Dendrimers based on ruthenium(II) and osmium(II) polypyridine complexes and the approach of using complexes as ligands and complexes as metals†

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The use of the "complexes as ligands and complexes as metals" synthetic strategy for the preparation of luminescent and redox-active Ru(II) and Os(II) dendrimers, the dominant synthetic approach for this novel class of compounds, is reviewed. A few comments on the photophysical and redox properties of the metal dendrimers are provided and an overview of alternative synthetic approaches is also presented.

1 Introduction

Polynuclear metal complexes based on ruthenium(II) and/or osmium(II) polypyridine building blocks constitute a class of compounds which has attracted the attention of many researchers in the last decade and continue to be subject to an ever increasing research effort.[1] This is due to the fact that these species play a central role in many fields of both fundamental and applied research. Primarily this is because the building blocks exhibit an unusual combination of properties rarely found simultaneously in other compounds. The relevant properties of Ru(II) and Os(II) polypyridine complexes are: (i) good stability of the ground as well as the excited and redox

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† Dedicated to Dr R Zimmermann (BD) on the occasion of his 60th birthday.

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states; (ii) absorption in the visible region, due to intense spin-allowed (and in the case of osmium compounds, also spin-forbidden) metal-to-ligand charge transfer (MLCT) bands; (iii) relatively long-lived (typically in the microsecond time range) and luminescent excited states. Emission is usually due to radiative deactivation of the lowest-lying 3MLCT level(s); (iv) reversible metal-centered oxidation and ligand-centered reduction processes at accessible potentials; (v) tunability of all the properties by a judicious choice and combination of the ligands.[2] This unique combination of properties has indeed allowed Ru(II) and Os(II) polypyridine complexes to be perfect candidates for many types of investigation, mostly based on their photophysical and redox properties.[1,2]

The contemporary presence of several Ru(II) and/or Os(II) polypyridine complexes within the same polynuclear structure adds new properties to the multimetal arrays, due to the supramolecular nature of these systems,[1,3–6] besides the basic properties of the building blocks cited above. The new properties depend on the electronic interactions between the various subunits, which is in turn due to the connections used and the topography of the systems. Among the various (supramolecular) properties that Ru(II)- and Os(II)-based polynuclear complexes can exhibit, photoinduced energy transfer processes within the arrays and simultaneous multielectron redox processes are particularly intriguing since they can lead to *useful functions*, such as light-harvesting antenna effect for solar energy conversion purposes and multielectron/hole storage.[1]

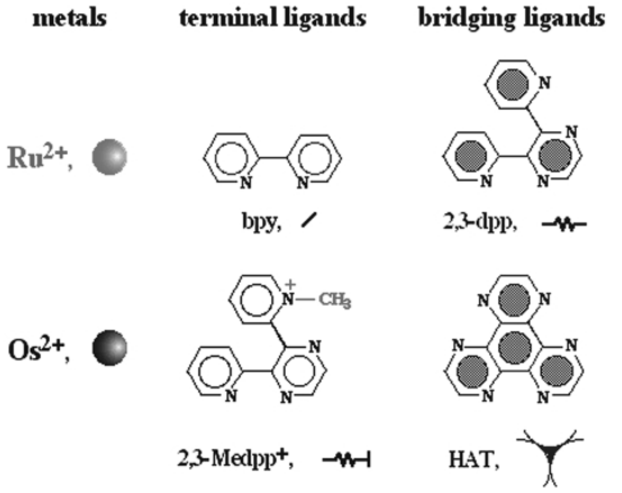
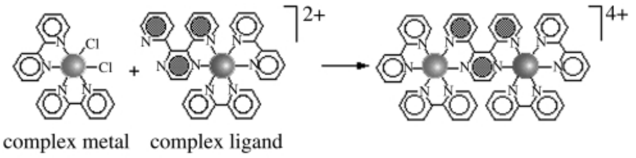


Fig. 1 Some fundamental components of metal dendrimers with designated symbols and representations.



complex metal complex ligand
1 2 3

Fig. 2 Application of the "complexes as ligands and complexes as metals" approach to the synthesis of a dinuclear compound.

Among polynuclear metal complexes, *metal-based dendrimers* are particularly interesting for several reasons: (i) the topography of the dendritic assembly is well-defined, an aspect which is relevant for preparing species with made-to-order properties and functions; (ii) the dendritic structure allows the incorporation of a large number of metal-based subunits in a limited space, employing relatively few synthetic steps. In the last few years, many dendrimers based on ruthenium and osmium polypyridine complexes have been prepared and their absorption spectra, photophysical properties and redox behavior were investigated.[7,8] These studies highlighted that Ru(II) and Os(II) dendrimers, when properly designed, behave as quite efficient artificial light-harvesting antennae[7] and can exhibit a large variety of multiredox patterns.[7,9,10] Therefore, many photo- and/or redox-induced functions, based on the particular properties of the ruthenium- and osmium-containing dendrimers, can be envisaged. This has indeed stimulated a growing interest over the past few years as far as the development of synthetic strategies for preparing luminescent and redox-active metal-based dendrimers is concerned.

In this review we will discuss in detail the synthetic strategy most frequently adopted for the synthesis of dendrimers based on ruthenium and osmium polypyridine complexes, that is the so-called "complexes as ligands and complexes as metals" strategy, which allowed the synthesis of the luminescent and redox-active dendrimers containing the largest numbers of metal subunits. The ligands most commonly used in the complexes that will be discussed here are shown in Fig. 1, together with the corresponding graphic symbols. A brief discussion on alternative synthetic strategies will also be presented.

