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Recent advances in luminescent polymetallic dendrimers containing the 2,3-bis(2′-pyridyl)pyrazine bridging ligand

Sebastiano Campagna *, Cinzia Di Pietro, Frédérique Loiseau, Béatrice Maubert, Nathan McClenaghan, Rosalba Passalacqua, Fausto Puntoriero, Vittorio Ricevuto, Scolastica Serroni

Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina, via Sperone 31, 98166 Villaggio S. Agata, Messina, Italy

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Contents

Abstract

Some new developments in the area of metal-based light-harvesting dendrimers based on the 2,3-bis(2′-pyridyl)pyrazine bridging ligand are presented, with particular regard to unidirectional energy transfer, enhanced light absorption, coupling dendritic structures with electron donors, and measurement of some of the ultra-fast processes occurring in this class of compounds. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ruthenium complexes; Osmium complexes; Luminescence; Energy transfer; Dendrimers

1. Introduction

Modular polymetallic systems based on Ru(II) and Os(II) polypyridine subunits have attracted a high degree of interest due to the unique combination of spectroscopic, redox and excited-state properties inherent in the building blocks employed [1], which confer particular properties to the polynuclear arrays. The correct choice of building blocks instils predictable properties in the resulting architectures, in particular as far as the energy transfer processes within the supramolecular edifices are concerned [2]. These qualities, coupled with enhanced absorption on increasing nuclearity leads to light-harvesting capabilities. Predictability depends onthe energy levels of the units employed and the sequence of connectivity, along with redox considerations. Among polymetallic species, those having a dendrimer-type structure are particularly interesting, in that such a structure is well adapted to fulfil the requirements of an artificial light-harvesting antenna in certain instances [3,4]. With this in mind, many Ru(II)- and Os(II)-based dendrimers have been prepared and their redox and photophysical properties have been investigated [4–7].

Our group has largely contributed to this research area during the past decade. In collaboration with

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* Corresponding author. Tel.: +39-090-676-5737; fax: +39-090-393-756.
E-mail address: photochem@chem.unime.it (S. Campagna).

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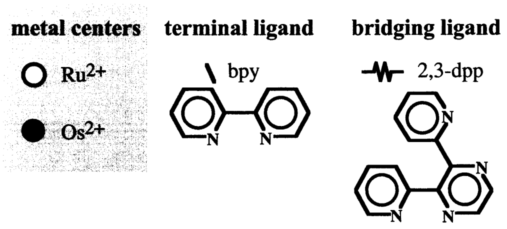

Fig. 1. Some of the components used in the polymetallic dendrimers discussed in this article with their designated symbols.

colleagues in Bologna and Pisa we have synthesised and studied a large class of luminescent and redox-active Ru(II) and Os(II) dendrimers, principally utilising 2,3-bis(2′-pyridyl)pyrazine (2,3-dpp) as the bridging ligand [6,8]. Previously we reported species of varying composition and nuclearity (with up to 22 metal centres in the larger examples, belonging to the third generation of such dendrimers [8c,8d]). Most of the components used in the construction of these dendrimers are shown in Fig. 1, whilst some examples of the species investigated are shown in Fig. 2.

However, the properties of some of the larger reported dendrimer species are not fully satisfactory: for example, in dendrimers of the second (and successive) generation, the use of only two types of metal centres, namely Ru(II) and Os(II), proved problematic (and for the moment impossible) in obtaining efficient periphery-to-centre energy transfer. The reasons for this behaviour have been discussed extensively [6] and can be summed up on considering that the lowest-lying excited state involving the intermediate chromophore(s) is at higher energy than the lowest-lying excited states of both the central and the peripheral chromophores. As a consequence, these intermediate chromophore(s) constitute a barrier to the periphery-to-centre energy transfer (for example in **1**, see Fig. 3).

