Polynuclear metal complexes of nanometre size. A versatile synthetic strategy leading to luminescent and redox-active dendrimers made of an osmium(II)-based core and ruthenium(II)-based units in the branches

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A docosanuclear metal complex of nanometric size and dendritic shape made of an osmium(II)-based core and containing 21 ruthenium(II)-based units in the branches has been prepared. The key building blocks are the $[Os(2,3\text{-dpp})_3]^{2+}$ 'complex ligand', and the $[Ru(2,3\text{-Medpp})_2Cl_2]^{2+}$ and $[\{Ru(bpy)_2(m\text{-}2,3\text{-dpp})\}_2RuCl_2]^{4+}$ 'complex metals' {2,3-dpp = 2,3-bis(2-pyridyl)pyrazine; 2,3-Medpp$^+$ = 2-[2-(1-methylpyridiniumyl)]-3-(2-pyridyl)pyrazine; bpy = 2,2′-bipyridine}. The first step of the synthesis is the formation of the tetranuclear $[Os\{(m\text{-}2,3\text{-dpp})Ru(2,3\text{-Medpp})_2\}_3]^{14+}$ species in which the peripheral ligands 2,3-Medpp$^+$ are 2,3-dpp ligands with the second chelating site inactivated (protected) by methylation. This species is obtained from the reaction of the $[Os(2,3\text{-dpp})_3]^{2+}$ 'complex ligand' core, which contains three open chelating positions, with three equivalents of the $[Ru(2,3\text{-Medpp})_2Cl_2]^{2+}$ 'complex metal', where the labile Cl^- ligands can be replaced by the chelating units of the core. Successive demethylation (deprotection) of the tetranuclear compound opens the six peripheral chelating sites. At this stage, the divergent synthesis can be iterated {reaction with six equivalents of the $[Ru(2,3\text{-Medpp})_2Cl_2]^{2+}$ 'complex metal'} with formation of the protected decanuclear compound $[Os\{(m\text{-}2,3\text{-dpp})Ru[(m\text{-}2,3\text{-dpp})Ru(2,3\text{-Medpp})_2]_2\}_3]^{32+}$. Alternatively, in a convergent approach, the reaction of the deprotected tetranuclear species with six equivalents of the trinuclear $[\{Ru(bpy)_2(m\text{-}2,3\text{-dpp})\}_2RuCl_2]^{4+}$ 'complex metal' leads to the docosanuclear $[Os\{(m\text{-}2,3\text{-dpp})Ru[(m\text{-}2,3\text{-dpp})Ru\{(m\text{-}2,3\text{-dpp})Ru(bpy)_2\}_2]_2\}_3]^{44+}$ species. The absorption spectra, luminescence properties, and electrochemical behaviour of $[Os(2,3\text{-dpp})_3]^{2+}$, $[Os(m\text{-}2,3\text{-dpp})_3\{Ru(2,3\text{-Medpp})_2\}_3]^{14+}$, $[Os\{(m\text{-}2,3\text{-dpp})Ru[(m\text{-}2,3\text{-dpp})Ru(2,3\text{-Medpp})_2]_2\}_3]^{32+}$, and $[Os\{(m\text{-}2,3\text{-dpp})Ru[(m\text{-}2,3\text{-dpp})Ru\{(m\text{-}2,3\text{-dpp})Ru(bpy)_2\}_2]_2\}_3]^{44+}$ have been investigated.

Miniaturization of components for the construction of useful devices is currently pursued by a 'large-downward' approach. This approach, however, which leads physicists to deal with progressively smaller molecular aggregates, becomes difficult or even impossible when the size of the miniaturized component has to be in the dimension of nanometres.

Chemists can construct nanometre-size species by a 'small-upward' approach starting with molecular components. This approach is very appealing since it allows the assembly of functionally integrated molecular building blocks to obtain molecular-level devices.[1]

Assembly of molecular components into large and functional arrays (supramolecular species) can be based on a variety of intermolecular forces such as hydrogen bonds, donor–acceptor interactions, stacking interactions, or on coordination and covalent bonds.[2] When the molecular building blocks contain transition metals, a strategy called 'complexes as metal/complexes as ligand' can allow the construction of large polynuclear metal complexes *via* metal–ligand coordination bonds.[3,4] In the last few years we have synthesized a variety of polynuclear transition-metal complexes having dendrimer type structure and exhibiting interesting photophysical and electrochemical properties.[5] The largest metal-based dendrimer reported by our group contains 22 Ru^{II} centres.[6] The interest in these species is not only related to their size, but also to the presence of chemically different units since each unit introduces into the supramolecular structure its own 'pieces of information' (in the form of specific properties such as excited states, redox levels, *etc.*). One of the advantages of the 'complexes as metal/complexes as ligand' synthetic strategy is that one can introduce the desired building block at each stage of the synthesis. We have taken advantage of this flexibility to build up a new docosanuclear dendrimer which contains an osmium(II) core and three branches, each one containing 7 ruthenium(II) units.

The metals and ligands used to build up our compounds are shown in Fig. 1 together with their graphic symbols and abbreviations. Fig. 2 shows the schematic representations of relevant compounds dealt with in this paper. The abbreviations indicate the type and number of metal atoms contained in the compound, and the nature of the peripheral ligands (d = deprotected 2,3-dpp ligands; p = protected 2,3-dpp ligands; t = terminal monochelating ligands).

Results and Discussion

Synthetic strategies

Dendrimers can be constructed by two different approaches.[7] One approach, called divergent or 'inside out', starts with an initial core containing *n* reactive sites. To this core (zero-generation of the dendrimer), *n* units (building blocks) can be connected. This process affords the first generation of the dendrimer. If the peripheral units of the dendrimer so obtained still contain reactive sites, the process can be iterated, yielding a second-generation dendrimer, and so on. For example, if the chosen core and each building block both contain three chelating reactive sites (as is the case of our compounds, see later), the peripheral reactive sites will progress as follows: 3 (zero generation); 6 (first generation); 12 (second generation); 24 (third generation), *etc.*

An alternative strategy is the convergent (or 'outside in')

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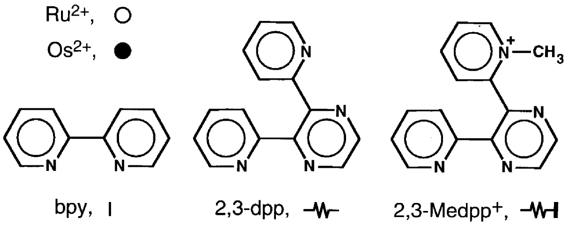

Fig. 1 Metals, ligands, and abbreviations used

construction of the dendrimer, whereby preformed branched arms are attached to a more or less large core.

The 'complexes as metal/complexes as ligand' synthetic strategy[3,4] can be exploited both for the divergent and the convergent approaches. Such a strategy is based on the use, as building blocks, of metal complexes that possess free chelating sites and metal complexes containing labile ligands (Fig. 3). The complexes with free chelating sites play the role of ligands ('complex ligands'), and those with labile ligands play the role of metals ('complex metals'). The reaction of complex ligands with complex metals in the appropriate stoichiometric ratio then leads to complexes of higher nuclearity (Fig. 3).

The divergent iterative approach requires the availability of a bifunctional species. In dealing with coordination compounds, such species have to be complexes capable of behaving both as a ligand and as a metal. A simple example is the compound $Ru(2,3\text{-dpp})_2Cl_2$, shown in Fig. 4. Unfortunately, a species like this is unavoidably self-reactive because the free chelating sites of one molecule would substitute the labile ligands of another molecule, leading to a mixture of dispersed and uncontrolled nuclearities. Thus, in order to carry on a divergent synthesis, potentially bifunctional species, where one of the two functions is temporarily blocked, have to be used. This is the case of the preparation of the complex metal $[Ru(2,3\text{-Medpp})_2Cl_2]^{2+}$,[6b] obtained by using the 'protected' ligand 2,3-Medpp$^+$,[4b] where one of the two chelating sites is methylated. The protection is stable in the reaction conditions used when $[Ru(2,3\text{-Medpp})_2Cl_2]^{2+}$ acts as a complex metal. Subsequent demethylation of the product restores the presence of free chelating sites, *i.e.* its complex ligand ability. An iterative, divergent synthesis is therefore possible, as shown in Fig. 5.

