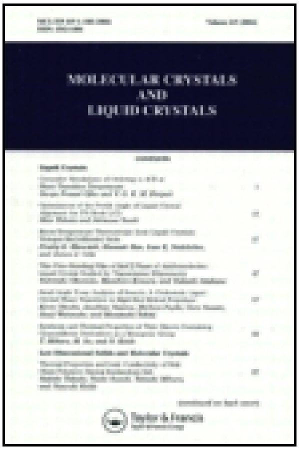

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"Small-Upward" Approach to Nanostructures: Dendritic Polynuclear Metal Complexes For Light Harvesting

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"SMALL-UPWARD" APPROACH TO NANOSTRUCTURES: DENDRITIC POLYNUCLEAR METAL COMPLEXES FOR LIGHT HARVESTING

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Abstract. A synthetic strategy is described to obtain supramolecular dendritic structures of nanometric dimensions made of metal complex units which absorb light all over the UV and visible spectral region. Specific metal and/or ligands can be placed in designed sites of the supramolecular array by an appropriate choice of the building blocks. A made-to-order control of the patterns of electronic energy transfer can thus be achieved. Supramolecular species containing up to 22 metal atoms have been prepared and their light absorption, luminescence, and energy transfer properties have been investigated.

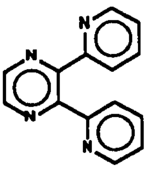
Introduction

The current approach to miniaturization of electronic components is based on a "large-downward" approach.[1] Further miniaturization, however, as well as the development of a variety of molecular machines,[2] will most likely require a "small-upward" approach, based on the assembly of functionally integrated building blocks into structurally organized arrays.^{3} Supramolecular chemistry^{3} has shown that molecular components can indeed be assembled to give species of nanometric dimensions. This bridge from molecules to materials is most promising and will certainly be the object of extensive research in the near future.

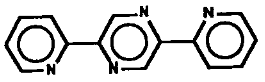
Metal complexes of pyridine-type ligands with some transition metal ions (particularly, Ru(II) and Os(II)) are since long know to exhibit very interesting photophysical and redox properties.^{4} Assembly of building blocks that contain such "pieces of information" can lead to supramolecular species capable of performing useful light induced functions (Photochemical Molecular Devices).^{2c} We have developed a synthetic strategy to link together in a made-to-order sequence any desired number of metal-containing building blocks of the type described above. This allows us to prepare supramolecular species where the pattern of electronic energy transfer is synthetically controlled.

Synthetic Strategy

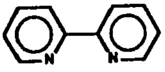
The metals used to obtain polynuclear species are Ru(II) and Os(II). The ligands used are the 2,3- and 2,5-bis(2-pyridyl)pyrazine (abbreviated as 2,3- and 2,5-dpp) bridging ligands (BL), and the 2,2'-bipyridine (bpy) and 2,2'-biquinoline (biq) terminal ligands (L).