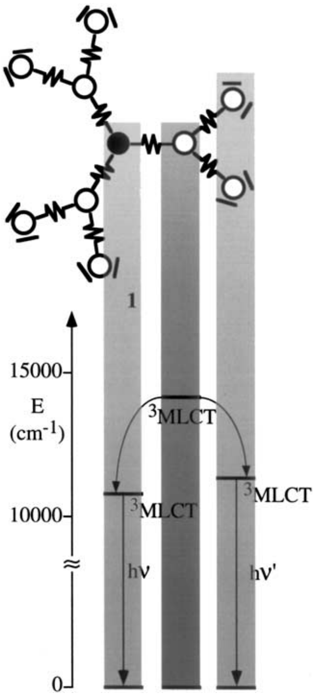

Fig. 3. Schematic representation of $OsRu_9$, **1**, with its energy-level diagram. The lowest energy levels of the various subunits are not in a cascade arrangement, and the absorbed energy is emitted from both the central and peripheral units [6].

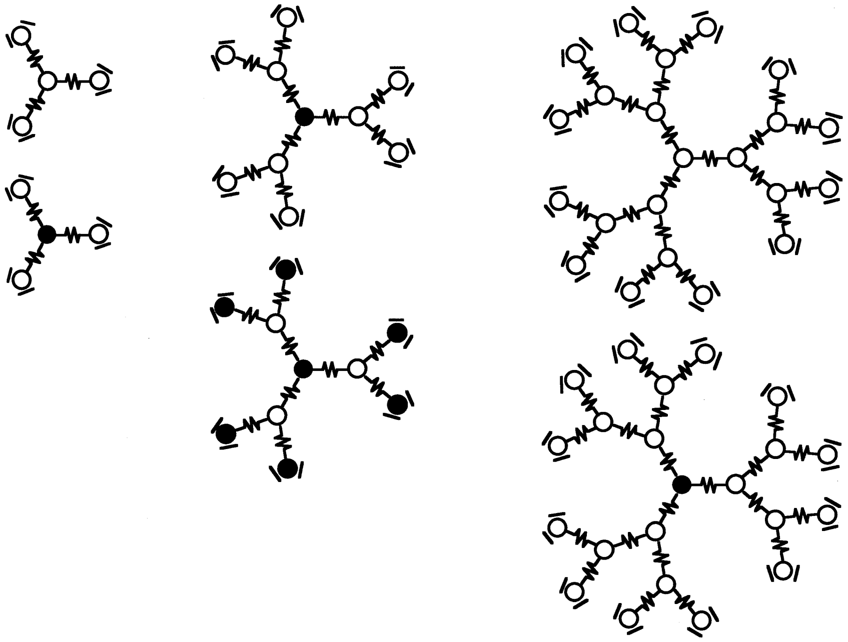

Fig. 2. Examples of homo- and heterometallic dendrimers, shown schematically. The symbols are explained in Fig. 1. Left to right—tetranuclear, decanuclear and docosanuclear species.

Here we report a synopsis of our recent progress in the study of this class of metal dendrimers.

2. Decanuclear metal dendrimers containing three different metal centres

As stated above and displayed in Fig. 3, by using Ru(II) and Os(II) centres alone we have been unable to obtain efficient periphery-to-centre energy transfer in larger species. Therefore, we decided to include different metal centres in the dpp-based dendrimers, besides Ru(II)- and Os(II)-based chomophores. Suitable alternative metal-containing subunits for introduction at the periphery have to be characterised by high-energy excited states. In this manner, we do not modify the energy of the inner chromophores, but rather we eliminate the option to direct the light energy absorbed by the intermediate chromophores towards the peripheral subunits and the energy is, therefore, necessarily directed towards the centre. To realise this idea we prepared the decanuclear compound **2**, [Os{(μ-2,3-dpp)Ru-[(μ-2,3-dpp)$PtCl_2$]$_2$}$_3$]$(PF_6)_8$ or $OsRu_3Pt_6$, in which the external layer of metal-subunits is constituted by $PtCl_2$ units, shown schematically in Fig. 4 [9]. The absorption spectrum in the visible region of **2** is dominated by the metal-to-ligand charge-transfer (MLCT) bands involving Ru(II) and Os(II) centres, with only a minor contribution from the Pt(II) subunits.