It should be clarified that in this review we will focus on systems in which all the subunits of the dendrimers are made of Ru(II) or Os(II) polypyridine complexes. Dendrimers in which Ru(II) or Os(II) complexes are only present at the core or at the periphery of the structures (not synthesized by the complexes as ligands/complexes as metals strategy) will not be discussed. For selected references concerning this latter type of Ru(II)- and Os(II)-containing dendrimers, interested readers can refer to some recent reviews.[8,9]

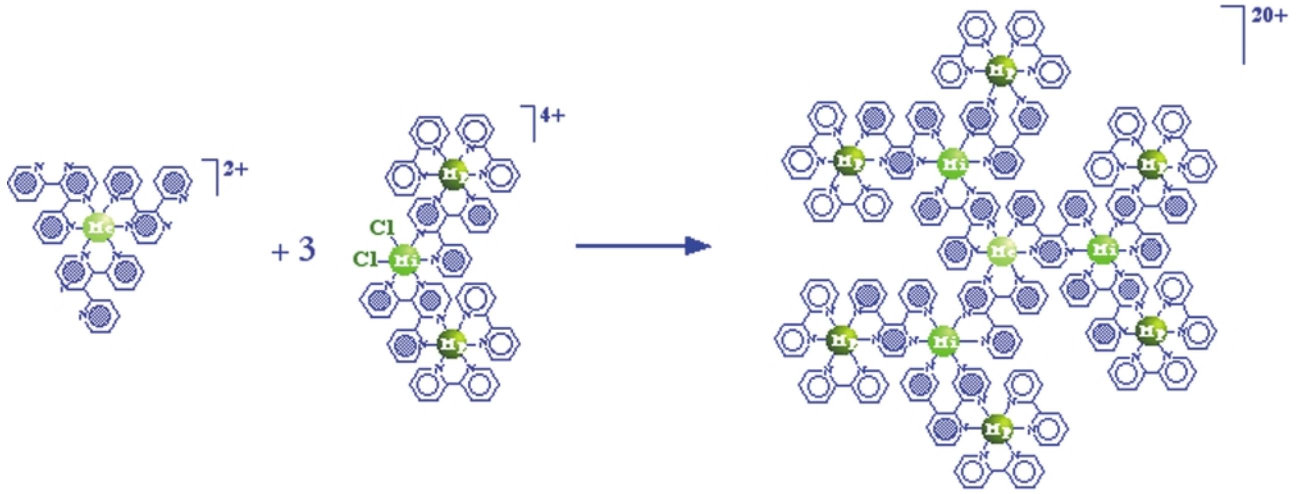


Fig. 3 Synthetic route to decanuclear metal complexes (Mc = core metal; Mi = intermediate metal; Mp, = peripheral metal).

2 “Complexes as ligands and complexes as metals” synthetic strategy

2.1 Basic concepts

This synthetic strategy is an example of modular synthetic chemistry,[11,12] a general approach that is becoming more and more widely adopted in chemical synthesis and is founded on concepts arising from supramolecular chemistry. The basic concept is that to obtain large (supra)molecular edifices, it is convenient to prepare simpler (multi)component structures (modules) and to assemble them into structurally-organized systems by taking advantage of some specific complementary reaction sites.

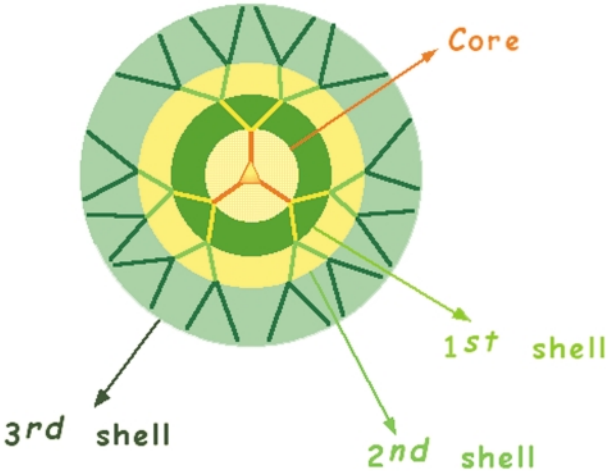


Fig. 4 Schematic representation of a dendrimer. Concentric circles signify a new dendrimer generation, while different colors indicate different shells.

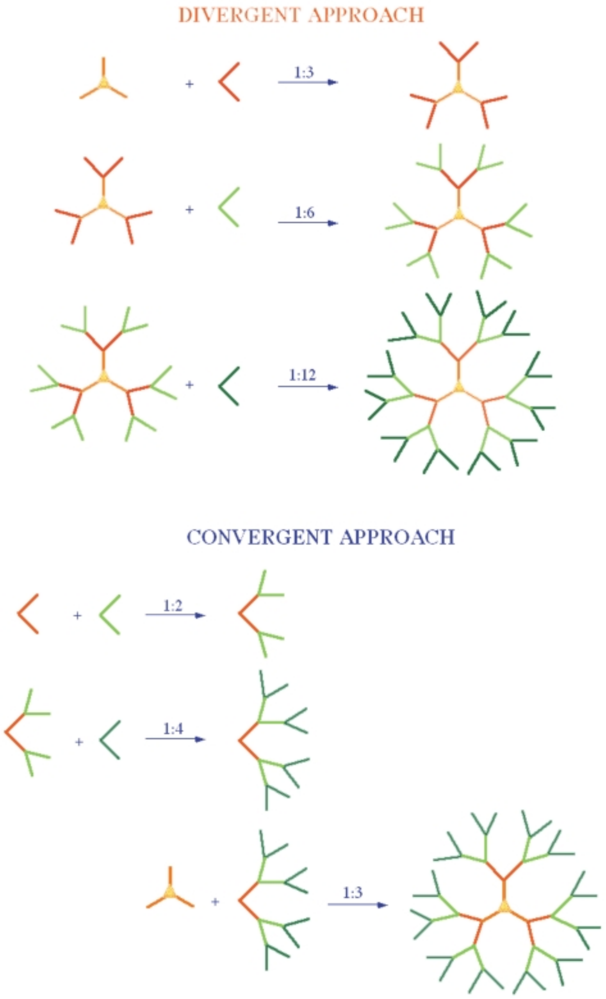


Fig. 5 Divergent and convergent approaches towards dendrimer synthesis.

