

Designing Dendrimers Based on Transition-Metal Complexes. Light-Harvesting Properties and Predetermined Redox Patterns

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Introduction

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 nanometers. Chemists can construct nanometer-sized species by a "small-upward" approach starting with molecular components. This approach is very appeal-

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ingsince it allows the assembly of functionally integrated molecular building blocks.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.^{1,2} When the molecular building blocks contain transition metals, a strategy called "complexes as metals/complexes as ligands"^{3,4} can allow the construction of large polynuclear metal complexes via metal–ligand coordination bonds.

In the past few years, a great number of luminescent polynuclear transition-metal complexes have been synthesized.⁵ At the same time, in the field of organic chemistry, there has been an extraordinary development in research dealing with highly branched treelike species, variously called cascade molecules, arborols, or, more commonly, dendrimers.⁶ Such compounds are interesting from a fundamental viewpoint and promising for a variety of applications.

Of particular interest are the dendrimers that incorporate some specific properties in their building blocks such as the capability to absorb visible light, to give luminescence, and to undergo reversible multielectron redox processes. Such species, in fact, could find applications as components in molecular electronics^{1a} and as photochemical molecular devices^{1b} for solar energy conversion^{1b,7} and information storage.¹ Transition-metal complexes of polypyridine-type ligands⁸ are ideal components to build up dendrimers of this type. We have therefore developed divergent and convergent synthetic procedures based on the "complexes as metals/complexes as ligands" strategy to prepare luminescent and redox-active dendrimers.⁹ Species containing up to 22 metal-based units have been obtained. The interest in these dendrimers is related not only 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 absorption spectra, luminescence, redox levels, etc.). As we will see below, one of the advantages of the "complexes as metals/complexes as ligands" synthetic strategy is that one can use the desired building block at each stage of the synthesis, thereby introducing specific pieces of information in selected positions of the supramolecular array.

The metals and ligands used to build up our compounds are shown in Figure 1 together with their graphic symbols and abbreviations.

Synthetic Strategy

Mononuclear transition-metal complexes are synthesized by combining metal ion (M) and free ligands (L), as shown in eq 1. In the "complexes as metals/complexes as ligands"

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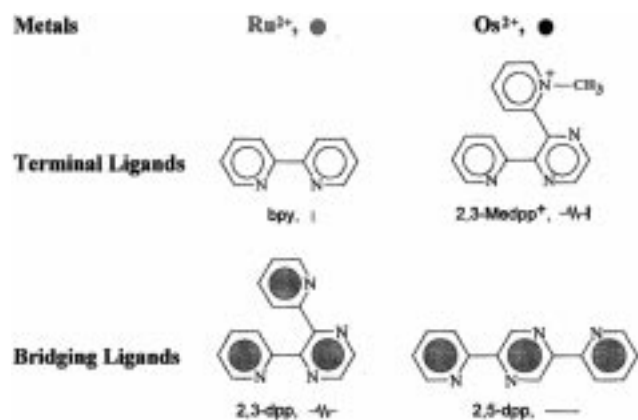


FIGURE 1. Formulas of the ligands, abbreviations, and graphic symbols used to represent the components of the dendrimers.



strategy,^{3,4} one uses complexes (building blocks) in the place of the metal (M) and/or of the ligands (L). The place of M can be taken by mono- or oligonuclear complexes that possess easily replaceable ligands, so that they can give rise to species with unsaturated metal coordination sites ("complex metals"), and the place of L can be taken by mono- or oligonuclear complexes which contain free chelating sites ("complex ligands").

Complexes of very high nuclearity can be obtained with this strategy if suitable polynuclear building blocks are available.^{10–12} An example is illustrated in Figure 2, which shows the reaction of a mononuclear complex ligand having three free chelating sites with three equivalents of a trinuclear complex metal, to form a decanuclear species.¹⁰ By a clever choice of the reaction partners, it is possible to obtain compounds where different metals and ligands can be located in the desired positions of the supramolecular structure.

Dendrimers can be constructed by two different approaches.⁶ One is the convergent (or "outside in") construction, whereby preformed branched arms are attached to a more or less large core, as shown in the example of Figure 2. An alternative and more general strategy is that called divergent (or "inside out"). The latter is an iterative procedure which starts with an initial core containing n reactive sites. To this core (0th 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.

The divergent iterative approach requires the availability of 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 could be the compound Ru(2,3-dpp)₂Cl₂, shown in Figure 3.¹¹ Unfortunately, a species like this is unavoidably self-reactive under the preparative conditions because the free chelating sites of one molecule would substitute the labile ligands of another molecule, leading to a mixture of species having dispersed and uncontrolled

nuclearities. To obtain satisfactory results, one of the two functions has to be temporarily blocked. This is the case of the [Ru(2,3-Medpp)₂Cl₂]²⁺ species (Figure 3), obtained by using the "protected" ligand 2,3-Medpp⁺,^{3b} where one of the two chelating sites is methylated. The protection is stable under the reaction conditions used when [Ru(2,3-Medpp)₂Cl₂]²⁺ acts as a complex metal. Subsequent demethylation of the product restores the presence of free chelating sites, that is its complex ligand ability. An iterative, divergent synthesis is therefore possible, as shown in Figure 4.¹¹ Moreover, each deprotected compound of the divergent approach can be used as a ligand core in a convergent process with complex metals to yield dendrimers of higher generation (Figure 4).