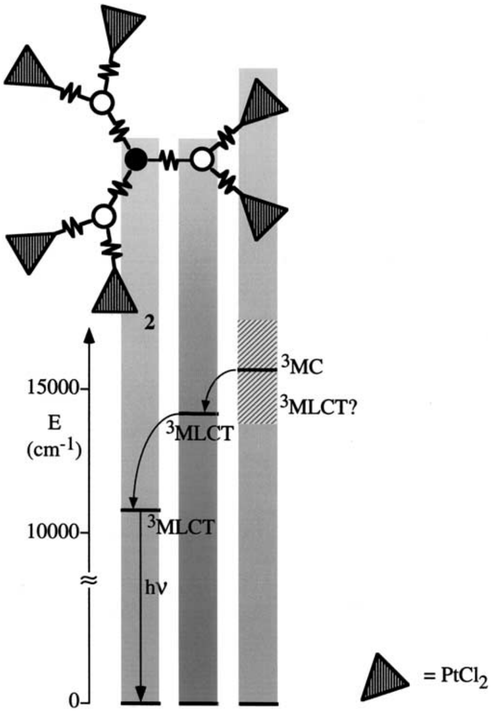

Fig. 4. Schematic representation of, $OsRu_3Pt_6$, **2**, where the appropriate energy gradient is present such that all the energy is channelled to the emissive central unit [9].

Table 1
Spectroscopic and photophysical data in deaerated CH_3CN

Compound	Absorption λ_{max} (nm) (ε, M^{-1} cm^{-1})	Luminescence 298 K		
		λ_{max} (nm)	τ (ns)	References
$OsRu_3$	549 (40 000)	875	18	8d
$OsRu_9$	550 (117 000)	780, 860 [a]	65	8d
$OsRu_3Pt_6$	520 (67 000)	875		[9]

For the absorption, the lowest-lying energy maxima are given.

[a] The higher energy maximum is due to the peripheral ruthenium chromophores, and the other one to the osmium core.

In this sense, the absorption properties of such a decanuclear compound (in principle, a second-generation dendrimer) are more reminiscent of a tetranuclear species (a first-generation dendrimer) than to those of Ru/Os dendrimers of the same generation (see Table 1). The pertinent states of $OsRu_3Pt_6$ follow the energy order of the lowest excited states of the units: [Os(μ-2,3-dpp)$_3$]$^{2+}$ < [(bpy)$_2$Ru(μ-2,3-dpp)]$^{2+}$ < [Ru(μ-2,3-dpp)$_3$]$^{2+}$ < [(μ-2,3-dpp)$PtCl_2$]$^{2+}$. The energy of the lowest excited state of the (μ-2,3-dpp)$PtCl_2$ could not be predicted with the same degree of confidence as the other metal centres, however, its position in the above series is apparently higher than that of [Ru(μ-2,3-dpp)$_3$]$^{2+}$. Indeed, the excitation of the intermediate, Ru-based, chromophores of the decanuclear $OsRu_3Pt_6$ compound leads to population of the Os core with quantitative efficiency, as demonstrated by excitation spectroscopy [9]. The matching between absorption and excitation spectra also indicates that even the light absorbed by the Pt(II) subunits contribute to the emission. Therefore, in the complex $OsRu_3Pt_6$, a clear antenna effect is observed, thus making this the first decanuclear species where all the energy absorbed is efficiently transferred to a single unit. The emitting state (formally triplet) MLCT involves Os^{2+} and the bridging ligand μ-2,3-dpp, with an emission maximum at 875 nm at room temperature (r.t.) in acetonitrile [9].

It should also be noted that the labile, terminal chloride ligands could be substituted in order to introduce additional functionalities at the periphery, or perhaps to anchor this species onto a surface.

3. Light-harvesting metal dendrimers appended with organic chromophores

Another approach to obtain unidirectional periphery-to-core energy transfer, whilst introducing larger number of chromophores relies upon the modification of the peripheral ligands employed. Replacing 2,2′-bipyridine with a substituted bipyridine such as those shown in Fig. 5, allows the introduction of a large number of