Mononuclear transition metal complexes are typically synthesized by reacting metal ions (M) and free ligands (L) as shown in eqn. (1).

$$M + nL \rightarrow ML_n \qquad (1)$$

The “complexes as ligands and complexes as metals” approach is based on the use of complexes in the place of simple metal ions and free ligands.[13] The place of M in eqn. (1) is therefore taken by mono- or oligonuclear complexes which possess ligands that can be readily substituted, so that species with unsaturated metal coordination sites can be easily generated under the reaction conditions employed (“complex metals”), and the place of L can be taken by mono or oligonuclear complexes which contain free chelating sites (“complex ligands”). To make the discussion clearer, a very simple case is shown in Fig. 2. In this reaction, $Ru(bpy)_2Cl_2$ plays the role of a complex metal in that the two chloride ligands are easily removed in refluxing ethanol, leaving the ruthenium coordination sites unsaturated, while $Ru(bpy)_2(2,3\text{-dpp})^{2+}$ plays the role of complex ligand in that the free chelating site of 2,3-dpp can fill the coordination sites of the $Ru(bpy)_2Cl_2$ partner, after removal of the chlorides. This leads to the preparation of the dinuclear homometallic complex $[(bpy)_2Ru(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]^{4+}$. It should be noted that the reaction in Fig. 2 was chosen in order to clarify the basic concept of the “complexes as ligands and complexes as metals” (“cal/cam”) approach. In fact, the dinuclear complex shown in the figure is more effectively prepared in a single step by reacting the 2,3-dpp free ligand and $Ru(bpy)_2Cl_2$ in the appropriate ratio. However, the procedure in Fig. 2 becomes necessary in the case of heteronuclear complexes, that is when the target molecule contains different metals and/or different peripheral ligands on the two metals.

The “cal/cam” approach reveals its full potential when polynuclear and/or multifunctional complex ligands and complex metals are available. This is exemplified in Fig. 3, where a trifunctional mononuclear complex ligand (containing free chelating sites) and a monofunctional, trinuclear complex metal are reacted to form a decanuclear complex. The reaction shown in Fig. 3 warrants some consideration. (i) A complex of high nuclearity is prepared in a single step by taking advantage of the complementary functionalities of the reaction partners. (ii) The topography of the final structure is fully controlled, in the sense that: the metal center in the central position (M_c) of the decanuclear species is the metal originally belonging to the trifunctional complex ligand; the metal centers in the intermediate positions (M_i) are the metals of the trinuclear complex metal carrying the leaving chloride ligands; and the metals in the peripheral positions (M_p) are the peripheral metals of the parent trinuclear complex metal. An analogous control on the position of the bridging ligands can also be obtained. (iii) The decanuclear species is a second generation dendrimer, obtained by a convergent synthesis (a topic better addressed later). It should be considered that point (ii) in particular is due to the stability of the Ru– and Os–polypyridine linkages. In fact, a prerequisite for the application of this method is that ligand scrambling does not occur.

Decanuclear complexes, such as the one showed in Fig. 3 immediately lead us into the dendrimer field. Dendrimers are perfectly branched synthetic macromolecules having numerous chain ends all emanating from a single core (Fig. 4).[14–17] Because of their structure, they resemble a tree (dendrimer is indeed a contraction for dendron, the greek word for tree, and polymer). In a dendrimer, one can recognize the core and successive layers of concentric shells, containing an increasing number of identical (at least within each shell) repetitive subunits (Fig. 4). Depending on the number of shells, dendrimers of various generations can be defined. Dendrimers are usually prepared by two approaches (Fig. 5): one involves a divergent iterative coupling and activation protocol from the core (divergent approach), whilst the other is based on the preparation of dendrimer branches (dendrons) and the connection of the various branches to a single focal point, *i.e.* the core (convergent approach). However, alternative strategies have also been reported.[18–20] The synthesis of decanuclear complexes schematized in Fig. 3 is an example of the convergent approach. As mentioned above, decanuclear complexes of the type discussed here are second generation dendrimers, in which the complex ligand $[Mc(dpp)_3]^{2+}$ plays the role of the core in the final structure, with each one of the three trinuclear complex metals acting as dendrons.

Several decanuclear dendrimers containing Ru(II) and Os(II) subunits have been prepared by this approach, containing different metals in the various "shells" and different peripheral ligands, thanks to the availability of different complex metal dendrons and complex ligand cores.[7] Different schematic

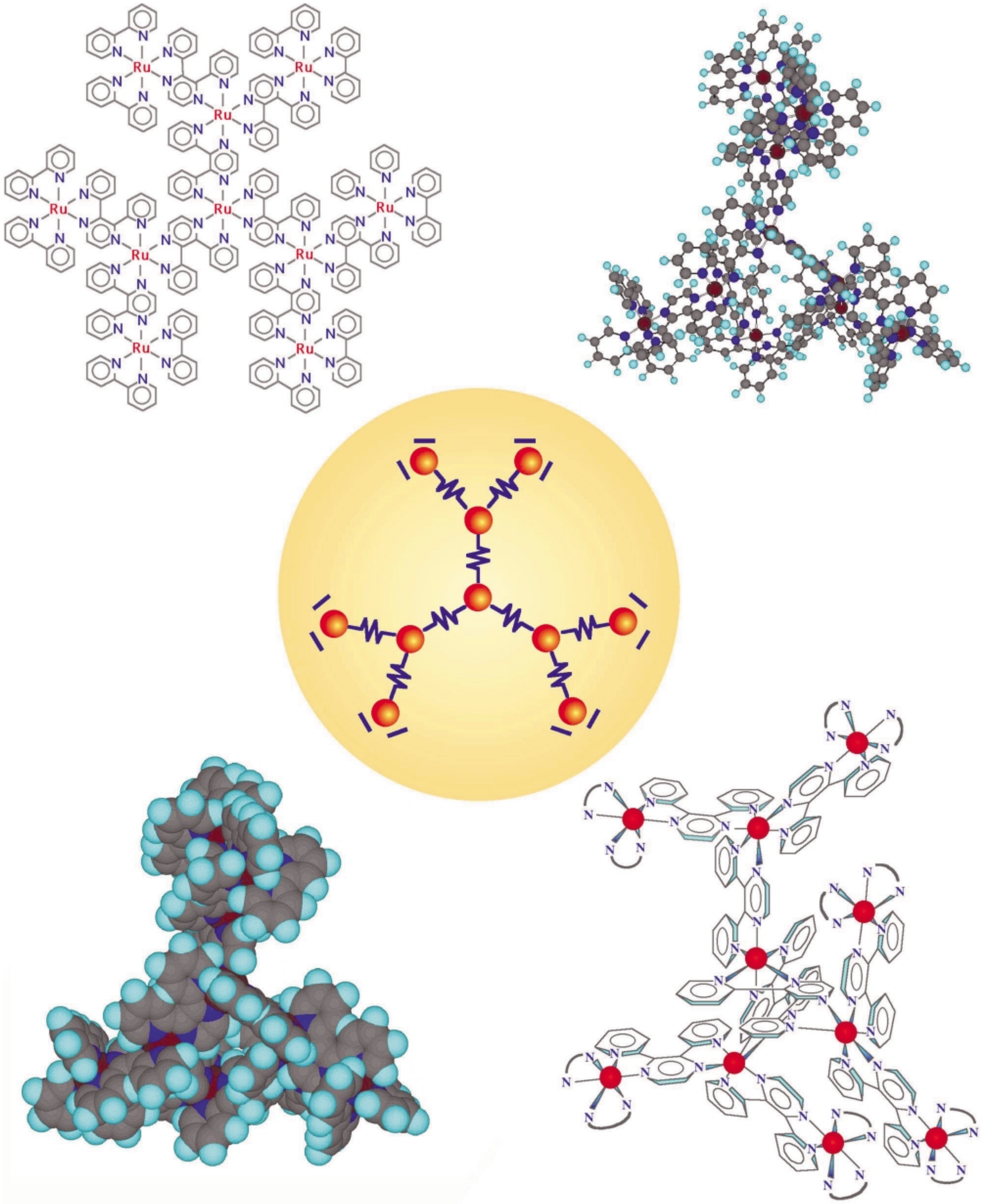
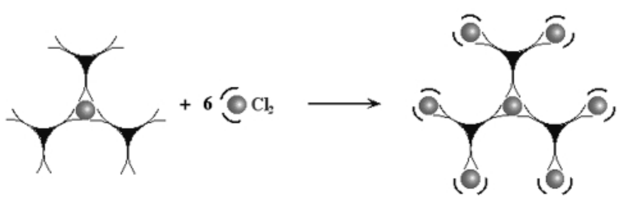