It should also be emphasized that each deprotected compound of the divergent approach can be used as a ligand core in a convergent process with complex metals to yield dendri-

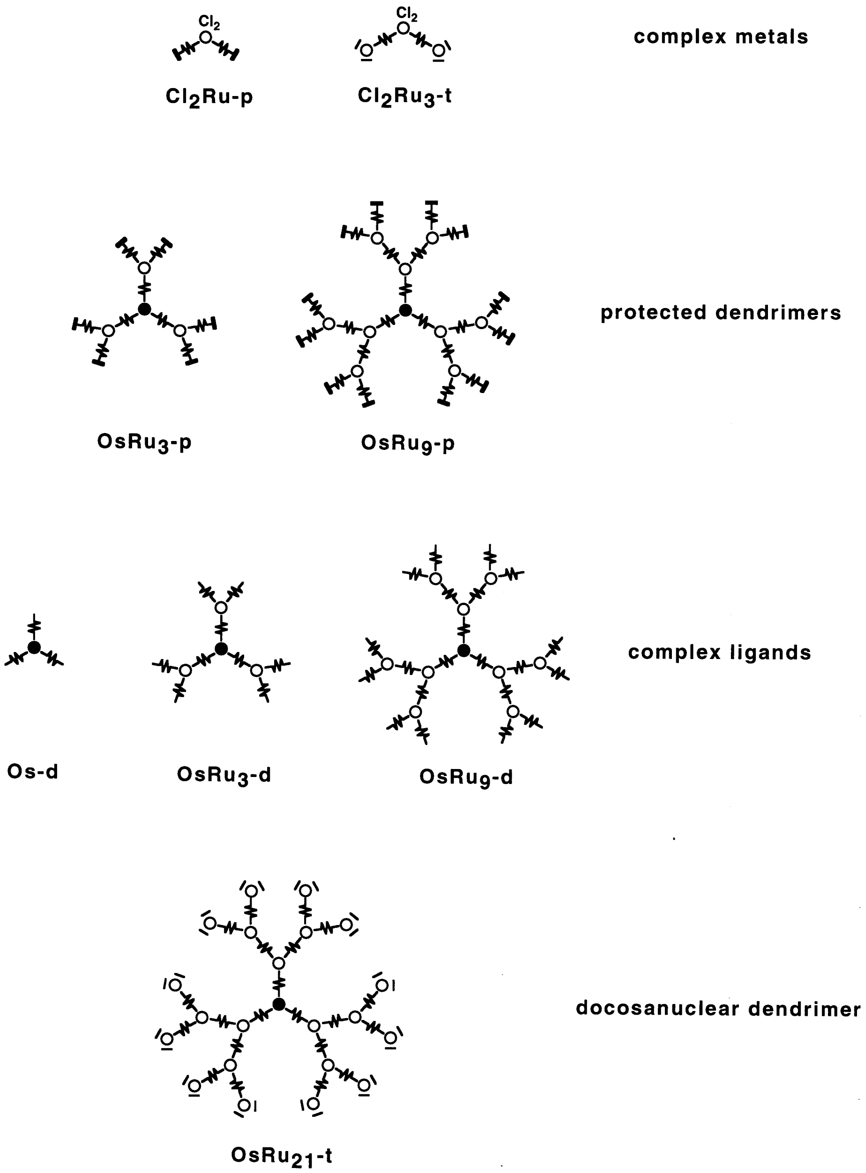

Fig. 2 Schematic representation of the compounds used for and/or obtained by our synthetic strategy. The graphic symbols used to represent metals and ligands are explained in Fig. 1. In the label used to designate each compound, the number indicates the nuclearity (number of metal ions), the letter indicates the type of the peripheral ligands (d, deprotected bridging ligand; p, protected bridging ligand; t, terminal monochelating ligand).

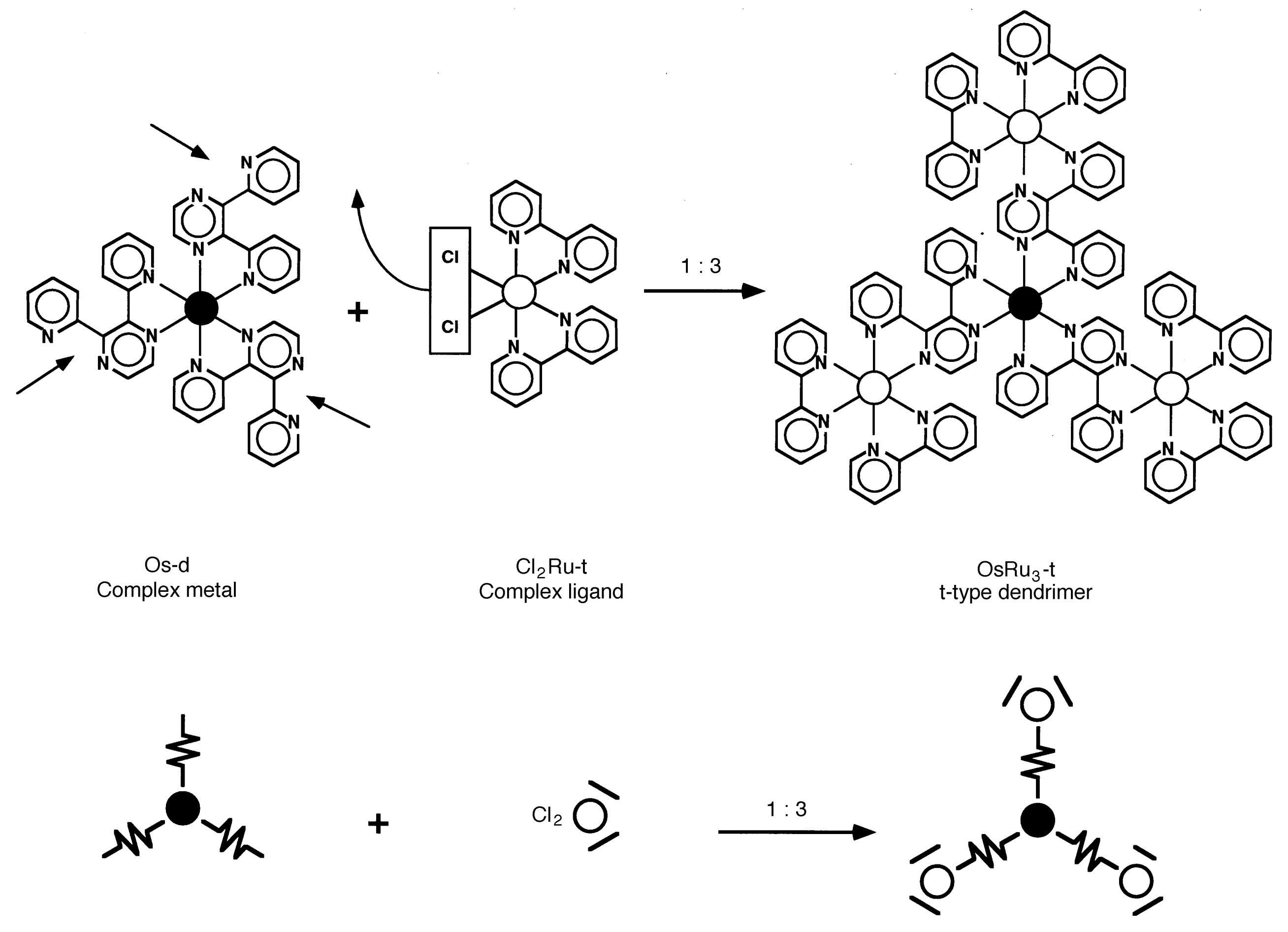

Fig. 3 Schematic representation of the reaction between the mononuclear Os-d complex metal and the mononuclear Cl_2Ru-t complex ligand to give the tetranuclear $OsRu_3$-t complex. Arrows indicate free chelating sites of Os-d and labile ligands of Cl_2Ru-t.