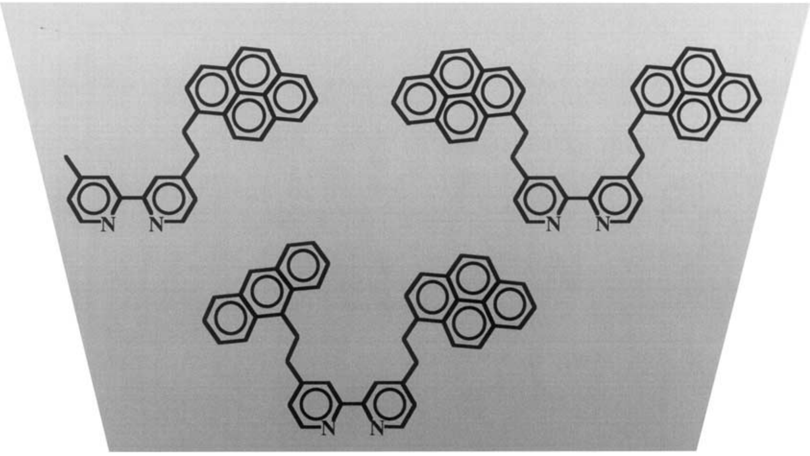

Fig. 5. Bi- and trichromophoric ligands, which can be introduced as terminal ligands in metal dendrimers.

chromophores (for example, pyrenyl subunits) at the periphery of metal containing dendrimers; yet significantly in fewer synthetic steps. On this basis, we prepared a tetranuclear mixed-metal dendrimeric complex bearing six pyrenyl chromophores at the periphery (**4**, Fig. 6) [10]. This species represents the first example of a new class of metal dendrimers. In fact, most of the metal dendrimers reported so far belong to two general classes: (i) species in which the metal-based chromophores are present in all positions of the dendrimeric array [3,5,6,8] and (ii) species in which a single metal-based chromophore is located at the core of the dendrimer, surrounded by purely organic wedges bearing chromophores at the periphery (Fig. 7) [3,5,11]. Compound **4** couples some properties of the two types of dendrimers, (i) and (ii), discussed above. The four metal-based subunits constitute a (i)-type dendrimer, and the six appended pyrenyl chromophores resemble the peripheral subunits of (ii)-type dendrimers. Therefore, it can be considered a (iii)-type light-harvesting metal-containing dendrimeric species as the rigid polynuclear skeleton is combined with an additional shell of organic chromophores, appended using flexible linkages, which serve as energy donors. As in the case of the parent heterometallic tetranuclear species, **3**, energy is funnelled to the emissive core. As anticipated, the emission spectrum of **4** (Fig. 8) closely matches that of the parent tetranuclear species **3**, suggesting that the origin of the emission is the same i.e. involving the triplet Os → μ-2,3-dpp CT excited state [10]. Excitation spectroscopy once more confirms quantitative energy transfer, regardless to the excited state initially populated by light excitation.

The absorption spectrum of **4** (Fig. 9) warrants some additional comment. At wavelengths longer than 550 nm, the Os and Ru MLCT bands dominate the spectrum and in the UV region the typical pyrene-centered bands [12] are evidenced. However, an additional, broad absorption band is present at around 450 nm, which cannot be assigned to specific individual

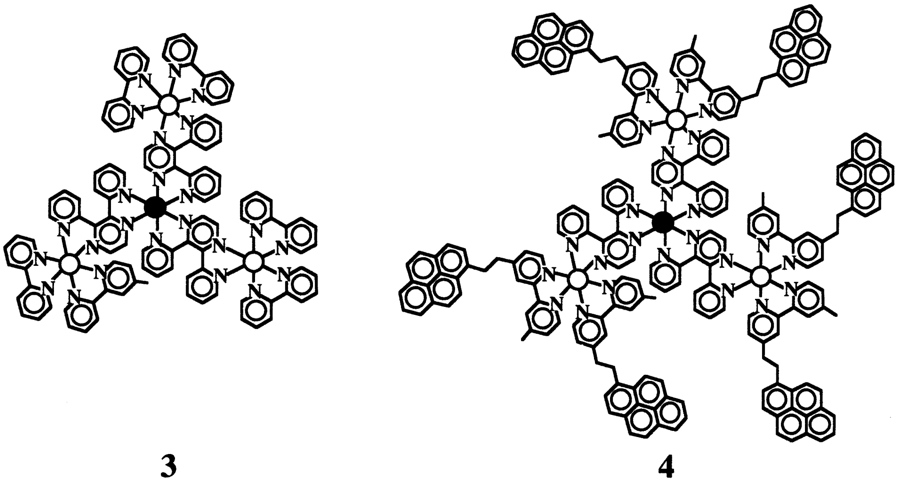

Fig. 6. Parent heterometallic tetranuclear antenna system, **3**, and corresponding tetranuclear species bearing an extra sphere of pyrenyl chromophores, **4** [10]. It should be considered that compound **4** exists as a mixture of isomers (geometrical and optical ones). The drawing represents only one isomer.

