Bottom-up strategy to obtain luminescent and redox-active metal complexes of nanometric dimensions

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ABSTRACT

By using the "complexes as metals and complexes as ligands" synthetic strategy, it has been possible to obtain oligonuclear metal complexes which contain up to 22 metal ions. Complexes containing two different types of metal ions (Ru and Os; Ru and Rh; Os and Rh; Ru and Ir) have also been prepared. The light absorption, luminescence, and redox properties of these polynuclear compounds can be varied by changing (i) the nuclearity, (ii) the nature of metal ions, bridging ligands and/or terminal ligands, and (iii) the position of the various components in the supramolecular structure. Because of their strong absorption in the visible spectral region and the possibility to predetermine the direction of energy migration, these compounds could be used as photochemical molecular devices for harvesting solar energy.

A. INTRODUCTION

Chemical synthesis has since long been considered a realm of organic chemistry. According to Cram, "synthetic organic chemists fall into two groups: those who prepare old naturally occurring compounds and those who prepare new compounds. The synthetic targets of the former group are provided by the evolutionary chemistry of Nature. The synthetic targets of the latter group are designed by the investigator" [1]. In the last decade outstanding progress has been made in the field of the synthesis of metal complexes, and it can now be stated that as far as the preparation of new (non-natural) compounds is

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concerned, metal coordination chemistry competes in imagination and achievements with organic chemistry.

In this paper we would like to review some results obtained on the synthesis of luminescent and redox-active polynuclear metal complexes of dendritic structure. The synthetic strategy is, as we shall see below, very flexible and allows us to obtain arrays of nanometric dimensions where different metal ions, bridging ligands, and terminal ligands can occupy predetermined sites. In this way, the light absorption, luminescence, and redox properties of these polynuclear compounds can be varied. In particular, it is possible to obtain a synthetic control of the direction(s) of electronic energy transfer after light absorption. This is a step towards the construction of nanometer-sized antennas for harvesting solar energy and other molecular devices capable of performing light-induced functions [2].

B. SYNTHETIC STRATEGY

Mononuclear transition metal complexes are synthesized by combining metal ion (M) and free ligands (L), as shown in eq. (1):

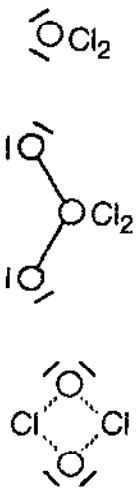
$$M + nL \longrightarrow M(L)_n \qquad (1)$$

In the last few years we have been developing a procedure to synthesize oligonuclear metal complexes of desired nuclearity and chemical structure [3-9]. Such a procedure is based on the use of *complexes* (building blocks) in the place of the metal (M) and/or ligands (L) in the synthetic reaction (1). The place of M can be taken by mono- or oligonuclear complexes that possess easily replaceable ligands, and the place of L can be taken by mono- or oligonuclear complexes which contain free chelating sites (*"complexes as metals"* and *"complexes as ligands"* strategy).

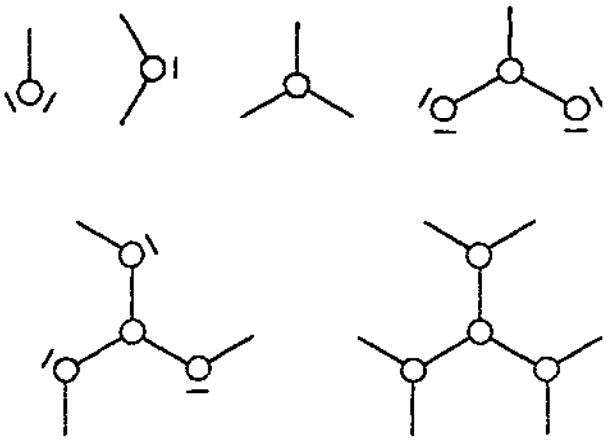
Some of the building blocks used in our syntheses are sketched in Scheme 1, where the metals and ligands used and their symbols are also indicated. It is worth noting that the use of the "complex metal" $[(phpy)_2M(Cl)_2M(phpy)_2]^{2+}$ building blocks (M = Rh(III) or Ir(III)) has recently allowed us [10] to introduce Rh(III) and Ir(III) in polynuclear compounds which were previously based only on Ru(II) and/or Os(II). The synthetic routes followed to obtain complexes of nuclearity 4, 10 and 22 are illustrated in Schemes 2-4. In each equation, the first reactant plays the role of a metal and the second one plays the role of a ligand. More details on the synthetic procedures (and on the characterization of the compounds) can be found in the original papers. A model of a decanuclear complex containing 2,3-dpp as bridging ligand is shown in Figure 1.