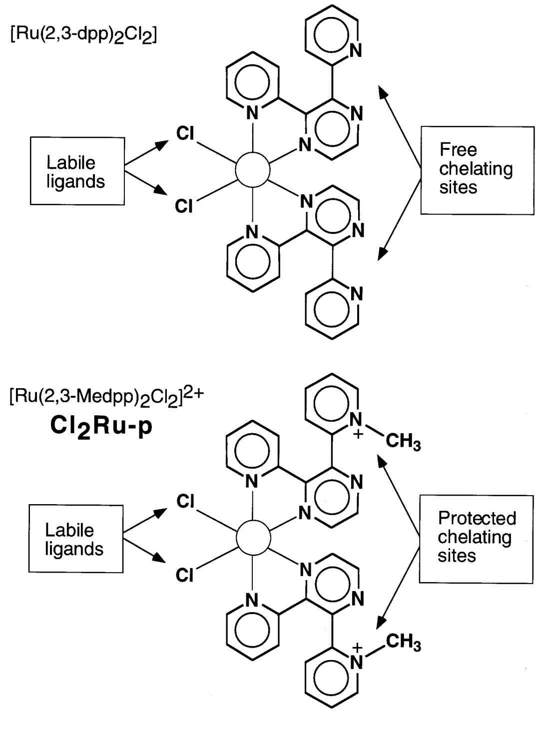

Fig. 4 Bifunctional self-reactive $Ru(2,3\text{-dpp})_2Cl_2$ complex and its protected $[Ru(2,3\text{-Medpp})_2Cl_2]^{2+}$ form

mers of higher generation (Fig. 5).[8] Such a strategy has been previously used to obtain homonuclear ruthenium(II) dendrimers containing up to 22 metal centres.[6]

As mentioned in the introductory section, the interest in highly branched polynuclear metal complexes, and more generally in dendritic species, is related to the 'small upward' construction of nanometre-size species. In this field, an important goal is the design and construction of dendrimers containing units of different chemical nature. An ordered array of different components can in fact generate valuable properties, such as the presence of cavities having different sizes, surfaces with specific functions, gradients for photoinduced directional energy and electron transfer, and sites for multi-electron transfer catalysis (Fig. 6).

The divergent and convergent synthetic strategies shown in Fig. 5 allow a step-by-step control of the growing process, so that building blocks containing different metals and/or ligands can be introduced at each step. In this work, we have used an $[Os(2,3\text{-dpp})_3]^{2+}$ core and $[Ru(2,3\text{-Medpp})_2Cl_2]^{2+}$ units in a divergent approach to prepare $[Os\{(\mu\text{-}2,3\text{-dpp})Ru(2,3\text{-Medpp})_2\}_3]^{14+}$ and $[Os\{(\mu\text{-}2,3\text{-dpp})Ru(2,3\text{-dpp})_2\}_3]^{8+}$ (tetranuclear dendrimers of the first generation) and then $[Os\{(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,3\text{-dpp})Ru(2,3\text{-Medpp})_2]_2\}_3]^{32+}$ and $[Os\{(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,3\text{-dpp})Ru(2,3\text{-dpp})_2]_2\}_3]^{20+}$ (decanuclear dendrimers of the second generation). Moreover the tetranuclear $[Os\{(\mu\text{-}2,3\text{-dpp})Ru(2,3\text{-dpp})_2\}_3]^{8+}$ core and the trinuclear $[\{Ru(bpy)_2(\mu\text{-}2,3\text{-dpp})\}_2RuCl_2]^{4+}$ units have been used in a convergent approach to obtain the docosanuclear $[Os\{(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,3\text{-dpp})Ru\{(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2\}_2]_2\}_3]^{44+}$ (third generation) dendrimer. To our knowledge, the docosanuclear compound is the first mixed-metal third-generation dendrimer prepared so far.

A further extension of this strategy towards the synthesis of

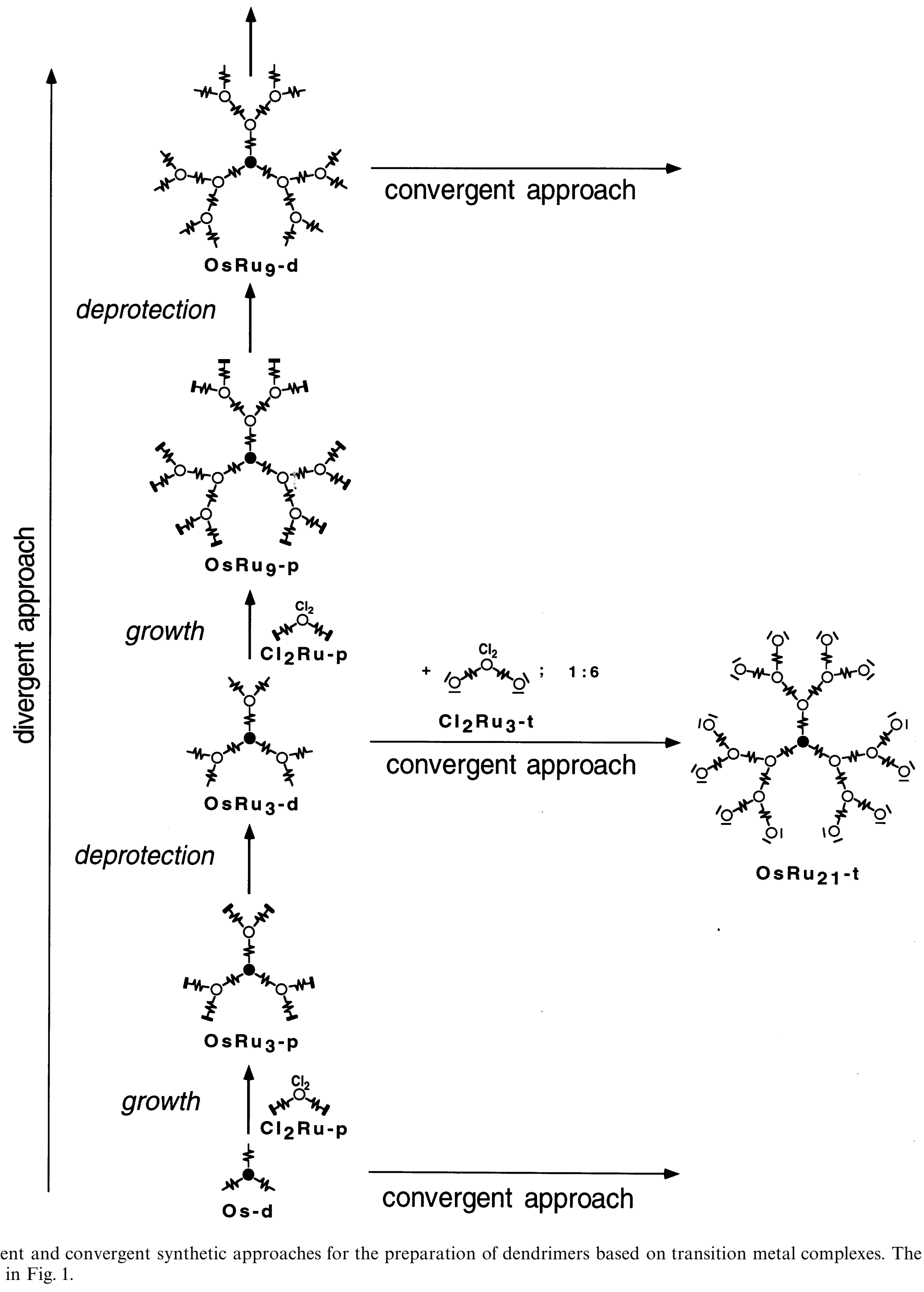

Fig. 5 Divergent and convergent synthetic approaches for the preparation of dendrimers based on transition metal complexes. The symbols used are explained in Fig. 1.