The convergent and divergent synthetic strategies shown in Figures 2 and 4 allow a step-by-step control of the growing process, since building blocks containing different metals and/or ligands can be introduced at each step.

For space reasons, in this Account, we will only deal with the properties of dendrimers containing Ru(II) and Os(II) as metals, 2,3-dpp and 2,5-dpp as bridging ligands, and bpy or biq as peripheral ligands (Figure 1). Similar dendrimers containing other metals,^{13,14} cyclometalated ligands,^{13,14} and protected or deprotected bridging ligands at the periphery^{11,12} have been described elsewhere.

General Properties

The dendrimers described in this paper are species with a well-defined composition, soluble in common solvents (e.g., CH₂Cl₂, CH₃CN, H₂O), and stable both in the dark and under light excitation. They carry an overall positive charge that is twice the number of the metal atoms. The species with high nuclearity exhibit a very extended, three-dimensional branching structure. For example, the species with 22 metals^{11,12} are made of 1090 atoms and have an estimated size of 5 nm. Besides the 22 metal atoms, they contain 24 terminal ligands and 21 bridging ligands. Such large species are expected to display endo- and exoreceptor properties, which are currently under investigation. Aggregation has been demonstrated by dynamic light scattering and conductivity experiments.¹⁵

In principle, these polynuclear metal complexes can exist as different isomers because the two coordinating nitrogen atoms of each chelating site of the bridging ligands are not equivalent. A 2D-COSY 400 MHz ¹H NMR spectrum of [Ru(2,3-dpp)₃]²⁺, which is the "core" in most of the described dendrimers, has shown that the purified material is a mixture of the *mer* and *fac* isomers in which the *mer* isomer predominates (92%).¹⁶ The polymetallic complexes can also be a mixture of several diastereoisomeric species since each metal center is also a stereogenic center. For these reasons structural investigations are difficult.¹⁶ Differences arising from the presence of isomeric species, however, are expected to be negligible in the electrochemical and spectroscopic properties described below.¹⁷

