorption coefficient, 10%; emission maxima, ±5 nm; excited state lifetimes, 10%; redox potentials, ±10 mV.

5. Conclusion

An efficient light-harvesting synthetic antenna species made of a dendritic-shaped metal dendrimer has been appended with electron donor PTZ subunits. The so-obtained multicomponent compound **1** exhibits two key features of natural photosynthetic systems, that is the antenna effect and an efficient photo-induced electron transfer involving the energy trap of the antenna component. Extensive work is under progress in our laboratories to synthesize new systems of this type and to kinetically characterize the electron transfer processes by ultrafast spectroscopy.

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