dendrimers containing units of different chemical nature can be based on the use, in the convergent approach, of branches containing metals and/or ligands different from those present in the core. Besides $[\{Ru(bpy)_2(\mu\text{-}2,3\text{-dpp})\}_2RuCl_2]^{4+}$,[4] interesting examples of trinuclear complex metal branches are $[\{Ru(biq)_2(\mu\text{-}2,3\text{-dpp})\}_2RuCl_2]^{4+}$,[8c,f] $[\{Ru(bpy)_2(\mu\text{-}2,5\text{-dpp})\}_2RuCl_2]^{4+}$,[4] $[\{Os(bpy)_2(\mu\text{-}2,3\text{-dpp})\}_2RuCl_2]^{4+}$,[4b,8f] $[\{Os(bpy)_2(\mu\text{-}2,3\text{-dpp})\}_2OsCl_2]^{4+}$,[9] $[\{Ru(bpy)_2(\mu\text{-}2,3\text{-dpp})\}_2OsCl_2]^{4+}$.[9]

General properties

The compounds reported in this paper are soluble in common solvents (*e.g.*, water, acetone and acetonitrile) and are stable both in the dark and under light excitation. In principle, they can exist as different isomers, depending on the *fac* or *mer* arrangement of the ligands around each metal centre. Furthermore, since each metal centre is a stereogenic centre, the preparation of polymetallic complexes necessarily leads to mixtures of several diastereoisomeric species. For these reasons structural investigations on these systems are difficult. Differences in the electrochemical and spectroscopic properties arising from the presence of isomeric species are not expected to be large.[10]

The species with high nuclearity exhibit a three-dimensional branching structure. Therefore, endo- and exo-receptor properties[7,11] can be expected (Fig. 6). The largest of our dendrimers contains 22 metal atoms, 21 bridging ligands, 24 peripheral ligands, and has an approximate size of 5 nm. We would like to stress that our dendrimers differ from most of those prepared

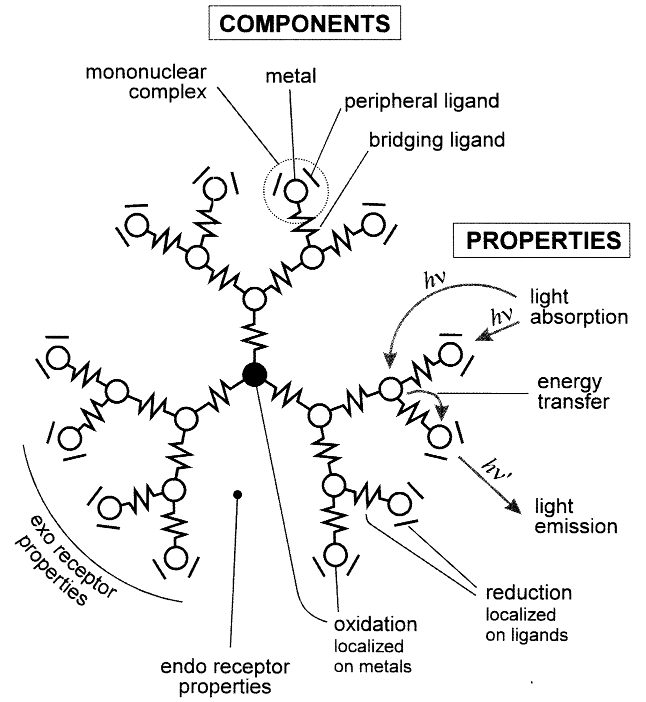

Fig. 6 Schematic representation of a docosanuclear dendrimer. Some properties are indicated.

so far for two fundamental reasons: (i) each metal-containing unit exhibits valuable intrinsic properties such as absorption of visible (solar) light, luminescence, and oxidation and reduction levels at accessible potentials;[12] (ii) by a suitable choice of the building blocks, they can incorporate many 'pieces of information' and therefore they can be used to perform valuable functions such as light harvesting, directional energy transfer, and exchange of a controlled number of electrons at a certain potential.[13,‡]

Previous investigations carried out on mono- and polynuclear compounds of the ruthenium(II) and osmium(II) polypyridine family[6,8,15,16] have shown that: (i) oxidation is metal centred; (ii) Os^{II} is oxidized at potentials considerably less positive than Ru^{II}; (iii) the electron donor power decreases in the ligand series bpy > 2,3-dpp > 2,3-$Medpp^+$ ⩾ m-2,3-dpp; (iv) the interaction between equivalent metal centres is noticeable for metals coordinated to the same bridging ligand, whereas it is negligible for metals that are further apart; (v) the interaction between equivalent ligands is noticeable for ligands coordinated to the same metal, whereas it is negligible for ligands that are further apart.

In the ruthenium(II) and osmium(II) polypyridine complexes luminescence originates from the lowest MLCT excited state which is formally spin forbidden.[12,17] Deactivation of the upper excited states to the lowest one is a very fast (picosecond timescale)[18] and highly efficient (100%)[19] process. In the 'localized molecular orbital' approach,[20] the excited electron and the corresponding hole are considered to be centred on the ligand and on the metal, respectively.

The ligands involved in our dendrimers exhibit different electron donor and electron acceptor properties. The electrochemical[6,8b,21] and luminescent[6,8b] behaviour of the complexes of the $[Ru(bpy)_n(2,3\text{-}dpp)_{3-n}]^{2+}$ family indicates that bpy is a better electron donor ligand than 2,3-dpp, and that monochelated 2,3-dpp is easier to reduce than coordinated bpy. When 2,3-dpp plays the role of a bis-chelating bridging ligand, its electron donor power toward a single metal decreases because the pyrazine ring is involved in the coordination of two metal centres, as evidenced by its reduction potential that becomes more positive by about 0.4 V.[6] Since the methylation of 2,3-dpp mainly concerns one of the pyridine rings, the electron donor and acceptor properties of the chelating site are only slightly affected; on the other hand a new easily reducible centre (the methylated pyridine ring) becomes present,[22] that is likely to contain the LUMO orbital of the complex.

In the dendritic species each metal-based unit will bring its own excited state and redox properties. It should be pointed out, however, that these properties are affected by intercomponent interaction (*vide infra*). From the above considerations, it follows that the energy order of the lowest excited states for the metal-based units relevant for our discussion (see later) is: $[Os(m\text{-}2,3\text{-}dpp)_3]^{2+} < [(m\text{-}2,3\text{-}dpp)Ru(bpy)_2]^{2+} < [Ru(m\text{-}2,3\text{-}dpp)_3]^{2+} < [(m\text{-}2,3\text{-}dpp)Ru(2,3\text{-}Medpp)_2]^{4+}$.

Absorption and emission properties

Fig. 7 shows the absorption spectra of $OsRu_{21}$-t and of the lower nuclearity $OsRu_9$-t and $OsRu_3$-t analogues. The spectra of the corresponding homonuclear Ru_{22}-t, Ru_{10}-t, and Ru_4-t complexes[6b] are shown in Fig. 8. In Fig. 9 the spectra of the protected $OsRu_3$-p and $OsRu_9$-p dendrimers are displayed. Absorption and emission data are collected in Table 1. As one can see, all the compounds exhibit intense ligand-centred (LC) bands in the UV region and moderately intense metal-to-ligand charge transfer (MLCT) bands in the visible. To a first approximation, each metal-based unit carries its own absorption properties in the polynuclear species, so that the molar absorption coefficients are proportional to the nuclearity

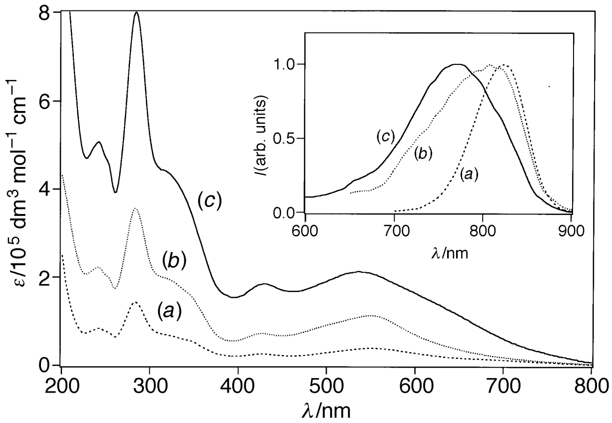

Fig. 7 Absorption spectra of (*a*) $OsRu_3$-t, (*b*) $OsRu_9$-t, and (*c*) $OsRu_{21}$-t in acetonitrile solution at room temperature. Inset shows their emission spectra under the same experimental conditions.