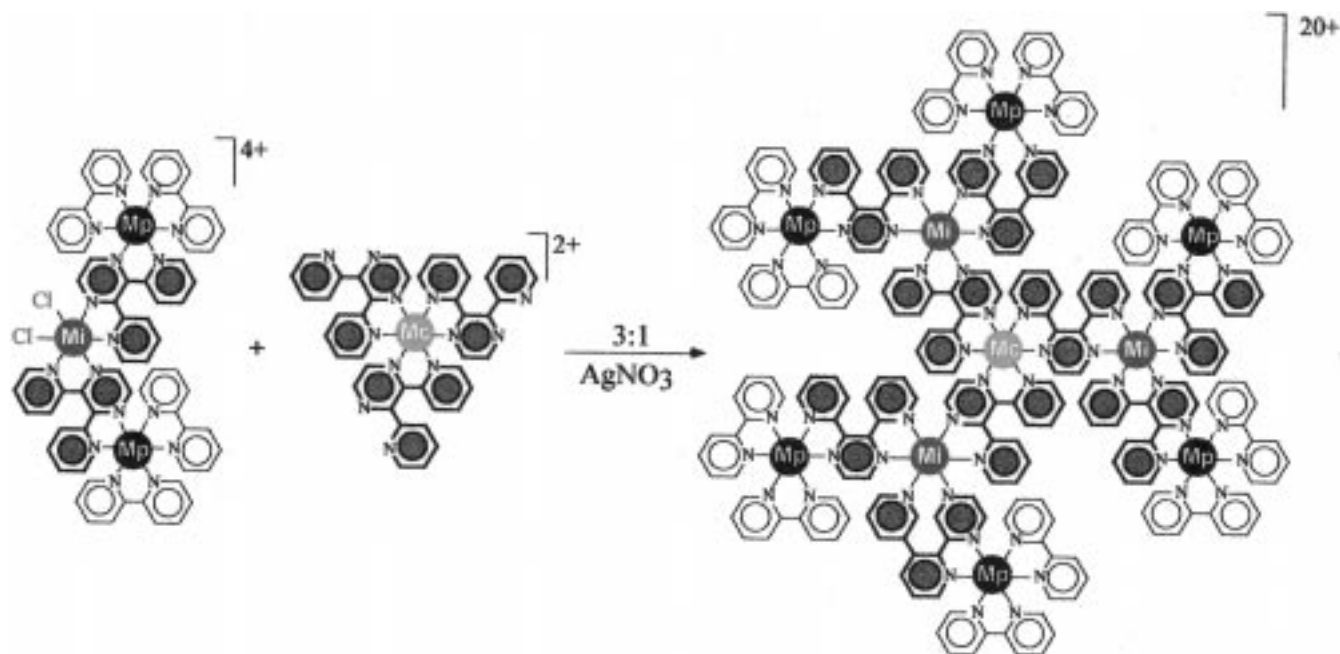


FIGURE 2. Schematic representation of the synthesis of decanuclear compounds.¹⁰ M_c , M_i , and M_p indicate the central, intermediate, and peripheral positions occupied by the metals. As one can see, the topology of the dendrimer depends on the building blocks used.

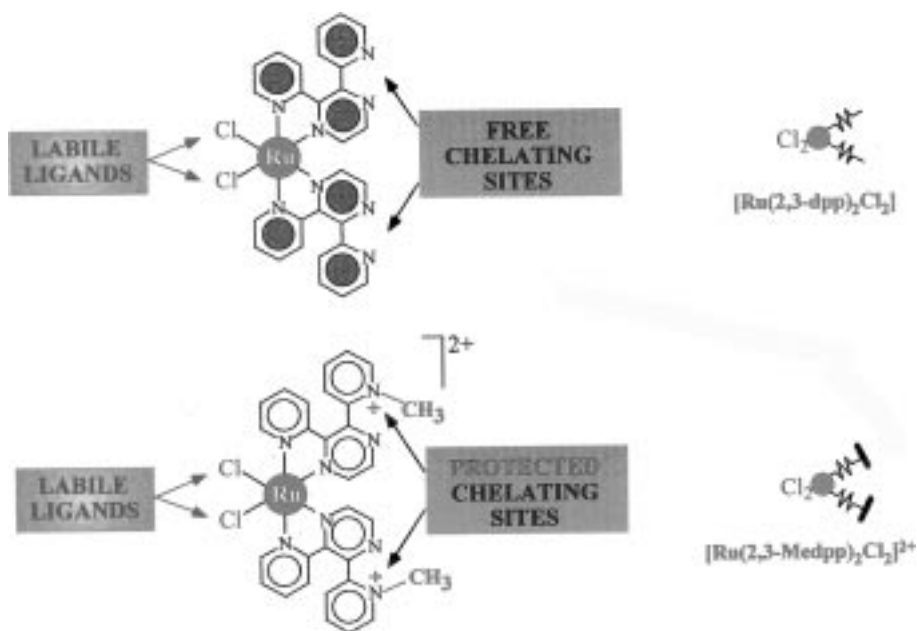


FIGURE 3. Schematic representation of the bifunctional $[Ru(2,3-dpp)_2Cl_2]$ and monofunctional $[Ru(2,3-Medpp)_2Cl_2]^{2+}$ complexes.

Each dendrimer can be viewed as an ordered ensemble of metal-based $[M(L)_n(BL)_{3-n}]^{2+}$ units ($M = Ru(II)$ or $Os(II)$; $L = bpy$ or biq ; $BL = 2,3-$ or $2,5-dpp$; $n = 0$ or 2) which are known^{4,9,18,19} to exhibit (i) intense ligand-centered (LC) absorption bands in the UV region and moderately intense metal-to-ligand charge-transfer (MLCT) bands in the visible region, (ii) a relatively long-lived luminescence in the red spectral region, due to the lowest 3MLCT level, (iii) reversible one-electron oxidation of each metal ion, and (iv) reversible one-electron reductions of each ligand. In the dendrimers, there is a small, but not negligible, electronic interaction between nearby mononuclear units, and therefore, the absorption spectrum and the electro-

chemical properties of the dendrimer are practically the "sum" of the spectra and redox patterns of the constituent units. The small electronic interaction, however, is responsible for new properties characteristic of the supramolecular array such as the occurrence of very fast (exoergonic) energy transfer between nearby units. This causes the quenching of the potentially luminescent units having higher energy 3MLCT levels and the sensitization of the luminescence of the units having lower energy 3MLCT levels. Therefore, big differences can be observed on comparing the luminescence spectra of a dendrimer and its separated units. The absorption spectrum, luminescence spectrum, and oxidation and reduction patterns