As shown in Schemes 2-4, the synthetic strategy used is versatile and selective, since the sites occupied by different metals and ligands in the structure of the polynuclear compounds can be synthetically predetermined by an appropriate choice of the building blocks. Recently we have also elaborated a strategy to grow up oligonuclear metal complexes in a tree-like structure according to a divergent approach (Scheme 5) [8,11].

"complex metals"

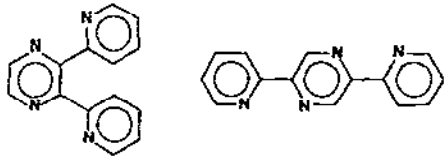


"complex ligands"



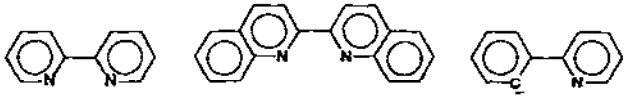
Metal ion, O: Ru^{2+}, Os^{2+}, Rh^{3+}, Ir^{3+}

Bridging ligand, ——:



2,3-dpp 2,5-dpp

Terminal ligand, I:



bpy biq phpy

Scheme 1

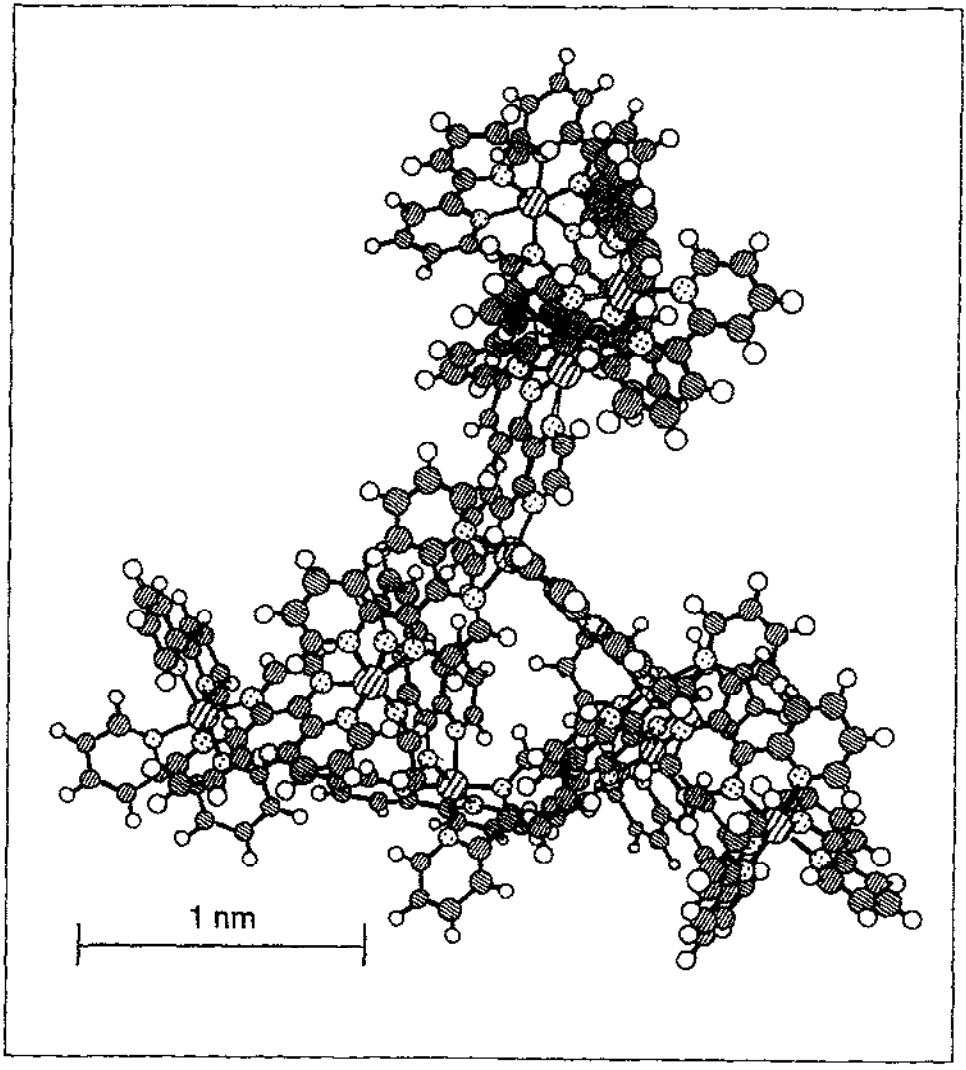
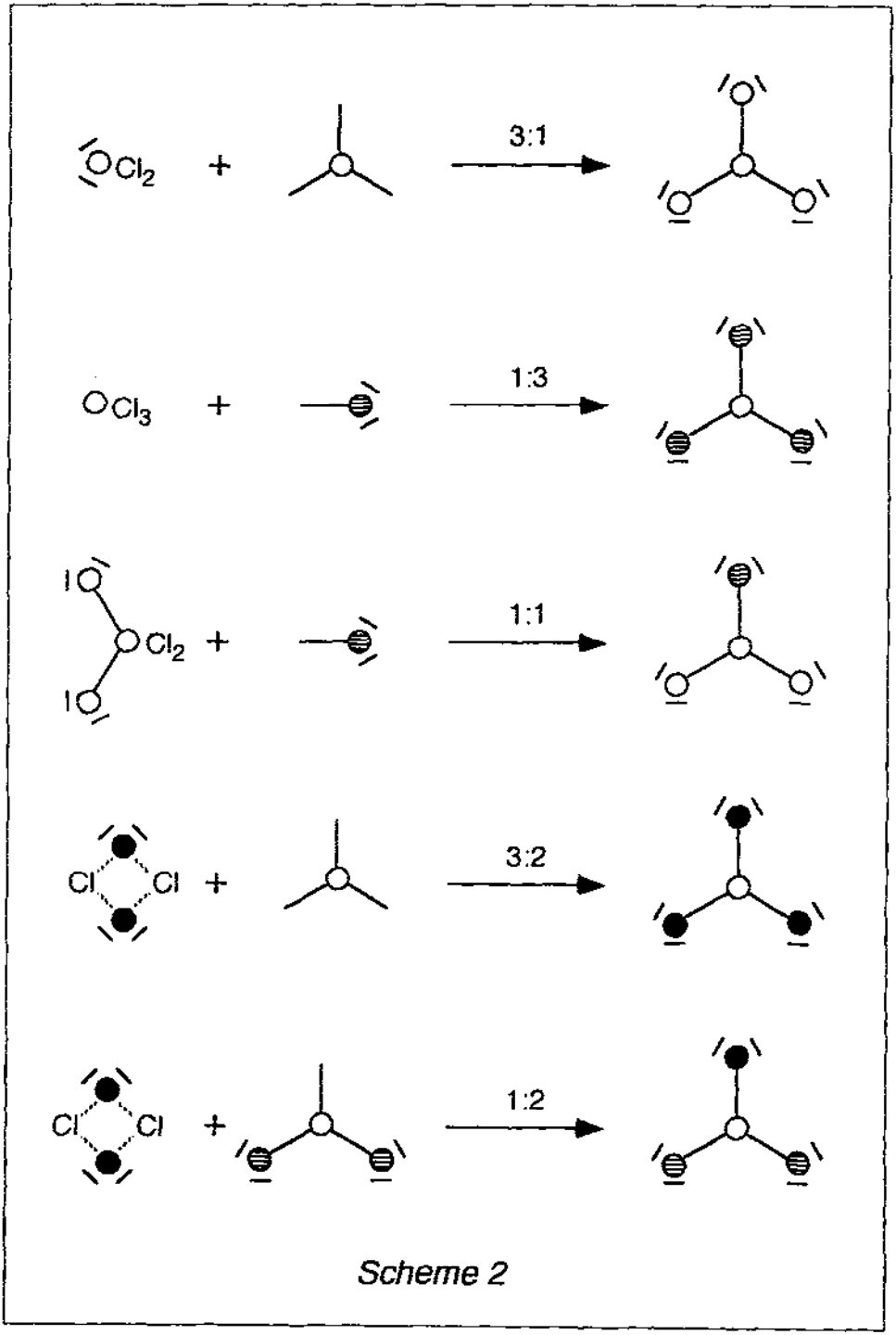