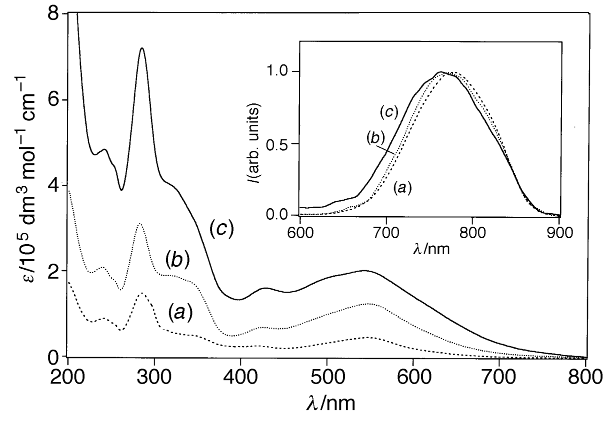

Fig. 8 Absorption spectra of (*a*) Ru_4-t, (*b*) Ru_{10}-t, and (*c*) Ru_{22}-t in acetonitrile solution at room temperature. Inset shows their emission spectra under the same experimental conditions.

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‡ Dendrimers made of different organic chromophores have been recently reported by Moore and coworkers.[14]

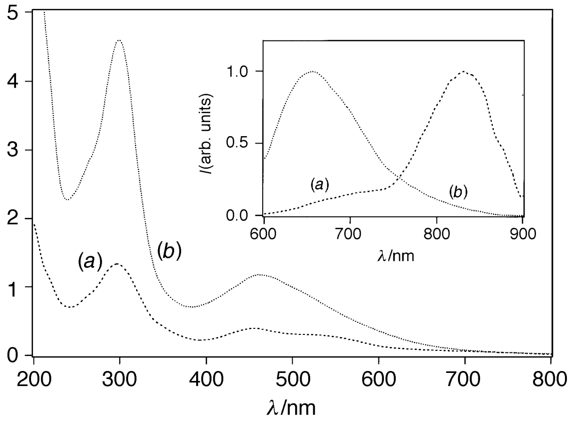

Fig. 9 Absorption spectra of (*a*) OsRu$_3$-p and (*b*) OsRu$_9$-p in acetonitrile solution at room temperature. Inset shows their emission spectra under the same experimental conditions.

Table 1 Spectroscopic and photophysical data^a

	absorption^b	luminescence		
	l_{max}/nm (e/dm^3 mol^{-1} cm^{-1})	$l_{max}{}^c$/nm	t^d/ns	$W_{em}{}^d/10^3$
Os-d^e	476 (18 000), 300 (27 800)	765	82	—
OsRu$_3$-p^f	526(sh) (34 500), 454 (45 000)	832	445^g	6.5
OsRu$_3$-t^h	551 (40 000), 283 (144 000)	875	18	1.0
Ru$_4$-t^i	545 (46 000), 285 (149 000)	811	60	1.0
OsRu$_9$-p	459 (118 000), 298 (460 000)	700	380	4.1
OsRu$_9$-t^j	550 (117 000), 283 (358 000)	808	65	*ca.*0.5
Ru$_{10}$-t^j	541 (125 000), 282 (329 000)	809	55	1.0
OsRu$_{21}$-t	547 (213 000), 284 (801 000)	805	200	0.85
Ru$_{22}$-t^k	542 (202 000), 284 (682 000)	786	45	0.30

[a] Acetonitrile solution, 298 K. [b] Lowest energy band in the visible and prominent absorption maximum in the UV region. [c] Corrected emission maxima. [d] Deaerated solution, unless otherwise noted. [e] See also ref. 8(*a*), 15 and K. Kalyanasundaram and Md. K. Nazeeruddin, *Chem. Phys. Lett.*, 1989, **158**, 45. [f] For preliminary data, see V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni and M. Venturi, *Coord. Chem. Rev.*, 1994, **132**, 1. [g] Air-equilibrated solution. [h] See also ref. 8(*a*). [i] See also ref. 8(*b*) and W. R. Murphy Jr., K. J. Brewer, G. Gettliffe and J. D. Petersen, *Inorg. Chem.*, 1989, **28**, 81. [j] Ref. 8(*f*). [k] Ref. 6.

(Fig. 8 and 9). Therefore the light harvesting capability increases with increasing nuclearity. It is well known that the transition from the singlet ground state to the lowest triplet MLCT level is more allowed in the osmium(II) than in the ruthenium(II) complexes. This results in a more intense tail in the red region of the spectra of the osmium-based complexes. This difference can be easily noted comparing the spectra of OsRu$_3$-t (Fig. 7) and Ru$_4$-t (Fig. 8).

In the p-type compounds the MLCT bands are displaced to higher energy compared to the analogous t-type compounds because the protected bridging ligand is a worse electron donor than bpy (Fig. 9).

All the dendrimers reported in this paper display luminescence in fluid solution at room temperature. The emission spectra of OsRu$_{21}$-t, OsRu$_9$-t and OsRu$_3$-t (Fig. 7, inset), Ru$_{22}$-t, Ru$_{10}$-t and Ru$_4$-t (Fig. 8, inset) and OsRu$_3$-p (Fig. 9, inset) are shown. The most important photophysical parameters are gathered in Table 1.

In the heteronuclear t-type dendrimers, the emission band moves to higher energy and broadens with increasing nuclearity (Fig. 7, inset). The emission of OsRu$_3$-t is characteristic of the osmium-based core, showing that energy transfer takes place from the three peripheral ruthenium-based moieties to the core. The corrected excitation spectrum shows that energy transfer occurs with unitary efficiency.[8a] In OsRu$_9$-t, the emission band clearly results from two different contributions (Fig. 7, inset), one due to the [Os(m-2,3-dpp)$_3$]$^{2+}$ core, and the other (at higher energy) due to the peripheral [(m-2,3-dpp)Ru(bpy)$_2$]$^{2+}$ units.[8f] This can be rationalized on the basis of the energy level diagram of Fig. 10(*a*). The lowest energy excited state is localized on the [Os(m-2,3-dpp)$_3$]$^{2+}$ core, and the energy of the peripheral [(m-2,3-dpp)Ru(bpy)$_2$]$^{2+}$ units is lower than that of the intermediate [Ru(m-2,3-dpp)$_3$]$^{2+}$ units. Therefore energy transfer from the peripheral units to the central one is at least in part prevented. For OsRu$_{21}$-t, a stronger contribution from ruthenium-based units is apparent (Fig. 7, inset). This is consistent with (i) a larger number of ruthenium-based units and (ii) the presence of intermediate ruthenium-based units having higher energy than the peripheral ones as in OsRu$_9$-t.

In the homonuclear ruthenium-based t-type dendrimers, luminescence occurs almost at the same wavelength (Fig. 8, inset) and exhibits comparable lifetimes and quantum yields regardless of nuclearity. This is an expected result because in all cases the lowest energy excited states are localized on the peripheral [(m-2,3-dpp)Ru(bpy)$_2$]$^{2+}$ units and there is a gradient for energy transfer from the centre to the periphery [Fig. 10(*b*)].[6,8f]

The emission properties of the p-type family can be interpreted on the basis of the discussion above.

Electrochemical properties

The electrochemical behaviour has been studied in argon-purged MeCN solution at room temperature. The polynuclear complexes contain a large number of redox-active units, and it is known from previous investigations on analogous complexes[6,8,12,21] that each metal centre can undergo a one-electron oxidation and each ligand can undergo at least one reduction process. The half-wave potential values are gathered in Table 2.