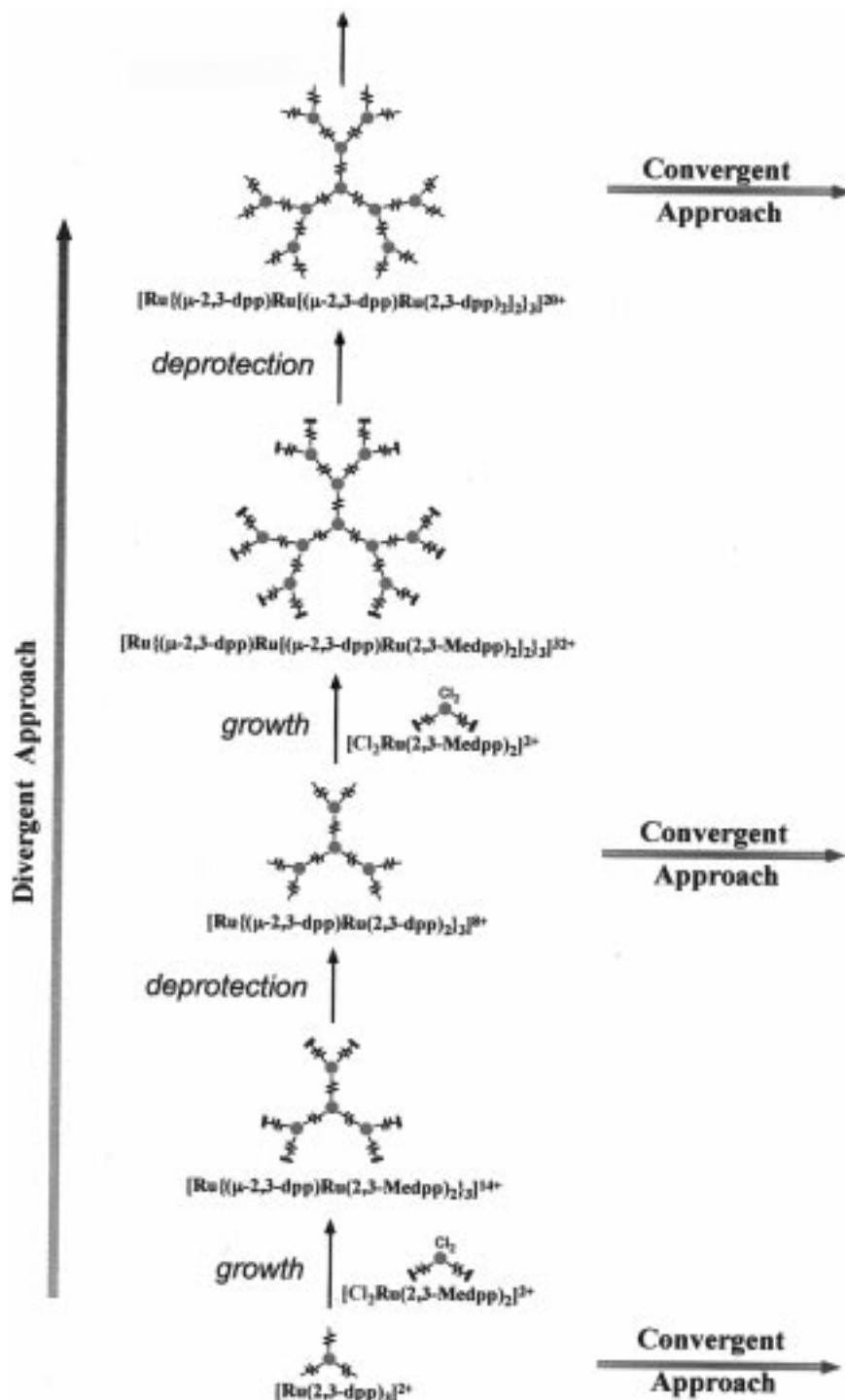


FIGURE 4. Divergent synthetic strategy to obtain polynuclear metal complexes of dendrimer shape.¹¹ Each deprotected compound of the divergent synthetic approach can be used as a core in convergent synthetic processes.

for the decanuclear $[\text{Ru}\{(\mu\text{-}2,3\text{-dpp})\text{Ru}(\mu\text{-}2,3\text{-dpp})\text{Ru}(\text{bpy})_2\}_2\}_3]^{20+}$ species are shown in Figure 5.¹⁰

Designing Dendrimers with Predetermined Redox Patterns

Electrochemical Behavior of the Component Units. The $[\text{M}(\text{L})_n(\text{BL})_{3-n}]^{2+}$ ($\text{M} = \text{Ru}(\text{II})$ or $\text{Os}(\text{II})$; $\text{L} = \text{bpy}$ or biq ; $\text{BL} = 2,3\text{-}$ or $2,5\text{-dpp}$; $n = 0$ or 2) mononuclear component units exhibit reversible redox processes. On oxidation, only one, metal-based process is observed. This process

occurs at a potential which depends (i) strongly on the nature of the metal ion ($\text{Os}(\text{II})$ is oxidized at a much less positive potentials compared to $\text{Ru}(\text{II})$) and (ii) less dramatically on the nature of the coordinated ligands, whose electron-donor power increases in the series $\mu\text{-}2,5\text{-dpp} \leq \mu\text{-}2,3\text{-dpp} < \text{biq} < \text{bpy}$.^{4,9,18}