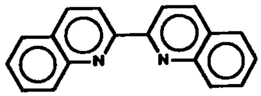
2,3-dpp



2,5-dpp



bpy

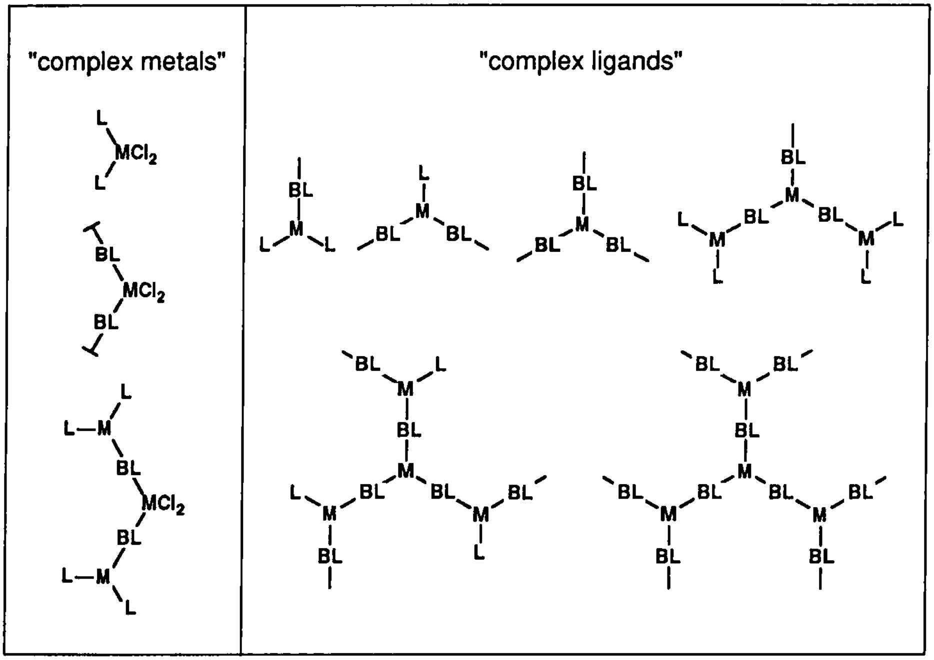


biq

To prepare mononuclear metal complexes one uses a simple reaction between metal ion and ligands (eq. 1). In order to obtain metal complexes of

$$M + nL \longrightarrow M(L)_n \tag{1}$$

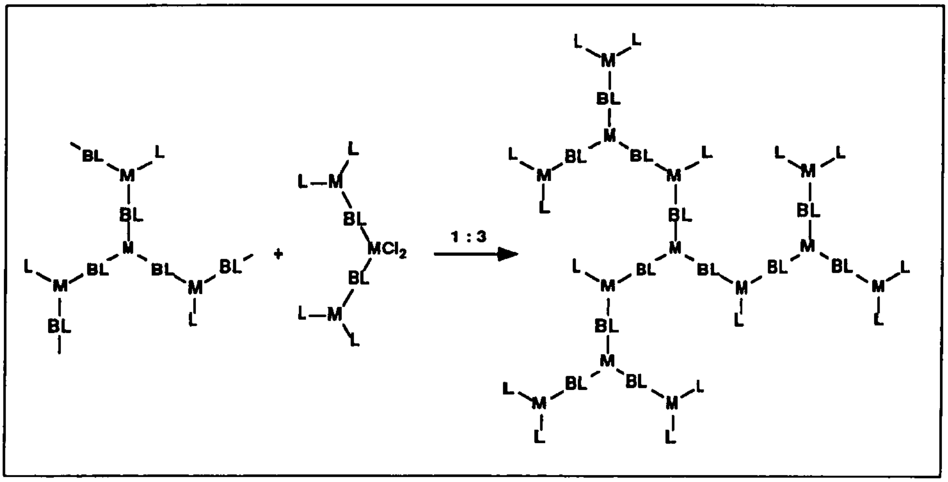
high nuclearity, one must replace M and/or L in eq. 1 with metal complexes (building blocks) that can play the role of metal and/or ligand ("complexes-as-metals/complexes-as-ligands" synthetic strategy).^{3j,5} The building blocks used in our syntheses are shown in Scheme 1. In some cases, a protection/deprotection procedure on the chelating sites of the complex-ligands has been performed by methylation-demethylation.[6] Details on the experimental conditions used for the synthetic reactions and for the purifications of the products are reported elsewhere.[3j,5,6] The synthetic route followed to obtain a complex of nuclearity 13 is shown in Scheme 2. An iterative reaction/deprotection procedure such as that shown in Scheme 3 can lead, in principle, to larger species by a divergent approach.