Oxidation. The polynuclear complexes examined here contain one osmium-based core and several ruthenium-based units. In all cases, the observed oxidation processes are reversible and, as expected,[6,8,12] oxidation of the osmium-based unit preceeds oxidation of the ruthenium-based ones. In the polynuclear compounds oxidation of the osmium-based core occurs at more positive potentials than in the mononuclear Os-d compound, according to the weaker electron donor power of m-2,3-dpp compared with 2,3-dpp (see General properties). The overall positive charge of the dendrimer increases strongly (i) with increasing nuclearity and (ii) on replacing the peripheral bpy ligands with protected 2,3-Medpp$^+$. The increase of positive charge has only little effect on the oxidation potential of the osmium-based core because (i) the increase in nuclearity is accompanied by an increase in the dendrimer size and (ii) the charges of the protected ligands are localized in the periphery of the structure.

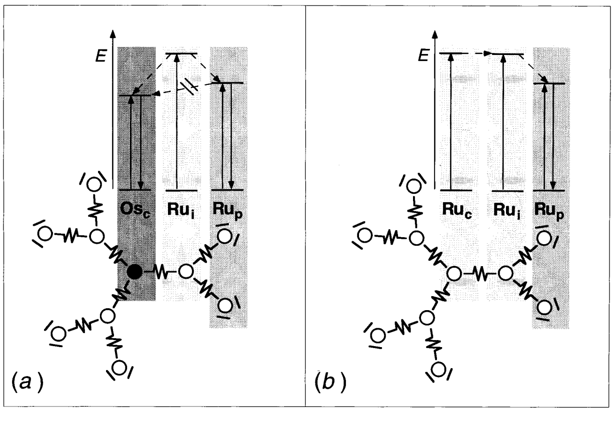

Fig. 10 Simplified schematic diagram showing the energy of the lowest excited state for the metal-based units along a branch of the OsRu$_9$-t (*a*) and Ru$_{10}$-t (*b*) dendrimers

Table 2 Electrochemical results in argon-purged acetonitrile solution at room temperature[a]

compound	$E_{1/2}^{\text{ox}}[n]^b$ (site)[c]	$E_{1/2}^{\text{red}}[n]^b$ (site)[c]
Os-d[d]	+1.21[1](Os)	−0.83[1](2,3-dpp), −1.04[1](2,3-dpp), −1.39[1](2,3-dpp)
$OsRu_3$-t[d]	+1.36[1](Os), +1.61[3](Ru_p)	−0.44[1](2,3-dpp), −0.62[1](2,3-dpp), −1.08[1](2,3-dpp), −1.20[*ca.*1](2,3-dpp)[e]
$OsRu_3$-p	+1.36[*ca.*1](Os)	−0.45[1](2,3-dpp), −0.78irr[6](2,3-$Medpp^+$), −0.99[1](2,3-dpp), −1.18[1] (2,3-dpp), −1.31[1](2,3-dpp)[e]
$OsRu_9$-t	+1.35[1](Os), +1.55[6](Ru_p)[f]	−0.43[1](2,3-dpp), −0.58[2](2,3-dpp), −0.68[6](2,3-dpp), −0.91[1][e]
$OsRu_9$-p	+1.45[1](Os), +1.82[3](Ru_i)	−0.78irr[12](2,3-$Medpp^+$), −1.00[*ca.*6](2,3-dpp)[e]
$OsRu_{21}$-t	+1.42[1](Os), +1.54[12](Ru_p)	−0.63[*ca.*12](2,3-dpp)[e]

[a] Potentials in volts *vs.* SCE; unless otherwise noted, the waves are reversible; for irreversible reductions (irr), the potential is evaluated from the DPV peaks; for the symbols used to indicate the compounds, see caption to Fig. 2. [b] Number of exchanged electrons. [c] Site(s) involved in the redox processes; the subscripts p and i on the metal stand for peripheral and intermediate positions. [d] Revised data; for previously reported data, see G. Denti, S. Campagna, L. Sabatino, S. Serroni, M. Ciano and V. Balzani, in *Photochemical conversion and storage of solar energy*, ed. E. Pelizzetti and M. Schiavello, Kluwer, Dordrecht, 1991, p. 27. [e] Other broad waves follow at more negative potential. [f] Revised data; for previously reported data, see ref. 8(*f*).

Oxidation of the osmium-based core can be followed by oxidation processes involving ruthenium-based units which occupy internal or peripheral sites (Fig. 2). In the deca- and docosa-nuclear compounds, all the internal ruthenium-based units are equivalent from the viewpoint of the first coordination sphere since each metal is surrounded by three bridging ligands, $[Ru(m\text{-}2,3\text{-dpp})_3]^{2+}$. The dendrimers, however, have an onion-shaped structure (Fig. 2) and therefore only the units that belong to the same shell are topologically equivalent and exhibit the same properties. Slightly different properties can be expected for units belonging to different inner shells.

The peripheral sites in our dendrimers can be of type t, or p, or d (Fig. 2). Since the d-type dendrimers give rise to electrode adsorption, we discuss only the t- or p-type compounds. Previous studies showed that the units belonging to the same shell (inner or peripheral) interact only weakly and are therefore oxidized simultaneously in multielectron processes.

For $OsRu_3$-p no oxidation process is observed after the oxidation of the osmium-based core. In $OsRu_9$-p, oxidation of the core is followed by a three-electron oxidation process at +1.82 V (Table 2). The number of electrons involved and the potential value (which is that found for the $[Ru(m\text{-}2,3\text{-dpp})_3]^{2+}$ inner units of Ru_4-p and Ru_{10}-p)[6b] suggest that this process is due to the simultaneous oxidation of the three equivalent ruthenium-based units occupying the intermediate positions in the dendrimer structure. The results obtained for $OsRu_3$-p and $OsRu_9$-p indicate that the peripheral p-type units cannot be oxidized in the potential window examined, as previously observed for the protected homonuclear ruthenium dendrimers.[6b] In the analogous $OsRu_3$-t and $OsRu_9$-t compounds, oxidation of the osmium core is always followed by the simultaneous oxidation of the peripheral t-type ruthenium-based units. Accordingly, for $OsRu_3$-t a three-electron process at +1.61 V, and for $OsRu_9$-t a six-electron process at +1.55 V are observed. The slightly more positive potential observed for the first complex is probably due to the closeness of the ruthenium units with the already oxidized osmium core. Even in the case of $OsRu_{21}$-t, oxidation of the osmium core is followed by the oxidation of the peripheral t-type units, as shown by the twelve-electron process observed at +1.54 V (Table 2). Previous studies[6] have shown that the oxidation of the peripheral t-type ruthenium-based units in the homonuclear ruthenium dendrimers occurs at a potential very similar to that found for the t-type heteronuclear compounds. These results show that the potential at which the oxidation of peripheral units takes place does not substantially depend on the nature of the internal part of the dendrimer.

Reduction. Because of the presence of a large number of polypyridine ligands, each capable of undergoing several reduction processes,[6b,21] the electrochemical reduction of polynuclear compounds of this type shows very complex patterns (for the mononuclear Ru-d compound, as many as 12 reduction processes have been evidenced[21] in the range −0.94 to −2.83 V). We will only discuss briefly the behaviour of the compounds of lower nuclearity, excluding the d-type compounds because of their electrode adsorption.

The mononuclear Os-d compound shows three one-electron processes. They correspond to the successive reduction of the three 2,3-dpp ligands which interact because they are linked to the same metal.

In $OsRu_3$-t the osmium-based core is linked to three $[Ru(bpy)_2]^{2+}$ units. It is well known that the bpy ligands are more difficult to reduce than the 2,3-dpp ligands.[21] Therefore even in this compound the first reduction processes should involve 2,3-dpp. Furthermore, it is expected that bridging 2,3-dpp is easier to reduce that monocoordinated 2,3-dpp. In agreement with such expectations, $OsRu_3$-t shows three one-electron reduction waves at less negative potentials than Os-d, assigned to the first reduction of the three bridging ligands. This series of waves is followed by a single wave, presumably due to the second reduction of a bridging ligand, and other high and broad waves assigned to overlapping second reduction of the other two bridging ligands and first reduction of the six bpy ligands.