Fig. 6 Different representations of the decanuclear homometallic compound $[Ru\{(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_3\}_3]^{20+}$ (**4**). Charges are omitted for clarity.

representations of one of these dendrimers, namely [Ru{(μ-2,3-dpp)Ru[(μ-2,3-dpp)Ru(bpy)$_2$]$_3$}$_3$]$^{20+}$ (**4**), are shown in Fig. 6, in which the three-dimensional nature of these species is apparent.

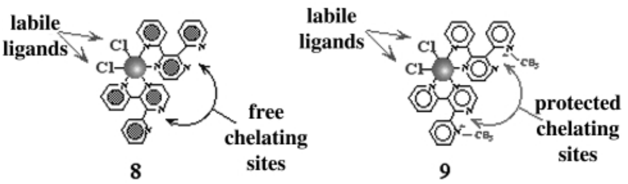
The “cal/cam” approach has also been used to prepare a heptanuclear Ru(II) complex by reacting a hexafunctional mononuclear complex ligand, [Ru(HAT)$_3$]$^{2+}$, with six Ru-(phen)$_2$Cl$_2$ complex metal subunits (Fig. 7).[21] Interestingly, this highly-branched first generation Ru dendrimer has also been investigated by scanning tunnelling microscopy, which allowed visualization of a single dendrimer[22] on a surface.



6 7 5

= 1,10-phenanthroline

Fig. 7 Schematization of the synthesis of heptanuclear compound **5**.



8 9

Fig. 8 Bifunctional (**8**) and masked bifunctional (**9**) species.

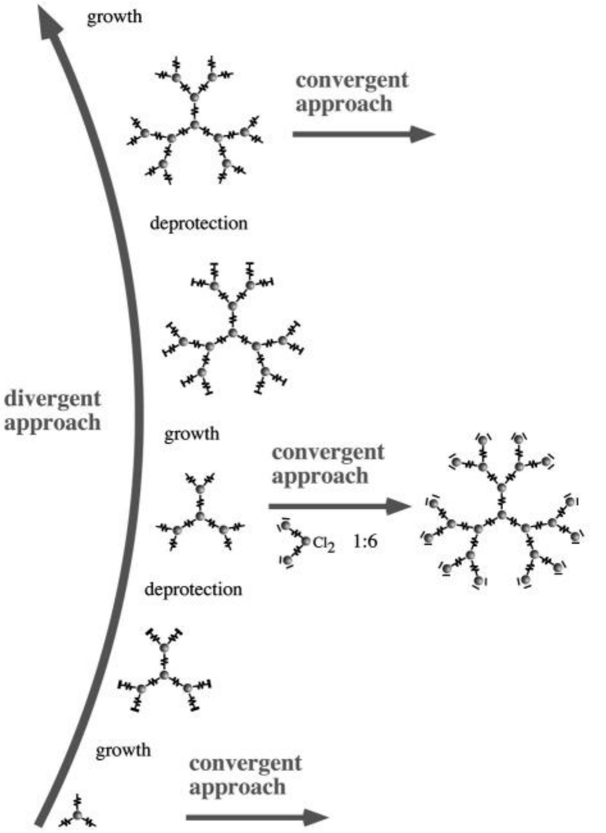
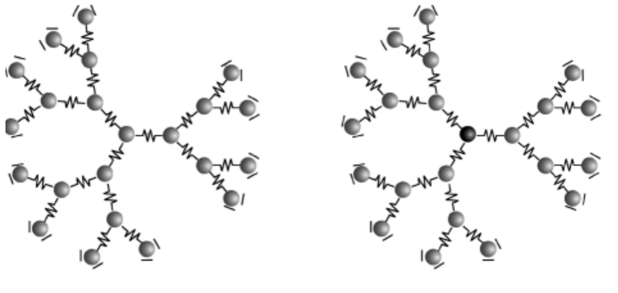


Fig. 9 The iterative divergent approach to metal dendrimers utilizing sequential growth and deprotection steps. Each deprotected compound can be used as a core in convergent synthetic processes.