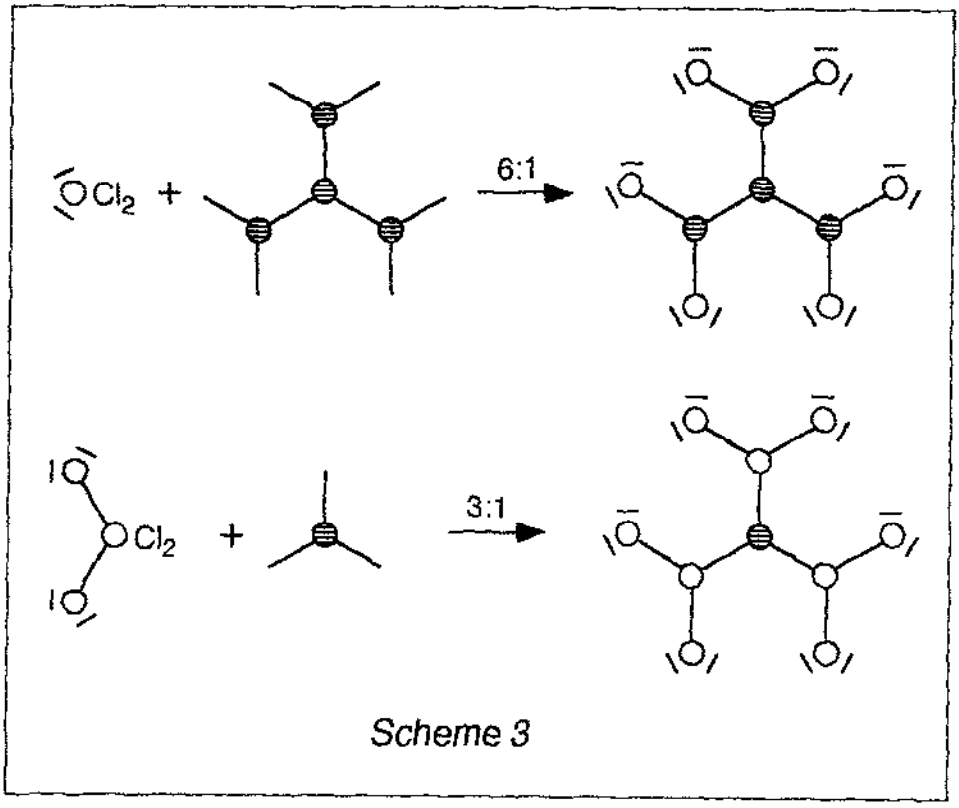
Fig. 1. Model of a decanuclear complex.

C. GENERAL PROPERTIES

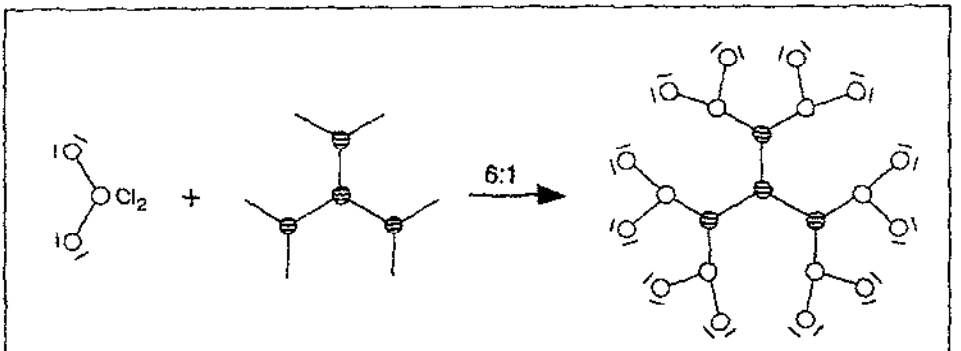
It should be emphasized that these polynuclear compounds are well characterized supramolecular species made of a defined number of metal-containing components. Neglecting the PF_6^- counter ions, the docosanuclear