In $OsRu_3$-p the osmium-based core is linked to three $[Ru(2,3\text{-Medpp})_2]^{4+}$ units. The methylated site of the 2,3-$Medpp^+$ ligand undergoes an irreversible reduction at −0.76 V.[22] Such a reduction process is practically unaffected by coordination of a metal on the other site of the ligand. In fact, it occurs practically at the same potential as in the free ligand.[22] Therefore in $OsRu_3$-p it is expected that the reduction pattern of the three inner bridging ligands, observed for $OsRu_3$-t, is perturbed by the reduction processes of the six peripheral protected ligands. The experimental results show that a small wave at −0.45 V is followed by an approximately six times larger wave at −0.78 V, followed by three small waves at −0.99, −1.18, and −1.31 V, and other large waves. Tentatively, we assign (i) the first wave to the one-electron reduction of an inner bridging ligand, as observed for $OsRu_3$-t, (ii) the big wave at −0.78 V to the simultaneous reduction of the six peripheral methylated sites, (iii) the two successive small waves to the first reduction of the two other inner bridging ligands, (iv) the small wave at −1.31 V to the second reduction of a bridging ligand, and (v) the following broad and large waves to overlapping second reduction of the other two bridging ligands and of the peripheral ligands.

For the decanuclear $OsRu_9$-t and $OsRu_9$-p, the reduction patterns are similar to those of the corresponding tetranuclear compounds, albeit much more complicated because of the presence of an intermediate shell containing six bridging ligands not exactly equivalent to the three inner ones. In addition, for $OsRu_9$-p, the irreversible reduction of the twelve protected peripheral ligands prevents the observation of one-electron process(es) that could be present at less negative potential. For $OsRu_{21}$-t, the first, broad, strongly asymmetric wave with a maximum at -0.63 V, corresponding to approximately 12 electrons, can be assigned to the reduction of bridging ligands, and the following huge waves with maxima at -1.43 and -1.76 V (not reported in Table 2), corresponding to large numbers of electrons, should be due to overlapping second reduction of the bridging ligands and first and second reduction of the peripheral bpy ligands.

Conclusions

The divergent and convergent synthetic strategies to the dendrimers described in this paper are characterized by a step-by-step control of the growing process. Therefore, building blocks containing different metals and/or ligands can be introduced at each step. We have used the $[Os(2,3\text{-dpp})_3]^{2+}$ core and $[Ru(2,3\text{-Medpp})_2Cl_2]^{2+}$ units in a divergent approach to prepare tetra- and deca-nuclear mixed-metal dendrimers. Moreover, we have used the tetranuclear $[Os\{(m\text{-}2,3\text{-dpp})Ru(2,3\text{-dpp})_2\}_3]^{8+}$ core and trinuclear $[\{Ru(bpy)_2(m\text{-}2,3\text{-dpp})\}_2RuCl_2]^{4+}$ units in a convergent approach in order to obtain the $[Os\{(m\text{-}2,3\text{-dpp})Ru[(m\text{-}2,3\text{-dpp})Ru\{(m\text{-}2,3\text{-dpp})Ru(bpy)_2\}_2]_2\}_3]^{44+}$ docosanuclear compound. To our knowledge, this compound is the first mixed-metal third-generation dendrimer prepared so far.

To a first approximation, in the dendrimers each metal-based unit carries its own absorption properties. Therefore the light harvesting capability increases with increasing nuclearity. All the dendrimers reported in this paper display luminescence in fluid solution at room temperature. Exoergonic inter-component energy-transfer processes are very efficient.

The dendrimers contain a large number of redox-active units. On oxidation, a reversible one-electron process of the osmium-based core occurs first, and is then followed by oxidation processes involving ruthenium-based units which occupy internal or peripheral sites. On reduction, complex patterns are observed because of the presence of a large number of polypyridine ligands (as many as 45 in the docosanuclear dendrimer), each capable of undergoing several reduction processes.

Experimental

Equipment and methods

Absorption spectra were obtained in acetonitrile solution at room temperature using a Perkin-Elmer 1-6 spectrophotometer. Luminescence spectra were obtained with a Perkin-Elmer LS-50 spectrofluorimeter. Emission lifetimes were measured with an Edinburgh 199 single-photon counting equipment. Emission quantum yields were measured at room temperature (20 °C) with the optically dilute method[23] calibrating the spectrofluorimeter with a standard lamp. $[Ru(bpy)_3]^{2+}$ in aerated aqueous solution was used as a quantum yield standard, assuming a value of 0.028.[24]

Electrochemical measurements were carried out in argon-purged acetonitrile solution at room temperature with a PAR 273 multipurpose equipment interfaced to a PC. The working electrode was a Pt microelectrode or a glassy carbon (8 mm^2, Amel) electrode. The counter electrode was a Pt wire, and the reference electrode was a SCE separated with a fine glass frit. The concentration of the complexes was 3×10^{-4} M and tetraethylammonium hexafluorophosphate 0.05 M was used as supporting electrolyte. Cyclic voltammograms were obtained at sweep rates of 20, 50, 200, 500 and 1000 mV s^{-1}; differential pulse voltammetry (DPV) experiments were performed with a scan rate of 20 mV s^{-1}, a pulse height of 75 mV, and a duration of 40 ms. For reversible processes the half-wave potential values are reported; the same values are obtained from the DPV peaks and from an average of the cathodic and anodic cyclic voltammetric peaks. For irreversible processes the reported values are those evaluated from the peak potentials in the DPV experiments. Both CV and DPV techniques have been used to measure the number of the exchanged electrons in each redox process,[25] utilizing $[Ru(bpy)_3]^{2+}$ as a reference compound, for which the oxidation and reduction processes are reversible and monoelectronic.[26] To establish the reversibility of a process, we used the criteria of (i) separation of 60 mV between cathodic and anodic peaks, (ii) close to unity ratio of the intensities of the cathodic and anodic currents, and (iii) constancy of the peak potential on changing sweep rate in the cyclic voltammograms.

Experimental errors in the reported data are as follows: absorption maxima, 2 nm; emission maxima, 5 nm; emission lifetimes, 10%; emission quantum yields, 20%; redox potentials, 20 mV. As far as molar absorption coefficients are concerned, the uncertainty in their absolute values is *ca.* 10% because of the highly diluted solutions used (10^{-5}–10^{-4} M).

Characterization of the dendrimers

Characterization of large molecules like dendrimers is a difficult task.[7] For neutral compounds, techniques based on colligative properties can be used to determine the molecular mass. Our compounds, however, are highly charged ions, and the use of the above techniques is not advisable because of the large number of counter ions. Mass spectrometry has not yet been developed for compounds carrying such a high electric charge, and light scattering can hardly be used because of the strong absorption in all the UV and visible spectral region.

In spite of the above difficulties, a reliable characterization of our dendrimers has been achieved by using a variety of techniques.

(1) Each compound (including precursors) was purified until TLC showed the presence of only one spot.

(2) Each building block was checked to be stable under the experimental conditions. It is already known that in such compounds no ligand or metal scrambling occurs, as shown by the synthesis of a number of tetra-,[8c] hexa-[4a] and deca-nuclear[8d,f] species containing different metals and/or ligands in predetermined sites of the structure.

(3) Each one of the reaction steps (Fig. 5) was accurately monitored as follows. (i) The reaction of the 'complex ligand' compounds (Os-d and $OsRu_3$-d) with the 'complex metal' Cl_2Ru-p was carried out under stoichiometric conditions. TLC analysis $[Al_2O_3, CH_2Cl_2\text{–}MeOH\ (9:1)]$ showed that in each case at least 90% of Cl_2Ru-p had reacted. (ii) For the product of the p-type compounds obtained in each growing step the ratio between aromatic and aliphatic protons in the ^1H NMR spectrum (where the strong signals of the methyl protons lie in a clean spectral window around d 4) was consistent with the expected formulations. (iii) IR analysis on the p-type compounds showed the absence of the 990 cm^{-1} band of unbridged 2,3-dpp.

The deprotection steps were carried out with a large excess of demethylating agent. The purified products did not show any ^1H NMR signal due to the presence of methyl groups, so we can exclude the presence of residual methylated sites (<1%).

The reaction of $OsRu_3$-d with the 'complex metal' Cl_2Ru_3-t (which was fully characterized by several techniques including FAB MS)[8f,27] was carried out under stoichiometric conditions until complete ($\geqslant 90$%) disappearance of Cl_2Ru_3-t (TLC analysis).