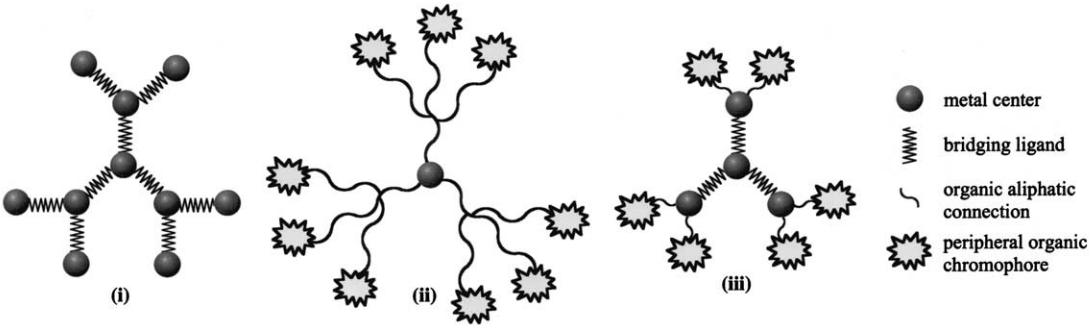

Fig. 7. Representations of two commonly studied class of metal-containing dendrimer, (i) and (ii); along with that represented by **4**, a (iii)-type dendrimer. Type-(i) species contain metal-ions in all positions of the polynuclear array; type-(ii) dendrimers comprise a metal centre with numerous peripheral organic chromophores, while type-(iii) species consist of a polynuclear architecture appended with organic chromophores.

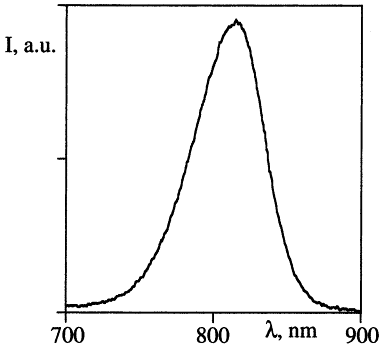

Fig. 8. Emission spectrum of **4** in acetonitrile fluid solution at r.t. The spectrum shown is uncorrected for photomultiplier response.

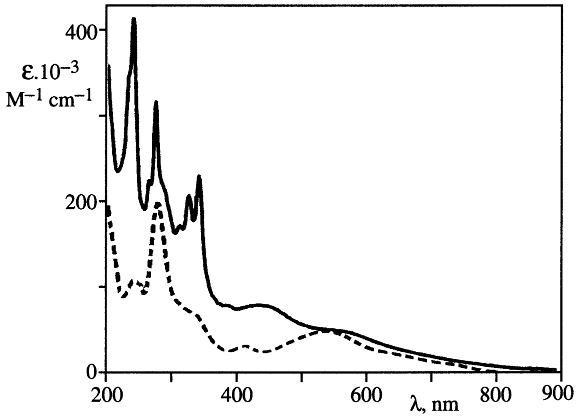

Fig. 9. Electronic absorption spectra of **3** (dashed line) and **4** (solid line) in acetonitrile at r.t. [10].