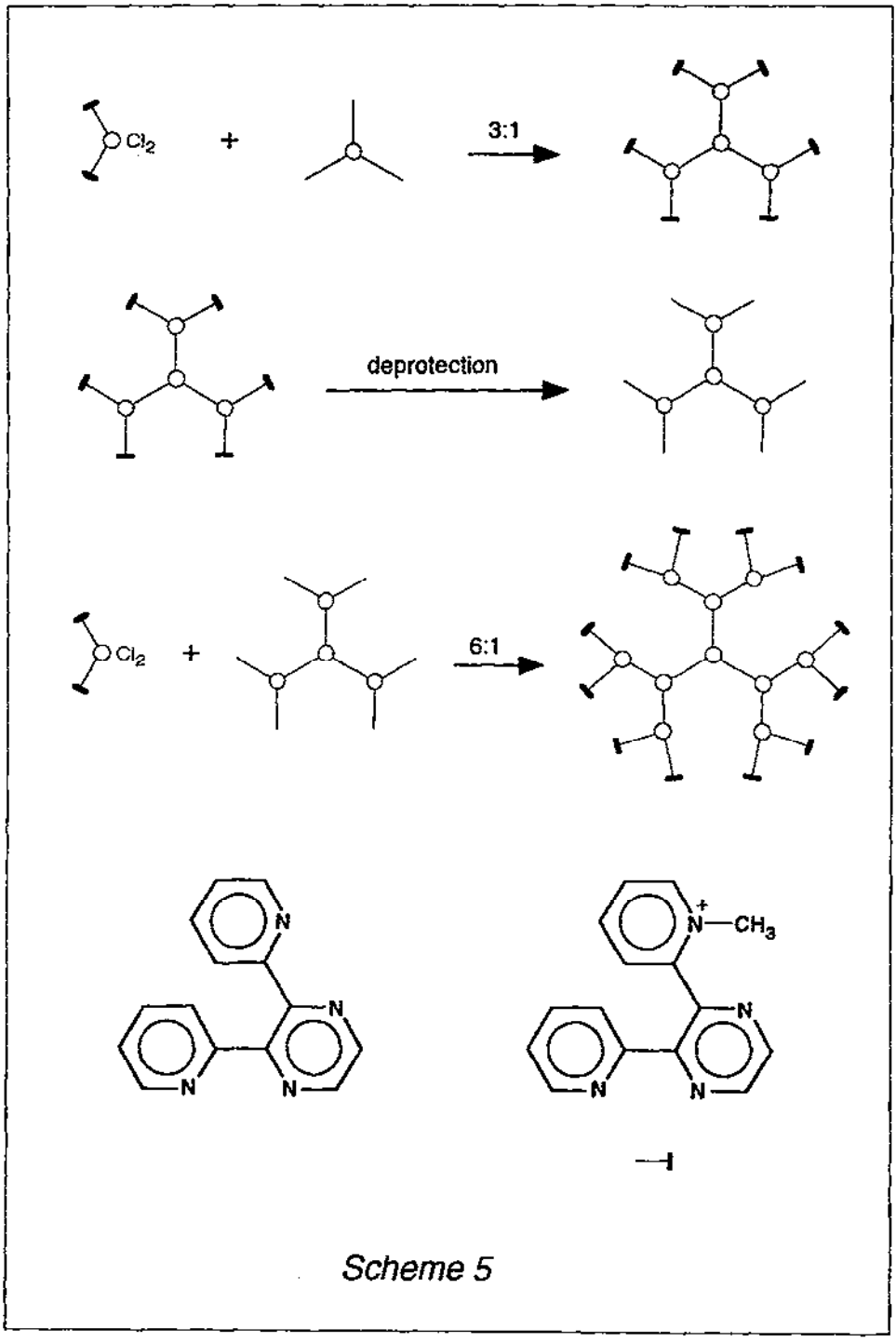
Scheme 2



Scheme 3



Scheme 4



Scheme 5

compound shown in Scheme 4 is made of 1090 atoms, has a molecular weight of 10890 daltons, and an estimated size of about 5 nm. Besides the 22 metal atoms, it contains 24 terminal bpy ligands and 21 2,3-dpp bridging ligands [8]. As one can understand from the model shown in Fig. 1, the species with high nuclearity exhibit a three dimensional branching structure of the type shown by otherwise completely different compounds based on polyamidoamines or other organic components [12,13]. Therefore endo- and exoreceptor properties can be expected (Fig. 2), which will be the object of future investigations. We would also like to point out that our complexes differ from most of the organic-type arborols or dendrimers prepared so far for two fundamental reasons: (i) each component exhibits valuable intrinsic properties such as absorption of visible (solar) radiation, luminescence, and redox levels at accessible potentials; (ii) by a suitable choice of the building blocks, different components can be placed in specific sites of the supramolecular array, as one can understand from Scheme 2 where five different synthetic routes to obtain tetranuclear complexes are reported. In other words, our dendrimers are species with a high "information" content and can therefore be exploited to perform valuable functions (Fig. 2).