(4) Consistent elemental analyses were obtained. It should be noted, however, that the C, H, and N values do not change significantly on increasing the dendrimer size. For this reason, we measured the ruthenium and osmium content of the $OsRu_{21}$-t species with atomic absorption spectrometry using a method described elsewhere.[28]

(5) The luminescence and electrochemical properties are fully consistent with the reported formulations.

Synthesis

The preparations of the complexes $[Os(2,3\text{-dpp})_3][PF_6]_2$ (Os-d),[15] $[Ru(2,3\text{-Medpp})_2Cl_2][PF_6]_2$ (Cl_2Ru-p),[6b] and $[Ru\{(m\text{-}2,3\text{-dpp})Ru(bpy)_2\}_2Cl_2][PF_6]_4$ (Cl_2Ru_3-t)[4a] have been previously reported. All the compounds dealt with in this paper have been characterized using the same methods previously described.[6b]

$[Os\{(m\text{-}2,3\text{-dpp})Ru(2,3\text{-Medpp})_2\}_3][PF_6]_{14}$ ($OsRu_3$-p). Solid $AgNO_3$ (0.009 g, 0.053 mmol) was added to a suspension of $[Ru(2,3\text{-Medpp})_2Cl_2][PF_6]_2$ (0.026 g, 0.027 mmol) in H_2O–EtOH (1 : 2, v/v) (10 ml). After 2 h stirring at room temperature, $[Os(2,3\text{-dpp})_3][PF_6]_2$ (0.011 g, 0.009 mmol) was added, and the reaction mixture refluxed for 72 h. After cooling to room temperature the AgCl formed was removed by repeated centrifugations, then the reaction mixture was rotary-evaporated to a small volume (about 3 ml) and a saturated methanolic solution of NH_4PF_6 (*ca.* 4 ml) was added. The solid so obtained was separated by filtration, dissolved in a small volume of MeCN and purified by flash chromatography on Sephadex G-10. From the eluate a wine-red solid was recovered by addition of CH_2Cl_2, partial evaporation *in vacuo* and filtration. A further recrystallization from MeCN–CH_2Cl_2 of the solid provided the product which was washed with small portions of CH_2Cl_2, then with Et_2O, and dried *in vacuo* (yield: 67%). Anal. calc. for $C_{132}H_{108}F_{84}N_{36}P_{14}OsRu_3 \cdot 2H_2O$: C, 33.3; H, 2.4; N, 10.6. Found: C, 33.3; H, 2.5; N, 10.5%.

$[Os\{(m\text{-}2,3\text{-dpp})Ru(2,3\text{-dpp})_2\}_3][PF_6]_8$ ($OsRu_3$-d). A solution containing $[Os\{(m\text{-}2,3\text{-dpp})Ru(2,3\text{-Medpp})_2\}_3][PF_6]_{14}$ (0.080 g, 0.17 mmol) and a very large excess of 1,4-diazabicyclo[2.2.2]octane (DABCO, 0.370 g, 3.3 mmol) in dry acetonitrile (15 ml) was refluxed for 6 d. After cooling of the solution to room temperature and addition of EtOH, the reaction mixture was concentrated to induce the precipitation of the crude product that was separated by filtration. This was then dissolved in a small amount of MeCN and purified by flash chromatography on Sephadex G-10. On adding Et_2O to the partially evaporated eluate the product precipitated as a brown powder, which was filtered off, washed with Et_2O, and dried *in vacuo* (yield: 75%). Anal. calc. for $C_{126}H_{90}F_{48}N_{36}P_8OsRu_3 \cdot 3H_2O$: C, 39.6; H, 2.5; N, 13.2. Found: C, 39.4; H, 2.4; N, 13.0%.

$[Os\{(m\text{-}2,3\text{-dpp})Ru[(m\text{-}2,3\text{-dpp})Ru(2,3\text{-Medpp})_2]_2\}_3[PF_6]_{32}$ ($OsRu_9$-p). Solid $AgNO_3$ (0.035 g, 0.208 mmol) is added to a suspension of $[Ru(2,3\text{-Medpp})_2Cl_2][PF_6]_2$ (0.100 g, 0.104 mmol) in H_2O–EtOH (1 : 2, v/v) (10 ml). After 2 h stirring at room temperature, $[Os\{(m\text{-}2,3\text{-dpp})Ru(2,3\text{-dpp})_2\}_3][PF_6]_8$ (0.065 g, 0.017 mmol) was added, and the reaction mixture was refluxed for 7 d. After cooling to room temperature the AgCl formed was removed by repeated centrifugations, then the reaction mixture was rotary-evaporated to a small volume (*ca.* 3 ml) and an excess of solid NH_4PF_6 was added. The solid so obtained was separated by filtration, dissolved in a small volume of MeCN and purified by flash chromatography on Sephadex G-25. From the eluate the brown–red product was recovered by addition of EtOH, partial evaporation *in vacuo* and filtration (yield: 25%). Anal. calc. for $C_{306}H_{246}F_{192}N_{84}P_{32}OsRu_9$: C, 33.8; H, 2.3; N, 10.8. Found: C, 33.7; H, 2.4; N, 10.6%.

$[Os\{(m\text{-}2,3\text{-dpp})Ru[(m\text{-}2,3\text{-dpp})Ru(2,3\text{-dpp})_2]_2\}_3][PF_6]_{20}$ ($OsRu_9$-d). A solution containing $[Os\{(m\text{-}2,3\text{-dpp})Ru[(2,3\text{-dpp})Ru(2,3\text{-Medpp})_2]_2\}_3][PF_6]_{32}$ (0.030 g, 0.003 mmol) and a very large excess of DABCO (0.185 g, 1.65 mmol) in dry acetonitrile (15 ml) was refluxed for 6 d. After cooling of the solution to room temperature and addition of EtOH, the reaction mixture was concentrated to induce the precipitation of the crude product which was separated by filtration. This was then dissolved in a small amount of MeCN and purified by chromatography on Sephadex G-25 (acetonitrile eluent). On adding Et_2O to the partially evaporated eluate the product precipitated as brown powder, which was filtered off, washed with Et_2O and dried *in vacuo* (yield: 90%). Anal. calc. for $C_{294}H_{210}F_{120}N_{84}P_{20}OsRu_9$: C, 39.5; H, 2.4; N, 13.2. Found: C, 39.4; H, 2.5; N, 13.1%.

$[Os\{(m\text{-}2,3\text{-dpp})Ru[(m\text{-}2,3\text{-dpp})[Ru(m\text{-}2,3\text{-dpp})Ru\text{-}(bpy)_2]_2]_2\}_3][PF_6]_{44}$ ($OsRu_{21}$-t). $[Ru\{(m\text{-}2,3\text{-dpp})Ru(bpy)_2\}_2Cl_2][PF_6]_4$ (0.106 g, 0.052 mmol) in 5 ml of water–ethanol (1 : 1, v/v) was treated with silver nitrate (0.014 g, 0.082 mmol). After the mixture had been stirred at room temperature for 2 h, a solution of $[Os\{(m\text{-}2,3\text{-dpp})Ru(2,3\text{-dpp})_2\}_3][PF_6]_8$ ($OsRu_3$-d) (0.032 g, 0.009 mmol) in ethylene glycol (3 ml) was added. The reaction mixture was refluxed for 7 d, then cooled to room temperature. AgCl was separated by repeated centrifugations, the mother-liquor concentrated by evaporation *in vacuo*, and an excess of solid NH_4PF_6, methanol (2 ml) and diethyl ether (10 ml) were added. The crude product was filtered off, dissolved in a small amount of MeCN and purified by chromatography on Sephadex G-75 (acetonitrile eluent). The eluate was rotary evaporated *in vacuo* to 2 ml, and the $OsRu_{21}$-t product was recovered as a purple powder by addition of about 20 ml of diethyl ether (yield: 76%). Anal. calc. for $OsRu_{21}$-t: Os, 1.1; Ru, 12.2. Found: Os, 0.9; Ru, 10.5%.

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