components. This band has been tentatively assigned to CT transitions between the electron-donating pyrenyl moieties and the easily reducible 2,3-dpp bridging ligands [10]. Indeed, similar transitions can be relatively high in intensity: for example, CT transitions in [3,3] paracyclophane–quinhydrones lead to molar absorbance values between 10^3 and 10^4 M^{-1} cm^{-1} depending on solvent polarity [13]. Significant charge transfer transitions corresponding to interactions between pyrenyl subunits and polypyridine ligands co-ordinated to Pt(II) have also been recently reported [14]. This somewhat unexpected result is very interesting: the light-harvesting properties of **4** compared with **3** are improved much more than initially foreseen by incorporating the additional peripheral chromophores. This is due to the coming into play of visible absorption bands which arise from new intercomponent (supramolecular) CT transitions, besides the UV pyrene-centered absorption bands. Such transitions may be subject to variation in energy depending on the solvent used, and may lead to tunable absorption properties. The correct choice of spacer(s) should also prove important, and one may draw on a vast range of organic linkages to govern flexibility, and other factors. This approach of appending additional chromophores through inert spacers should prove general and similarly other chromophores with the desired absorption properties (i.e. region of absorption and high molar extinction coefficients) could be similarly introduced.

4. Coupling light-harvesting antennae with reaction centres

Artificial systems designed to convert solar energy into chemical energy can follow the guidelines set by Nature, where photosynthetic processes rely upon co-operation of several components [15]. This is exemplified by the recent structural determination of photosystem I (from bacterium *Synechoccus Elongatus*) which is found to be of extreme complexity, consisting of 12 protein subunits and 127 co-factors comprising 96 chlorophylls, two phylloquinones, three iron-based clusters, 22 carotenoids, four lipids, one Ca^{2+} ion and 206 water molecules [16]. Of course, it is not possible to assemble such complicated arrays synthetically. Therefore, attempts to mimic natural photosynthetic processes rely upon emulating some of the key features and processes occurring, including light-harvesting antenna effects (discussed above), and reaction centres designed to afford a long-lived charge separated state.

In the former sections of this review the emphasis was placed upon increased absorption and unidirectional energy transfer, in other words additions to the family of light-harvesting antenna systems. In this section the focus is directed at coupling an inorganic polynuclear architecture with a covalently linked electron donor. Although much effort has been made to prepare artificial antenna systems [4] and charge-separation molecular devices [17], reports of coupled light-harvesting antenna/reaction centre species are rare [18]. As a first step in this direction, in collaboration with colleagues in Odense and Amsterdam, we prepared two multicomponent compounds in which an electron donor was coupled with a small trinuclear, dendron-like antenna system of the 2,3-dpp family [19]. The $[\{(bpy)_2Ru(\mu\text{-}2,3\text{-dpp})\}_2Ru(bpy)]^{6+}$ wedge can be considered as a small antenna, since it is a multichromophoric species in which fast energy transfer processes take place within the components. The electron donor employed was the much studied tetrathiofulvalene (TTF) subunit, which offers high stability and favourable redox properties [20]. The new species investigated, $[\{(bpy)_2Ru(\mu\text{-}2,3\text{-dpp})\}_2Ru(bpy\text{-}TTF_1)](PF_6)_6$ (**6**); and $[\{(bpy)_2Ru(\mu\text{-}2,3\text{-dpp})\}_2Ru(bpy\text{-}TTF_2)](PF_6)_6$ (**7**), are shown in Fig. 10, along with the parent species, **5**, which is structurally similar, but lacking the extra electron donor unit. Interaction between redox-active sites is found to be weak from an electrochemical viewpoint, on the basis of minimal modification of redox-potentials of the various subunits when compared with model compounds [19].

Whilst the parent polymetallic compound is luminescent, with emission arising from the deexcitation of a triplet Ru → μ-2,3-dpp CT state (emission maximum at 802 nm), involving one of the two peripheral Ru ions, no emission was observed from the TTF-containing trinuclear complexes at r.t. This is conducive with a photoinduced electron transfer pathway, with an electron being transferred from the TTF moiety to the excited Ru-based luminophore (Fig. 11). The driving force for such a process was estimated as −0.4 eV, showing that reductive quenching in the trinuclear complex is a thermodynamically favourable process [19].