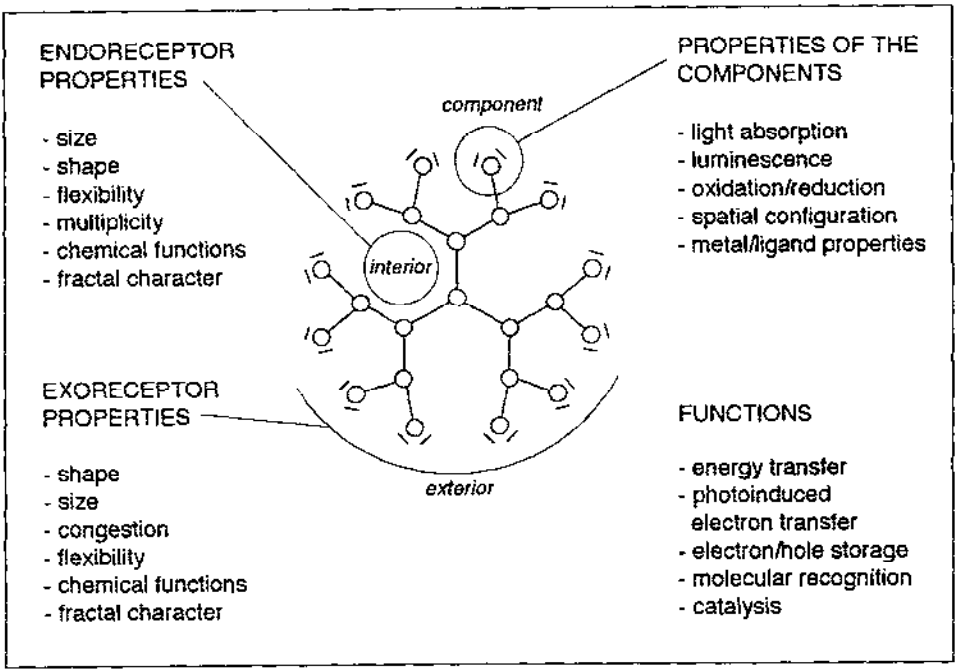


Fig. 2. Properties and functions of a transition-metal based dendrimer.

D. ABSORPTION, EMISSION, AND REDOX PROPERTIES

Each metal containing building block is characterized by its own absorption, luminescence and redox properties. The absorption bands are related to ligand centered (LC, in the UV region) and metal-to-ligand charge transfer (MLCT, in the visible region). Luminescence originates from the lowest excited state which is a ^{3}MLCT level, except for the Rh-based cyclometallated units where the lowest excited state is a ^{3}LC level. Oxidation is metal centered and reduction is usually ligand centered [14-17].

In the supramolecular structure of the polymetallic species there is a relatively weak electronic interaction among the building blocks which causes (i) some shift in the MLCT absorption bands and redox potentials and (ii) fast energy transfer from the lowest luminescent level of each unit to the lowest one of the entire supramolecular structure [3,5]. Luminescence usually originates from such a lowest excited state. The absorption and luminescence data for a family of tetranuclear compounds are collected in Table 1. The absorption and luminescence spectra of some of these compounds are shown in Fig. 3. It is