The reduction processes are essentially ligand localized. The reduction potential of each ligand depends on its electronic properties and, to a smaller extent, on the nature of the metal and the other ligands coordinated to

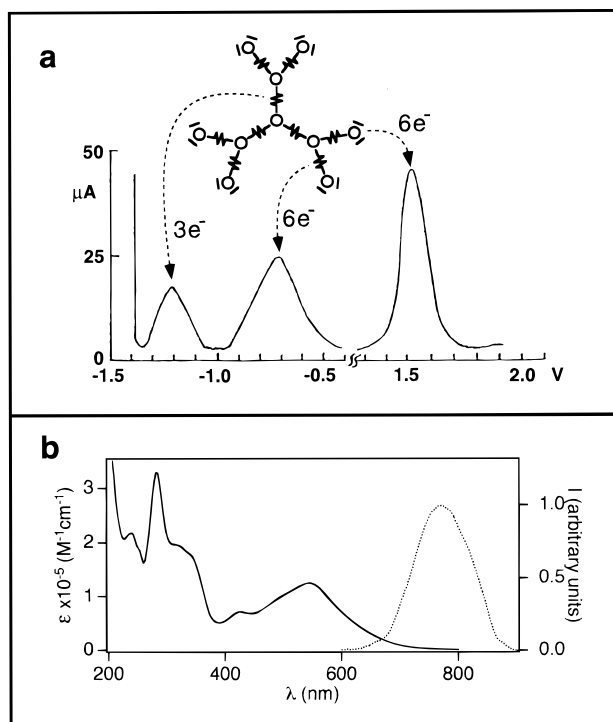


FIGURE 5. (a) Differential pulse voltammogram for oxidation and reduction and (b) absorption (full line) and luminescence (dotted line) spectra of the decanuclear $[\text{Ru}\{(\mu\text{-}2,3\text{-dpp})\text{Ru}(\mu\text{-}2,3\text{-dpp})\text{Ru}(\text{bpy})_2\}_2\}_3](\text{PF}_6)_{20}$ species in acetonitrile solution.¹¹

the metal. The first reduction potential becomes more negative in the ligand series $\mu\text{-}2,5\text{-dpp} < \mu\text{-}2,3\text{-dpp} < \text{biq} < \text{bpy}$. Each L ligand is reduced twice, and each BL ligand is reduced four times in the potential window $-0.5/-3.1$ V.²⁰

Electrochemical Behavior of Dendrimers. In the dendritic species, each unit brings its own redox properties, more or less affected by intercomponent interactions. Metal–metal and ligand–ligand interactions are noticeable for metals coordinated to the same bridging ligand and for ligands coordinated to the same metal, whereas they are negligibly small for metals or ligands that are sufficiently far apart.

It is well-known²¹ that supramolecular species containing a number of identical noninteracting centers exhibit current–potential responses having the same shape as that obtained with the corresponding molecule containing a single center. Only the magnitude of the current is enhanced by the presence of additional electroactive centers. Therefore, in the described dendrimers, equivalent and noninteracting units undergo electrochemical processes at the same potential. This allows us to control the number of electrons lost or gained at a certain potential by placing in the dendrimer the desired number of suitable, equivalent, and noninteracting units.

Very interesting oxidation patterns have been obtained for decanuclear dendrimers.¹⁰ In the $[\text{Ru}\{(\mu\text{-}2,3\text{-dpp})\text{Ru}(\mu\text{-}2,3\text{-dpp})\text{Ru}(\text{bpy})_2\}_2\}_3]^{20+}$ compound, the peripheral Ru-based units are expected to be oxidized at less positive potentials than the internal ones because the bpy ligands are better electron donors than the 2,3-dpp bridging

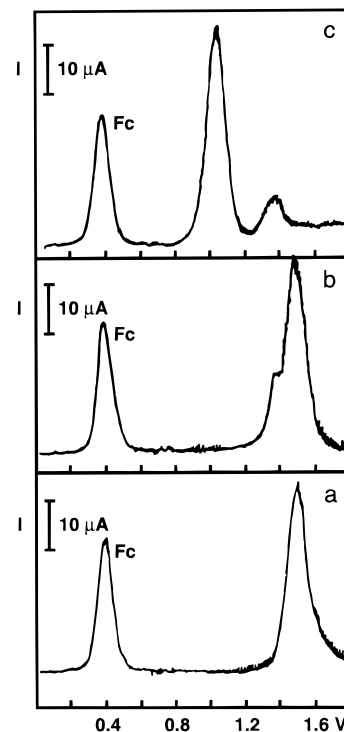


FIGURE 6. Oxidation pattern for some decanuclear complexes.^{10–12} Fc indicates the oxidation peak of ferrocene, used as an internal standard.

ligands. Furthermore, the six peripheral Ru-based units are not expected to interact with one another because they are not directly connected. According with this expectation, the first oxidation process observed for this dendrimer (+1.53 V) involves the exchange of six electrons at the same potential (Figure 6a). Successive oxidation of the other metal-based units cannot be observed presumably because the accumulation of the large positive charge, due to the oxidation of the peripheral units, displaces the oxidation process of the other units to more positive potentials outside the examined potential window.