2.2 The protection–deprotection divergent approach

An important breakthrough in the field of metal-dendrimer synthesis resulted from the implementation of an iterative process within the “cal/cam” synthetic framework, based on a protection–deprotection protocol of polypyridine chelating sites.[13] In fact, all the divergent syntheses of dendrimers rely upon an iterative coupling of subunits and require the availability of a species carrying two types of functional groups. In the “cal/cam” approach, this means the availability of a species which can behave both as a complex ligand and as a complex metal. A simple example is the compound Ru(2,3-dpp)$_2$Cl$_2$ (**8**,Fig. 8). However, a species like this is self-reactive under the preparative conditions because the free chelating site of one molecule could substitute the labile chlorides of another molecule, leading to an uncontrolled mixture of species. The key step towards the preparation of the required compound was the synthesis of the monomethylated 2,3-Medpp$^+$ ligand (Fig. 1), which allowed the preparation of the [Cl$_2$Ru(2,3-Medpp)$_2$]$^{2+}$ complex. This latter complex is a masked bifunctional compound, in that it is a complex metal but also a potential complex ligand: its potential as a complex ligand can be activated by demethylation. Reacting the masked bifunctional complex [Cl$_2$Ru(2,3-Medpp)$_2$]$^{2+}$ with [M$_c$(2,3-dpp)$_3$]$^{2+}$ cores affords tetranuclear protected compounds (first generation dendrimers). After deprotection, the reaction could be iterated. The general procedure is shown in Fig. 9.

In this approach one can distinguish two essential steps, the deprotection and the growth reactions. Any growth reaction leads to successive generation of the dendrimers, while the deprotection step leads to different dendrimers of the same generation. It is also interesting to note that each deprotected dendrimer can be used as a core in convergent synthetic processes. Actually this strategy was employed in the syntheses of the two largest dendrimers of this series obtained so far, the docosanuclear species (*i.e.* containing 22 metal centers) schematically shown in Fig. 10. Both compounds were prepared by reacting the appropriate tetranuclear deprotected species (*i.e.* hexafunctional complex ligands, carrying six free chelating sites at the periphery) with six trinuclear complexes of the type shown in Fig. 3 (a multifunctional complex metal species).

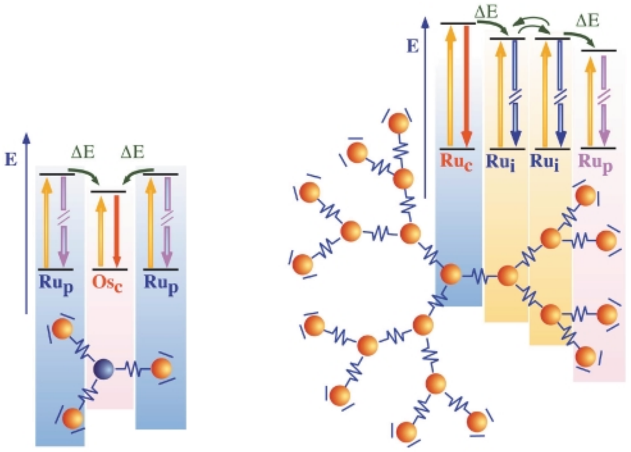


10 11

Fig. 10 Representation of two docosanuclear metal dendrimers. Charges are omitted for clarity.

2.3 Some comments on the photophysical and redox properties of Ru(II) and Os(II) dendrimers containing 2,3-dpp bridges

As mentioned in the Introduction, the interest in Ru(II) and Os(II) dendrimers is stimulated by their photophysical and redox properties, in particular their ability to behave as artificial light harvesting antennae and participate in multielectron redox processes. We shall not dwell on these properties which have been recently reviewed,[8–10] and are beyond the scope of this article, which deals principally with the synthetic approach. However, it is important to note that the topographical control allowed by the “cal/cam” approach translates into predetermined redox patterns and energy migration processes within the dendritic arrays. These few notes can be limited to the properties of the 2,3-bridged Ru(II) and Os(II) dendrimers **12** and **10** which are heterometallic tetranuclear and homometallic docosanuclear species, respectively. These selected examples typify the energy migration processes occurring in this type of compound, and are depicted in Fig. 11.[7] In the Os-containing tetranuclear species, the subunit containing the lowest-energy excited state of the entire array is the Os core.[7] In this case, quantitative energy transfer occurs from the peripheral Ru chromophores to the Os center, which acts as the energy trap of the antenna. Conversely, in the docosanuclear all-ruthenium third generation dendrimer, the lowest-energy excited states are MLCT levels centered at the twelve peripheral chromophores. Luminescence studies indicate that quantitative center-to-periphery energy migration occurs, demonstrating that energy transfer through isoenergetic dendrimer subunits is very fast and efficient.



12 **10**

Fig. 11 Energy migration patterns occurring in the heterometallic tetranuclear, first-generation dendrimer **12** and in the homometallic docosanuclear, third-generation dendrimer **10**.[17]

Very recent investigations aimed to clarify the rates and mechanisms of the energy migration processes within the Ru(II) and Os(II) dendrimers indicate that energy transfer between isoenergetic subunits in dendrimer-type polynuclear complexes bridged by 2,3-dpp ligands takes place in the femtosecond timescale (within 200 fs),[23] that is a timescale comparable with vibrational relaxation and singlet–triplet conversion (of course, down-hill energy transfer processes are expected to be even faster). Thus, intercomponent energy transfer probably involves non-thermally equilibrated states, which explains the ultrafast transfer rate obtained in this class of compounds, which are even faster than energy migration processes between the antenna subunits in natural photosynthetic arrays.

The cyclic voltammetry curve of hexanuclear complex **13** (Fig. 12) serves to highlight the rich redox properties exhibited by these dendrimers.[24] In this compound (prepared by coupling two equivalents of the trinuclear complex metal shown in Fig. 3 with one equivalent of the free ligand 2,3-dpp), as many as 26 reduction processes have been identified and assigned to specific subunits.