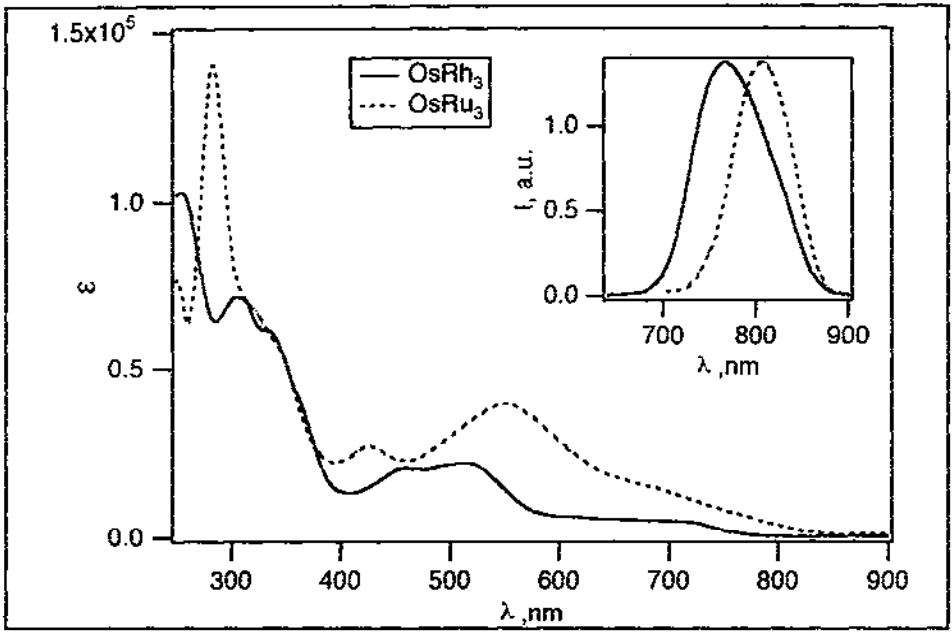


Fig. 3. Absorption and (inset) emission spectra of $OsRh_3$ and $OsRu_3$. Absorption spectrum of $OsRu_3$ is in acetonitrile; other spectra are in dichloromethane solution.

Table 1

Lowest energy absorption maxima (^{1}MLCT) and luminescence data of some tetranuclear compounds.[a]

Complex	Abbreviation	λ_{abs} (nm)	λ_{em} (nm)	τ_{em} (ns)	luminescent excited state [b]
$Os[(\mu\text{-}2,3\text{-}dpp)Ru(2,3\text{-}dpp)_2]_3^{8+}$	$OsRu_3$ open	520	c	c	$Os_c \rightarrow dpp$
$Os[(\mu\text{-}2,3\text{-}dpp)Ru(Me\text{-}2,3\text{-}dpp)_2]_3^{14+}$	$OsRu_3$ prot.	526	812	445	$Os_c \rightarrow dpp$
$Os[(\mu\text{-}2,3\text{-}dpp)Ru(bpy)_2]_3^{8+}$ [e]	$OsRu_3$	551	806	36	$Os_c \rightarrow dpp$
$[(bpy)_2Ru(\mu\text{-}2,3\text{-}dpp)]_2Ru(\mu\text{-}2,3\text{-}dpp)Os(bpy)_2^{8+}$	$RuRu_2Os$	618	960[d]	-	$Os_p \rightarrow dpp$
$Ru[(\mu\text{-}2,3\text{-}dpp)Rh(phpy)_2]_3^{5+}$ [e]	$RuRh_3$	458	655	360	$Ru_c \rightarrow dpp$
$Ru[(\mu\text{-}2,3\text{-}dpp)Ir(phpy)_2]_3^{5+}$ [e]	$RuIr_3$	495	795	160	$Ir_p \rightarrow dpp$
$Os[(\mu\text{-}2,3\text{-}dpp)Rh(phpy)_2]_3^{5+}$ [e]	$OsRh_3$	512	764	55	$Os_c \rightarrow dpp$
$Os[(\mu\text{-}2,3\text{-}dpp)Os(bpy)_2]_3^{8+}$	$OsOs_3$	675	>900	-	$Os_p \rightarrow dpp$
$Ru[(\mu\text{-}2,3\text{-}dpp)Ru(bpy)_2]_3^{8+}$	$RuRu_3$	542	780	50	$Ru_p \rightarrow dpp$

[a] Data in air-equilibrated acetonitrile solution at room temperature, unless otherwise noted. Luminescence maxima are uncorrected for photomultiplier response; [b] The subscript letter indicates the position of the involved atom: c = central, p = peripheral; [c] Very weak emission; [d] MeOH/EtOH 4:1 v/v glassy matrix at 90 K; [e] Data in dichloromethane.

worth noting that the nature of the luminescent excited state depends on the nature and location of the various units and that the properties of the luminescent unit (e.g.; the central Os-based component in the $OsRh_3$ and $OsRu_3$ species, Table 1) are affected by the neighbouring units. [10].