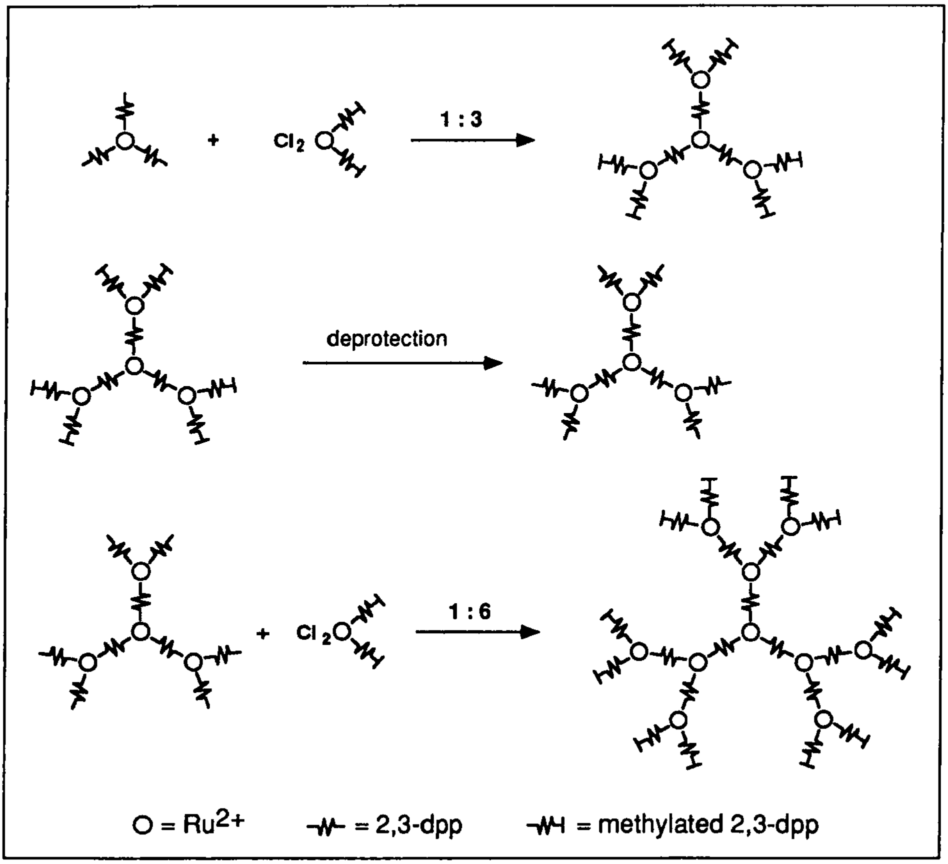
Scheme 1

Properties

In the compounds discussed in this paper, ligand coordination around each metal center takes place according to an octahedral geometry. Furthermore, the bridging ligands are not planar (particularly, 2,3-dpp). This leads to very complex, tridimensional structures for the polynuclear complexes. Fig. 1 shows a schematic view of a possible structure of the tridecanuclear compound.



Scheme 2



Scheme 3

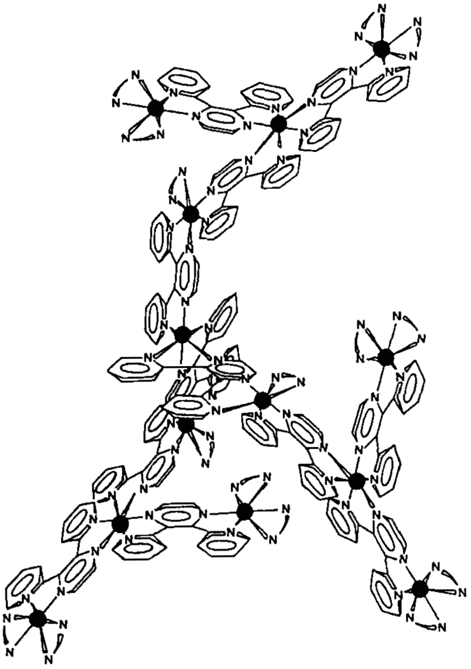


FIGURE 1 Schematic view of the tridecanuclear compound.