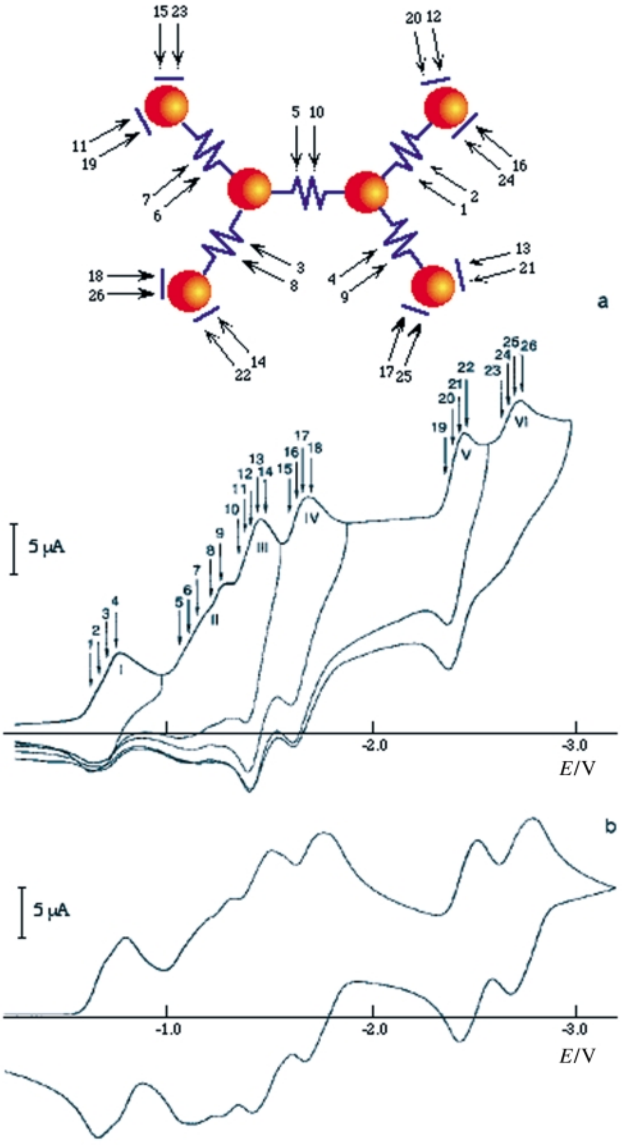


Fig. 12 a: Cyclic voltammetry (cv) curve of a hexanuclear dendrimer in *N*,*N*-dimethylformamide at −55 °C. The assignment of the observed processes to specific subunits of the compound is also shown. b: Digital simulation of the cv curve.[24]

3 Alternative approaches to Ru(II) and Os(II) polypyridine dendrimers

Beside the “cal/cam” synthetic strategy, another approach has been extensively employed for Ru(II) and Os(II) dendrimers. This approach relies on the possibility of preparing mono- or multimetal Ru(II) modules containing polypyridine ligands substituted with reactive sites and directly coupling these

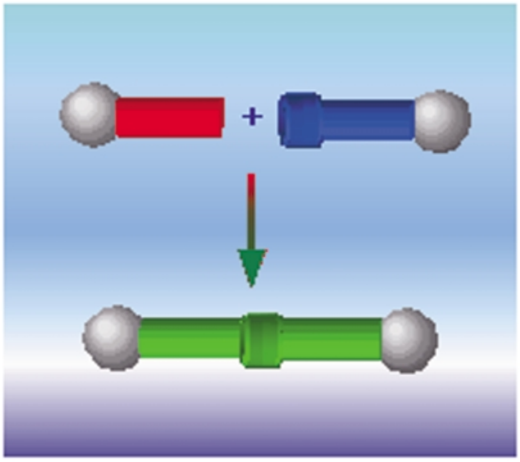
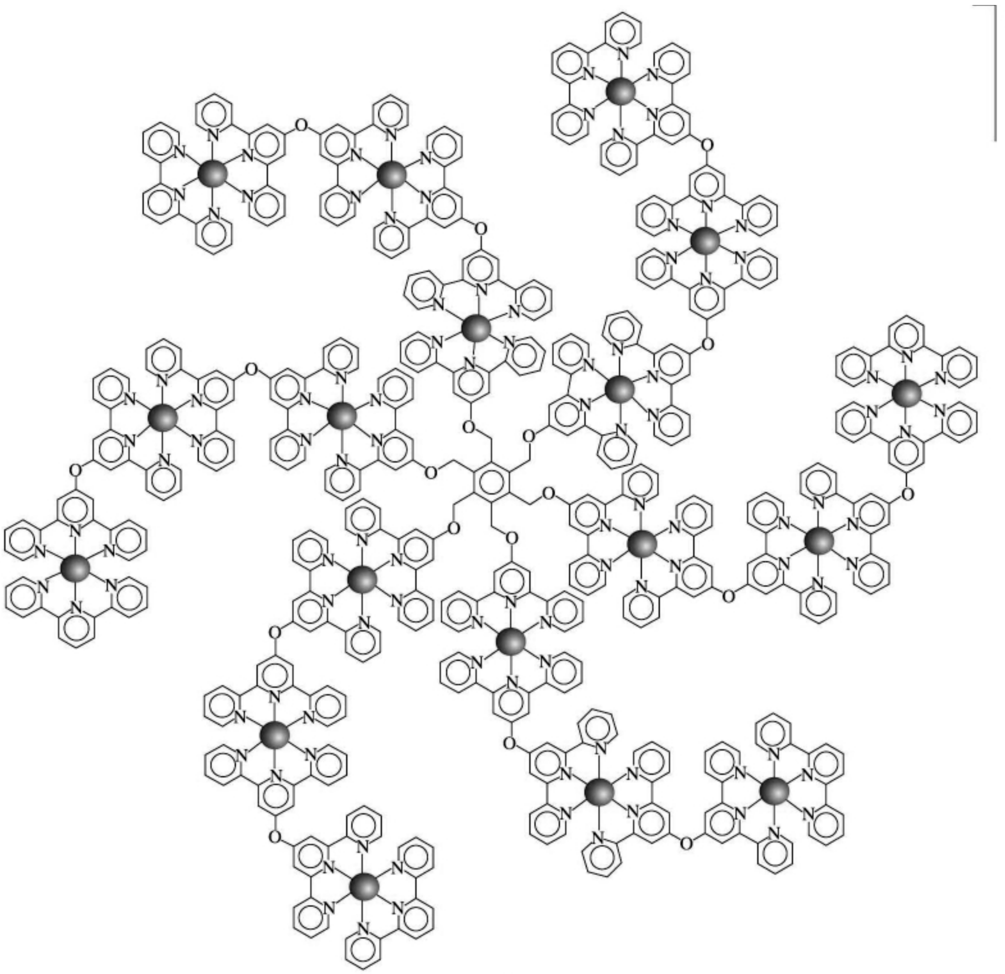
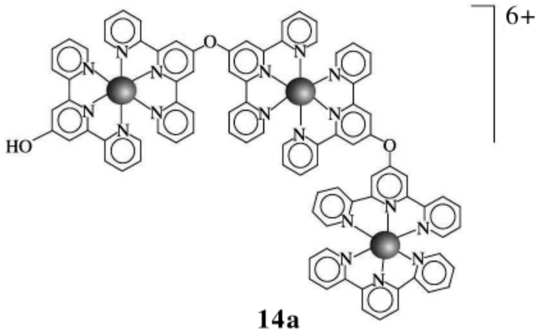