E. ANTENNA EFFECT

The natural photosynthetic systems show that for harvesting solar energy supramolecular arrays are needed which absorb as much visible light as possible and are capable to channel the resulting excitation energy towards a specific site of the array (*antenna devices*) [2,18]. The polynuclear metal complexes described in this paper are excellent light absorbers in the entire visible region. Furthermore, efficient energy transfer can take place among their components, as shown by the presence of only one luminescence band for compounds which contain more than one type of chromophoric units. The occurrence of energy transfer can be established by the quenching of the luminescence of the donor unit and the sensitization of the luminescence of the acceptor unit, and its efficiency can be estimated by comparing the absorption and excitation spectra. The energy levels involved in the energy transfer process are the lowest excited state of each component. Since the properties of the components are known, it is possible to design polynuclear complexes where the component with the lowest energy excited state is located in the desired position of the supramolecular structure. This allows a synthetic control of the direction of energy migration after light absorption.

The results obtained with the tetranuclear dimetallic compounds (Table 1) show that efficient energy migration takes place from the cyclometallated Rh-based to the Ru-based component in $RuRh_3$ [10], and from the Ru-based component to the Os- based component in $OsRu_3$ [19]. This allows us to design a decanuclear compound where the excitation energy is channelled from the periphery to the center of the supramolecular structure (Fig. 4) [20].

F. CONCLUSION

Much of the interest in polynuclear metal complexes is related to their size, shape, presence of different sites, and ordered location of such different sites. We have developed a strategy to obtain polynuclear complexes of nanometric dimensions and dendritic shape, which can contain many different sites (i.e., different metals and/or ligands) in a predetermined, synthetically controlled pattern. Because of the absorption, luminescence, and redox properties of each unit and the possibility to order such units in the supramolecular array, a high information content can be embedded in these species. In particular, made-to-order control of the number of electrons lost at a certain potential and of the direction of energy transfer can be achieved.

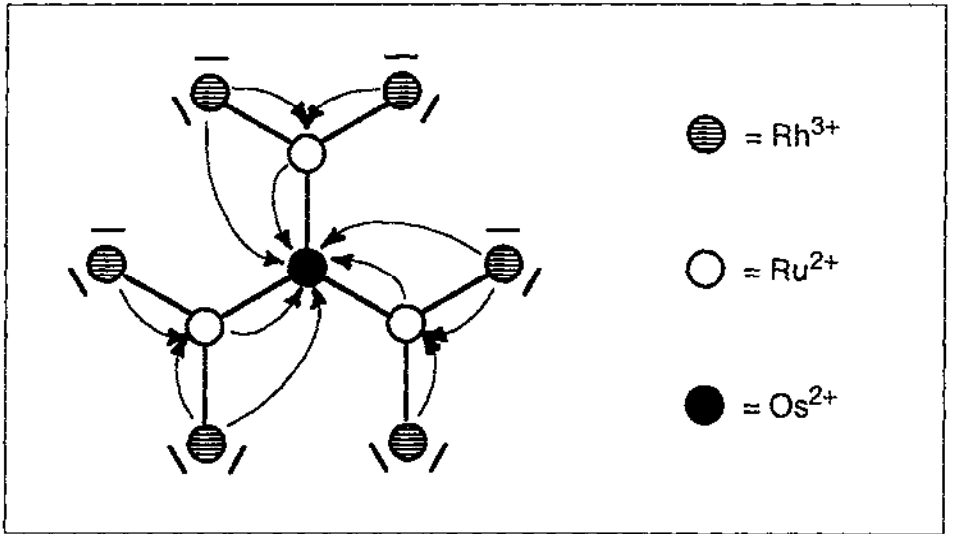


Fig. 4. Schematic representation of a decanuclear trimetallic complex featuring excitation energy migration towards the central metal.

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20 Work in progress in our laboratories.