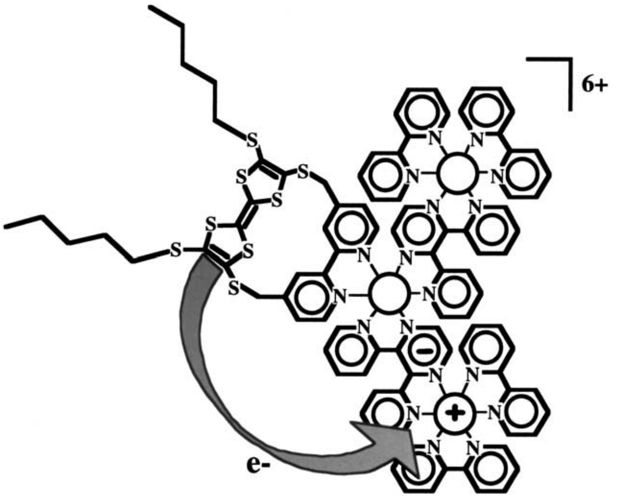

Fig. 11. Long-range photoinduced electron transfer, in **6**, from TTF to a non-adjacent (nominally Ru(III)) metal centre in a trinuclear antenna [19].

Transient absorption spectroscopy afforded a means to study this process further, and a rate constant of $3 \times 10^9\ s^{-1}$ was determined with **6**, a typical value for this type of exergonic, long-range electron transfer process. No evidence of the TTF radical was observed, suggesting that the back electron transfer process was perhaps even faster than the forward electron transfer process. At 77 K in a butyronitrile matrix, luminescence similar to that of the parent complexes was observed with an

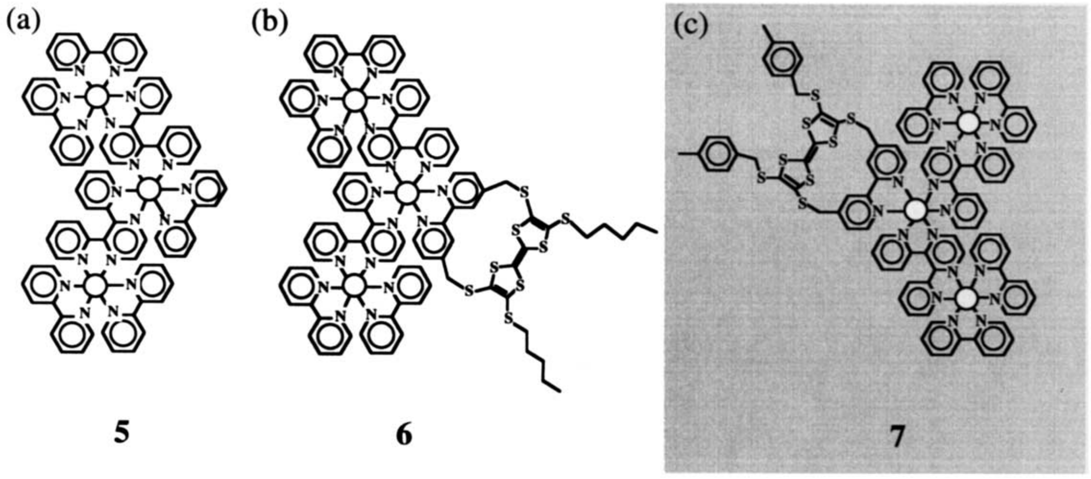

Fig. 10. (a) Luminescent model trinuclear antenna system, **5**; (b) Antenna system decorated with TTF_1, **6**; (c) Antenna system decorated with TTF_2, **7**. Room temperature luminescence is quenched in **6** and **7** by a photoinduced electron transfer pathway [19].

emission maximum at 710 nm. This is unsurprising as electron transfer can be significantly slowed down in a rigid matrix at this low temperature, due to the presence of significant nuclear barriers and destabilisation of the charge-separated states under these conditions.

The results obtained for novel compounds **6** and **7** are interesting from different view points: (i) the quencher subunit is connected to a metal which is not involved in the MLCT state subject to reductive quenching; (ii) the coupling of a trinuclear antenna compound with the electron donors TTF_1 and TTF_2, together with the efficiency of the electron transfer quenching of the trinuclear complex emission by TTF moieties, afforded the first functional antenna-reaction centre system involving metal complexes and one of the first systems of this type in general [21]. It is interesting to note that, for **6** and **7**, the luminescence of the entire array is totally quenched even though the redox-active quencher is not directly connected to the lowest-energy chromophore of the antenna. This observation could be important for the future design of functional antenna-reaction centre assemblies, as this suggests that, at least in some cases, it is not strictly necessary to directly connect the charge-separation subunit to the antenna energy trap.