Fig. 13 Schematic representation of the approach of connecting preformed metal (or multimetal) systems by coupling of complementary ligands. Grey spheres represent the metal centers; red and blue components are coordinating ligands bearing complementary substituents; the green component represents a newly formed bridging ligand.



14



14a

Fig. 14 The octadecanuclear dendrimer **14** of Constable and co-workers.[17] Compound **14a** is the trinuclear precursor (see text).

modules by means of high-yielding organic reactions on the coordinated ligands. In this way the bridging ligand is formed during the reaction. This approach is schematized in Fig. 13.

Constable and co-workers have prepared a large series of Ru(II) dendrimers by taking advantage of this alternative methodology, employing both convergent and divergent strategies.[17] In the majority of the cases, they used bridging ligands based on 2,2′,2″-terpyridine (terpy) subunits as chelating sites. One of the largest systems prepared by this team is the octadecanuclear complex **14**, shown in Fig. 14.[17] Synthesis was achieved by reacting six equivalents of trinuclear compound **14a**, which terminates with a hydroxy group (treatment with base generates the reactive intermediate), with one equivalent of hexakis(bromomethyl)benzene to generate the octadecanuclear compound by a convergent route.

Similar systems have been recently studied by Juris and co-workers who employed bpy analogues of the terpy-based systems shown in Fig. 14 to prepare the first-generation tetranuclear mixed-metal complex **15** shown in Fig. 15.[25] In particular the synthesis of this latter compound is an example of coupling the “cal/cam” approach and the strategy of performing organic reactions on preformed complexes. The first step was functionalization of the mononuclear osmium complex **16**, containing 4-bromo-2,2′-bipyridine, by grafting additional bpy units onto the coordinated ligands to obtain a complex ligand with three free chelating sites (**17**). The resulting complex ligand **17** was then reacted with the Ru(bpy)$_2$Cl$_2$ complex metal to afford **15**.

MacDonnell and co-workers also used the method of coupling reactive sites of complexed polypyridine ligands to generate metal dendrimers of first and second generation.[26,27] One of the species thus obtained is shown in Fig. 16. The most interesting point is that this group used chirally-resolved building blocks, so that the final structures are species which

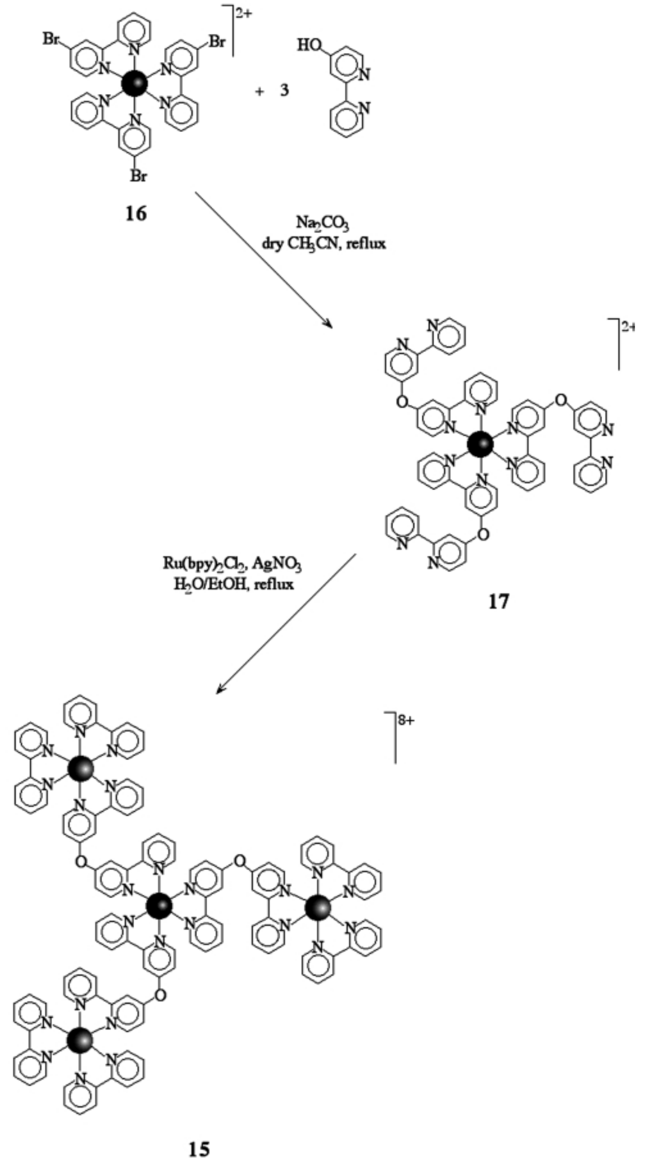
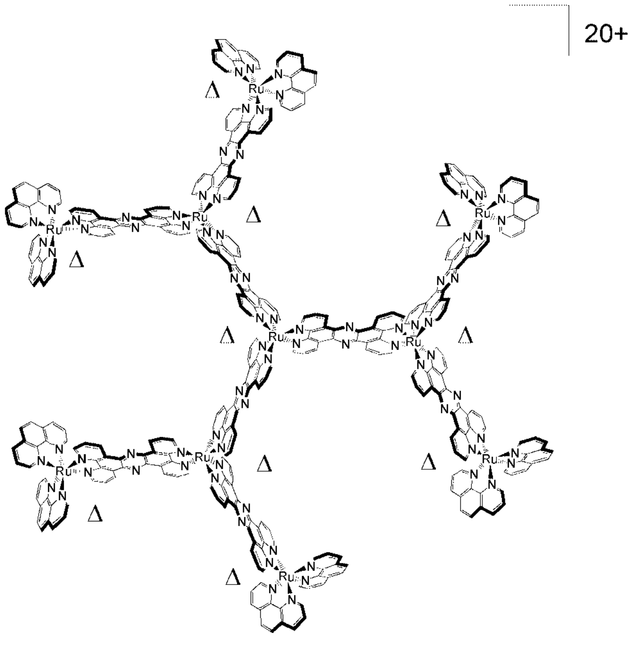


Fig. 15 Reaction scheme showing the synthesis of heterometallic compound **15**.[25]

also are enantiomerically pure, since the reactions take place with retention of configuration at the metal centers (which are not involved in the reaction process) and the new bridging ligand generated by the reaction does not introduce further chirality elements into the final species.