Dendrimers capable of showing distinct oxidation processes related to topologically different units can be designed by taking advantage of the fact that Os(II) is easier to oxidize than Ru(II) and that peripheral ligands are stronger electron donors than the bridging ligands. So, for the $[\text{Os}\{(\mu\text{-}2,3\text{-dpp})\text{Ru}(\mu\text{-}2,3\text{-dpp})\text{Ru}(\text{bpy})_2\}_2\}_3]^{20+}$ dendrimer, which is made of an Os(II)-based core and nine Ru(II)-based units, a 1–6 pattern is predicted for the electrons exchanged on oxidation. In agreement with these expectations, the differential pulse voltammogram of this compound (Figure 6b) shows a shoulder at +1.35 V, assigned to the one-electron oxidation of the central Os(II) metal ion, superimposed to a six time higher peak at +1.55 V, assigned to the simultaneous one-electron oxidation of the six peripheral noninteracting Ru(II) ions. Oxidation of the three intermediate Ru(II) ions is further shifted toward more positive potentials and cannot be observed in the accessible potential window.

For the $[\text{Os}\{(\mu\text{-}2,3\text{-dpp})\text{Ru}(\mu\text{-}2,3\text{-dpp})\text{Os}(\text{bpy})_2\}_2\}_3]^{20+}$ compound,¹⁰ made of an Os(II)-based core, three Ru(II)-

based units in the intermediate positions, and six Os(II)-based units in the peripheral positions, one expects a 6–1 pattern instead than the 1–6 one observed in the previous case. This is fully consistent with the differential pulse voltammetry results which show an oxidation peak at +1.05 V six times higher than a following peak at +1.39 V (Figure 6c). Following the considerations made for the previous dendrimer, it is easy to understand why the oxidation of the intermediate Ru(II)-based units is not observed.

For the docosanuclear dendrimer made of an Os(II)-based core and 21 Ru(II)-based units, a 1–12 pattern is obtained, corresponding to the one-electron oxidation at +1.42 V of the Os(II) ion, followed by the simultaneous oxidation at +1.54 V of the 12 equivalent and noninteracting peripheral Ru(II)-based units.¹²

Lower nuclearity compounds exhibiting 1–2, 1–3, and 2–2 electron exchange patterns on oxidation have also been designed.^{11,22–24}

Because of the presence of many polypyridine ligands, each capable of undergoing several reduction processes,²⁰ the electrochemical reduction of this type of dendritic compounds produces very complex electron exchange patterns. For example, the previously seen $[\text{Ru}\{\mu\text{-}2,3\text{-dpp}\}\text{Ru}\{\mu\text{-}2,3\text{-dpp}\}\text{Ru}(\text{bpy})_2\}_3]^{20+}$ compound shows a differential pulse voltammogram (Figure 5) with two, broad peaks (at –0.73 and –1.22 V) followed by several other overlapping peaks.¹¹ The first peak, which corresponds to the exchange of six electrons, is due to the one-electron reduction of the six outer equivalent bridging ligands. The width of the peak, compared to that observed on oxidation, suggests a non-negligible interaction between the two ligands coordinated to the same metal, resulting in two closely lying three-electron processes. The second broad peak, which involves three electrons, is assigned to the one-electron reductions of the three inner bridging ligands, occurring at close potential values. Since the interaction between reduced ligands depends also on the nature of the metal, the electron exchange pattern can be modified by replacing Ru(II) with Os(II).¹²

In conclusion, the electrochemical data offer a fingerprint of the chemical and topological structure of the dendrimers. Furthermore, the knowledge of the electrochemical properties of the $[\text{M}(\text{L})_n(\text{BL})_{3-n}]^{2+}$ mononuclear component units and the synthetic control of the supramolecular structure allow us to design dendrimers with predetermined redox patterns. The made-to-order synthetic control of the number of electrons exchanged at a certain potential makes such polynuclear complexes very attractive in view of their possible application as multi-electron-transfer catalysts.²⁵ Examination over a more extended oxidation potential window (in a solvent like liquid SO_2) should permit the observation of an even larger variety of oxidation patterns.

Ordered Molecular Arrays for Light Harvesting

Natural photosynthetic processes convert sunlight into chemical energy by means of a very specific supramolecular organization (roughly schematized in Figure 7a)

formed as the result of evolution.²⁶ Part of the natural photosynthetic system is devoted to optimize light absorption, i.e., to convert the incident sunlight into electronic energy of molecular components.²⁷ Such an electronic energy is then channeled, thanks to an appropriate energy gradient,²⁹ toward a “reaction center”³⁰ where the electronic energy is used to create charge separation, i.e., redox chemical energy. In subsequent thermal steps, the redox energy is used to transform low-energy chemical species such as water and carbon dioxide into high-energy chemical species such as carbohydrates (food, fuel) and dioxygen.