5. Ultrafast energy transfer in 2,3-dpp bridged dinuclear complexes

In all the luminescent metal dendrimers based on the 2,3-dpp bridging ligands that we have studied so far, the occurrence of photoinduced energy transfer has been essentially based on steady-state measurements, mostly utilising excitation and emission spectroscopy [6]. No indication of rates of the energy transfer processes has been obtained, even using picosecond time-resolved emission spectroscopy. In fact, even within this timescale, the energy transfer processes seem to have already occurred and the emission spectrum of each dendrimer recorded after a few picoseconds is coincident with the steady-state emission spectrum. Information obtained on the rate of these energy transfer processes should prove important both from a fundamental viewpoint and for future design of larger species. For example, the determination of the exact rate of energy transfer between neighbouring metal centres is of prime importance for the overall efficiency of a multistep transfer process in antennae and other photonic devices.

To gain insights into the excited state ultrafast dynamics of the Ru(II) and Os(II) polynuclear compounds of the 2,3-dpp family, we recently studied a series of dinuclear complexes with femtosecond pump-probe spectroscopy, in collaboration with the group of Leif Hammarström in Uppsala [22]. Some of the compounds examined are shown in Fig. 12. However, even by using polarised excitation pulses, we were only able to determine that the Ru-to-Os energy transfer rates in the dinuclear mixed-metal system shown in Fig. 12 (and therefore, probably between neighbouring metal-based chromophores in larger species based on the same subunits) is faster than the resolution available to us, which was 200 fs. Therefore, the problem of the determination of the exact energy transfer rate in mixed-chromophore species of this class of polynuclear compounds remains unsolved. In any case, our results gave us a number of pieces of information. Firstly, the timescale of energy transfer in these complexes is comparable to that of the thermalisation of MLCT excited states in Ru(II) and Os(II) polypyridine complexes (which can include singlet–triplet conversion and vibrational relaxation of the lowest MLCT state) [23]. The direct consequence is that energy transfer between neighbouring chromophores in dpp-bridged systems can occur from non-thermalised excited states, so that the process may even involve singlet MLCT states and conventional models (for example, Förster and Dexter mechanisms for energy transfer [24]) are inappropriate to describe these processes. Another consequence is that energy migration can also be very fast in symmetric complexes (RuRu, **8**, or OsOs, **10**, in Fig. 12), where $\Delta G = 0$ eV and a significant activation energy is predicted if the reactants were thermally equilibrated. This information may be useful for designing antennae with higher nuclearity, with stepwise energy transfer processes occurring between several centres. Considering an intermediate metal centre, the excitation energy must hop from one Ru → μ-dpp CT state to another which involves a different bridging dpp, i.e. an interligand hopping process for which $\Delta G \sim 0$. From the data accumulated for $Ru(bpy)_3^{2+}$, one would predict that this process is relatively slow, on a timescale of tens of ps [25]. However, interligand hopping from non-thermalised excited states can be much faster. It is, therefore, also probable that with an energy cascade involving several metal centres, excitation transfer can occur within 200 fs. This can be important in large antennae, photonic wires and other systems where a

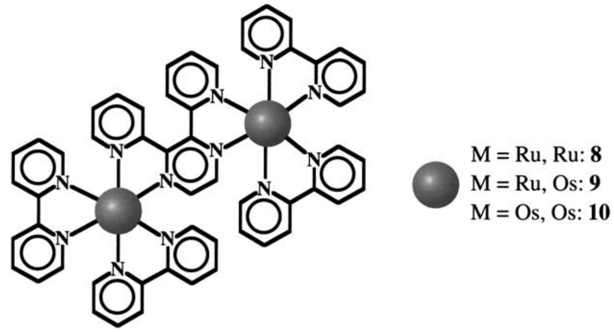

Fig. 12. Homometallic (**8** and **10**), and heterometallic (**9**) dinuclear species used in studies of ultrafast excited state processes [21]. The formal charges of the complexes are 4+ in all the cases.

rapid energy migration over a large distance is desired. A very rapid energy transfer in each step can efficiently compete with other excited-state deactivation pathways and result in small losses of excitation energy, even in systems characterised by multi-step processes.

Acknowledgements

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