4 Conclusions and outlook

The rapid development of the chemistry of luminescent and redox-active dendrimers has afforded the opportunity to investigate the photophysical and redox properties of large and topologically-controlled assemblies of chromophores. The “cal/cam” approach in particular has led to the preparation of highly efficient artificial antennas which promise to be very useful for designing complex solar energy conversion devices. In the coming years, besides the synthesis of novel Ru(II) and Os(II) polypyridine dendrimers, coupling these multicomponent species with particular substrates, such as electrodes and charge separation components, will probably be key goals. Research work addressing these issues is already underway and may lead to interesting and novel results.



$\Delta_6\Delta_3\Delta$–Ru$_{10}$

Fig. 16 One of the chirally-pure decanuclear second-generation dendrimers prepared by MacDonnell and co-workers.[27]

5 Acknowledgements

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6 References

1 V. Balzani, A. Juris, S. Campagna and S. Serroni, *Chem. Rev.*, 1996, **96**, 759 and references therein.
2 (*a*) A Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85; (*b*) T. J Meyer, *Acc. Chem. Res.*, 1989, **22**, 163.
3 F. Barigelletti and L. Flamigni, *Chem. Soc. Rev.*, 2000, **29**, 1.
4 A. Harriman and R. Ziessel, *Chem. Commun.*, 1996, 1707.
5 J.-P. Sauvage, J.-P. Collin, J.-C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola and L. Flamigni, *Chem. Rev.*, 1994, **94**, 993.
6 F. Scandola, C. Chiorboli, M. T. Indelli and M. A. Rampi, in *Electron Transfer in Chemistry*, ed. V. Balzani, Wiley-VCH, Weinheim, Vol. 3, p. 337.
7 V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni and M. Venturi, *Acc. Chem. Res.*, 1998, **31**, 26 and references therein.
8 V. Balzani, P. Ceroni, A. Juris, M. Venturi, S. Campagna, F. Puntoriero and S. Serroni, *Coord. Chem. Rev.*, in press.
9 (*a*) M. Venturi, S. Serroni, A. Juris, S. Campagna and V. Balzani, *Top. Curr. Chem.*, 1998, **197**, 193; (*b*) A. Juris, M. Venturi, P. Ceroni, V. Balzani, S. Campagna and S. Serroni, *Collect. Czech. Chem. Commun.*, 2001, **66**, 1.
10 A. Juris, in *Electron Transfer in Chemistry*, ed. V. Balzani, VCH-Wiley, Weinheim, 2001, Vol. 3, p. 665.
11 P. F. H. Scwab, M. D. Levin and J. Michl, *Chem. Rev.*, 1999, **99**, 1863.
12 J.-M. Lehn, *Supramolecular Chemistry*, Wiley-VCH, Weinheim, 1995.
13 (*a*) S. Serroni and G. Denti, *Inorg. Chem.*, 1992, **31**, 4251; (*b*) S. Campagna, G. Denti, S. Serroni, A. Juris, M. Venturi, V. Ricevuto and V. Balzani, *Chem. Eur. J.*, 1995, **1**, 211 and references therein.

14 D. A. Tomalia and H. D. Durst, *Top. Curr. Chem.*, 1993, **165**, 193.

15 A. Adronov and J. M. J. Fréchet, *Chem. Commun.*, 2000, 1701.

16 G. R. Newkome, C. Moorefield and F. Vögtle, *Dendrimers and Dendrons*, Wiley-VCH, Weinheim, 2001.

17 E. C. Constable, *Chem. Commun.*, 1997, 1073 and references therein.

18 J.-P. Majoral and A.-M. Caminade, *Top. Curr. Chem.*, 1998, **197**, 79.

19 F. Zeng and S. C. Zimmerman, *Chem. Rev.*, 1997, **97**, 1681.

20 A. W. Bosman, H. M. Janssen and E. W. Mejer, *Chem. Rev.*, 1999, **99**, 1665.

21 C. Moucheron, A. Kirsch-De Mesmaeker, A. Dupont-Gervais, E. Leize and A. Van Dorsselaer, *J. Am. Chem. Soc.*, 1996, **118**, 12834.

22 L. Latterini, G. Pourtois, C. Moucheron, R. Lazzaroni, J.-L. Brédas, A. Kirsch-De Mesmaeker and F. C. De Schryver, *Chem. Eur. J.*, 2000, **6**, 1331.

23 H. Berglund-Baudin, J. Davidsson, S. Serroni, A. Juris, V. Balzani, S. Campagna and L. Hammarström, submitted.

24 M. Marcaccio, F. Paolucci, C. Paradisi, S. Roffia, C. Fontanesi, L. J. Yellowless, S. Serroni, S. Campagna, G. Denti and V. Balzani, *J. Am. Chem. Soc.*, 1999, **121**, 10081.

25 (*a*) A. Borje, O. Kothe and A. Juris, *New J. Chem.*, 2001, **25**, 191; (*b*) A. Borje, O. Kothe and A. Juris, submitted.

26 S. Bodige, A. S. Torres, D. J. Maloney, D. Tate, G. R. Kinsel, A. K. Walker and F. M. MacDonnell, *J. Am. Chem. Soc.*, 1997, **119**, 10364.

27 M.-J. Kim, F. M. MacDonnell, M. E. Gimon-Kinsel, T. Du Bois, N. Asgharian and J. C. Griener, *Angew. Chem., Int. Ed.*, 2000, **39**, 615.