An intelligent approach toward the design of artificial systems for solar energy conversion is to take the natural energy conversion sequence as a model and see whether the natural devices can be replaced by artificial ones.

Absorption of Sunlight. As one can see from Figure 8, where the spectra of the tetra-, deca-, and docosanuclear Ru(II)-based dendrimers are shown, a great number of broad overlapping bands is present and, in the dendrimers of higher nuclearity, the molar absorption coefficient is huge throughout the entire UV–visible spectral region.

The bands in the UV region are ligand centered. The bands observed in the visible region are due to metal-to-ligand charge-transfer (MLCT) transitions. The energies of these transitions depend on the nature of the donor metal ion and the acceptor ligand and, to a minor extent, on the remaining coordination environment.⁸ Therefore, even in the case of homonuclear dendrimers, different types of MLCT transitions are present because there are two types of ligands (bridging and terminal ones) and topologically different positions for the metal ions (central, intermediate, peripheral).

Directional Energy Transfer. As we have seen above, in our dendrimers, the energy levels of the component building blocks are essentially maintained. Light excitation in the near UV–visible region populates ¹MLCT excited states of the various metal-based units. Investigations carried out on $[\text{Ru}(\text{bpy})_3]^{2+}$ with fast techniques indicate that the originally populated ¹MLCT excited states undergo relaxation to the lowest energy ³MLCT level in the subpicosecond time scale.³¹ If this behavior, as it seems likely, is of general validity for the various component units of the dendrimers, the actual result of light excitation is the population with unitary efficiency of the lowest energy ³MLCT level of the unit where light absorption has taken place. If each unit were isolated, as it happens in mononuclear complexes, competition between radiative (luminescence) and radiationless decay to the ground state would account for the deactivation of the ³MLCT level, with an overall rate constant, measured from the luminescence decay, in the range $10^6\text{--}10^8\text{ s}^{-1}$.⁸ Each isolated mononuclear $[\text{M}(\text{L})_n(\text{BL})_{3-n}]^{2+}$ component displays a characteristic luminescence, both in rigid matrix at 77 K and in fluid solution at room temperature.⁹

When the components are linked together in a supramolecular array, electronic energy can be transferred from an excited component to an unexcited one. The

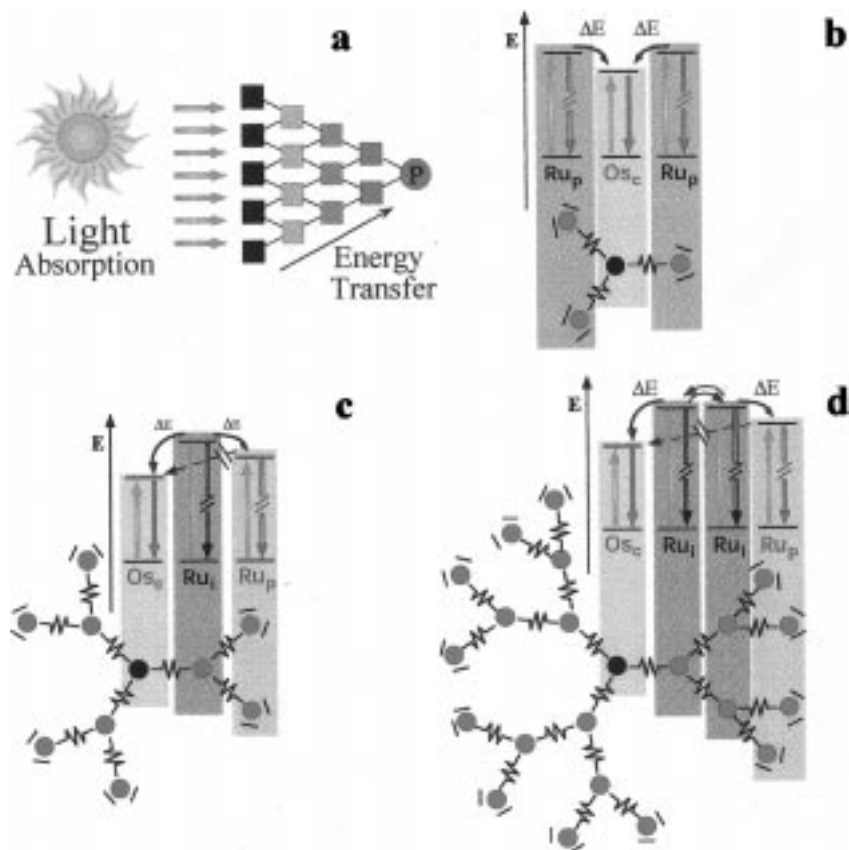


FIGURE 7. (a) Schematic representation of a light-harvesting system. Light is absorbed by an array of chromophores, and the electronic energy is then channeled to a reaction center (P). (b) Energy migration patterns for tetranuclear compounds. Energy migration patterns for a decanuclear (c) and a docosanuclear (d) complex.

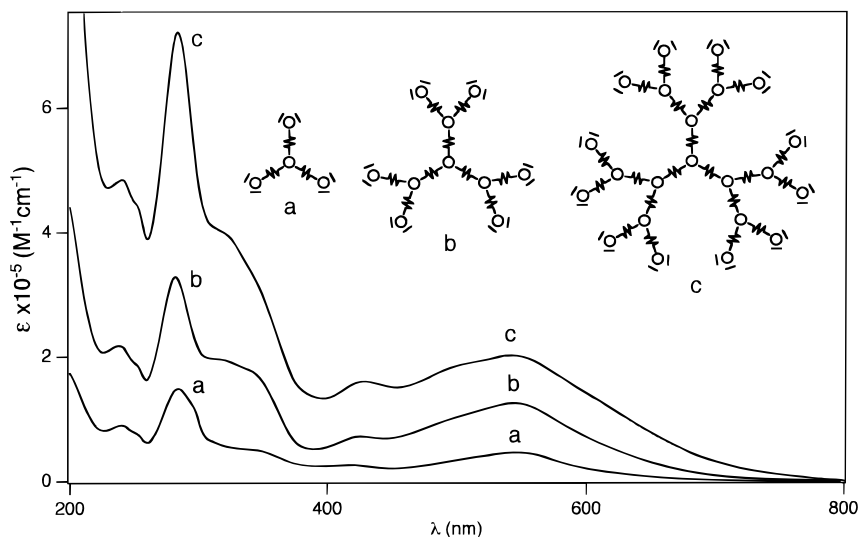


FIGURE 8. Absorption spectra of some dendrimers in acetonitrile solution at room temperature.

experimental results show that in the dendrimers exoergic energy transfer between contiguous units is so fast that the luminescence of the unit whose $^3\text{MLCT}$ level lies at higher energy can no longer be observed, with concomitant sensitization of the luminescence of the unit possessing a lower $^3\text{MLCT}$ level. The energy of the $^3\text{MLCT}$ level excited state of each unit depends on metal and ligands in a predictable way.³² Following the modular synthetic strategy described above, dendrimers can be

obtained with a high degree of synthetic control in terms of the nature and position of metal centers, bridging ligands, and terminal ligands. Thus, the synthetic control translates into a high degree of control on the direction of energy flow within these arrays.

In the case of tetranuclear compounds, all the four possible energy migration patterns have been obtained.^{34,35} For an example, see Figure 7b. By using different combination of metals and ligands, a variety of energy-

migration patterns have also been obtained for hexa-,²⁴ deca-¹⁰ and docosanuclear^{11,12} dendrimers. Two examples are shown in Figure 7c,d. Such examples show that in large structures unidirectional energy transfer (center-to-periphery or viceversa) cannot be obtained with only two types of metals (Ru(II) and Os(II)) and ligands (bpy and μ -2,3-dpp). We are currently investigating the possibility of placing suitable substituents on the terminal bpy ligands so as to raise the energy of the peripheral units and create a periphery-to-center energy gradient. We have also begun a systematic study aimed at extending the number of different metals and/or ligands that can be incorporated in the dendritic structures.^{13,14}

Conclusions and Perspectives

Dendrimers based on transition-metal complexes have been synthesized by using the "complexes as metals/complexes as ligands" synthetic strategy. Such a strategy offers 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. Each dendrimer can be viewed as an ordered ensemble of weakly interacting $[M(L)_n(BL)_{3-n}]^{2+}$ units ($M = Ru(II)$ or $Os(II)$; $L = bpy$ or biq ; $BL = 2,3-$ or $2,5-dpp$; $n = 0$ or 2). The absorption bands and the electrochemical properties of each unit are only slightly perturbed in the assembled structure, so that the absorption spectrum and redox pattern of a dendrimer resemble the "sum" of the spectra and redox patterns of the constituent units. The electronic interaction, however, is sufficiently strong to allow very fast (exoergonic) energy transfer between nearby units. The synthetic control translates into a high degree of control of the electrochemical behavior, light absorption properties, and direction of energy transfer. Therefore, these dendrimers can be used to perform valuable functions such as light harvesting, a fundamental property for solar energy conversion purposes, and reversible exchange (storage and release) of a controlled number of electrons at a certain potential, an attractive characteristics for the design of "molecular batteries" and multielectron-transfer catalysts.

Future work will be focused along the following directions: (i) synthesis of larger systems; (ii) synthesis of systems containing a greater variety of metals and ligands; (iii) synthesis of wedge-type arrays with full control of the direction of energy transfer.

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