A great number of mononuclear Ru(II) and Os(II) polypyridine-type complexes have been studied in the last twenty years.[4] Some important properties of these compounds can be summarized as follows: (1) intense ligand-centered (LC) absorption bands are displayed in the UV region, and moderately intense (ε_{max} ~1×10^4 $M^{-1}cm^{-1}$) metal-to-ligand charge transfer (MLCT) bands in the visible region; (2) a relatively long-lived luminescence (10^{-7} s time scale) is present in the red spectral region; this emission originates from the lowest triplet MLCT level; (3) reversible one-electron oxidation of the metal ion takes place in the potential window +0.6/+1.8 V (*vs* SCE); (4) reversible one-electron reduction of each ligand takes place in the potential window -0.5/-1.6 V. Important differences relevant to our discussion are as follows: (i) Os(II) complexes are oxidized at potentials considerably less positive than Ru(II) complexes; (ii) the MLCT absorption and luminescence bands lie at lower energies for the Os(II) complexes than for the Ru(II) ones; (iii) the energy of the LUMO of the (mono-coordinated) ligands decreases in the series bpy > biq > 2,3-dpp > 2,5-dpp; as a consequence, the lowest (luminescent) ^{3}MLCT level involves the lowest ligand of the above series which is present in the complex; (iv) the electron donor power decreases in the ligand series bpy > biq ≥ 2,3-dpp ~ 2,5-dpp. Because of these properties of the components and of the stabilization of the LUMO of 2,3-dpp and 2,5-dpp on coordination to a second metal center, it can be expected that for the metal-containing building blocks which are present in the polynuclear compounds the oxidation potential of the metal and the energy of the lowest (luminescent) excited state increase in the series $Os(bpy)_2(\mu\text{-}2,5\text{-}dpp)^{2+} \leq Os(bpy)_2(\mu\text{-}2,3\text{-}dpp)^{2+} < Os(biq)_2(\mu\text{-}2,5\text{-}dpp)^{2+} \leq Os(biq)_2(\mu\text{-}2,3\text{-}dpp)^{2+} < Os(\mu\text{-}2,5\text{-}dpp)_3{}^{2+} < Os(\mu\text{-}2,3\text{-}dpp)_3{}^{2+} < Ru(bpy)_2(\mu\text{-}2,5\text{-}dpp)^{2+} \leq Ru(bpy)_2(\mu\text{-}2,3\text{-}dpp)^{2+} < Ru(biq)_2(\mu\text{-}2,5\text{-}dpp)^{2+} \leq Ru(biq)_2(\mu\text{-}2,3\text{-}dpp)^{2+} < Ru(bpy)(\mu\text{-}2,5\text{-}dpp)_2{}^{2+} \leq Ru(bpy)(\mu\text{-}2,3\text{-}dpp)_2{}^{2+} < Ru(\mu\text{-}2,3\text{-}dpp)_3{}^{2+}$.

It can also be expected that in the polynuclear complexes the metal-metal interaction is noticeable for metals coordinated to the same bridging ligand, whereas it is very small between metals that do not share the same bridging ligand. Similarly, the ligand-ligand interaction is noticeable only for ligands coordinated to the same metal. The properties of the single metal-containing units and their interactions give rise to an interesting behavior of the polynuclear complexes in redox reactions[3j,5] and electronic energy transfer.

Light harvesting and electronic energy channelling

Solar energy conversion in natural photosynthetic systems is based on the presence of supramolecular arrays which absorb as much visible light as possible and are capable to channel the resulting excitation energy towards a specific site (antenna devices). The polynuclear complexes discussed in this paper exhibit intense absorption bands in the visible spectral region, as is shown by the spectrum of the tridecanuclear complex displayed in Fig. 2. Light excitation in the visible absorption bands populates ^{1}MLCT excited states in the various components. The originally populated ^{1}MLCT levels undergo relaxation to the lowest energy ^{3}MLCT level of the same component in the subpicosecond time scale. As a consequence, the actual result of light excitation is the population with unitary efficiency of the lowest energy ^{3}MLCT level of the component where light absorption has taken place. If each component were isolated, competition between radiative (luminescence) and radiationless decay to the ground state would account for the deactivation of the ^{3}MLCT level, with an overall rate constant, measured from the luminescence decay, in the range 10^6-10^8 s^{-1}. When the components are linked together in a supramolecular array, however, electronic energy can be transferred from an excited component to an unexcited one, according to well-known mechanisms.[7] 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 rate of energy transfer depends on the energetics of the process and on the electronic interaction between the components. Exoergonic energy transfer between components connected by the same bridging ligands is expected to be much faster than luminescence and radiationless decay.

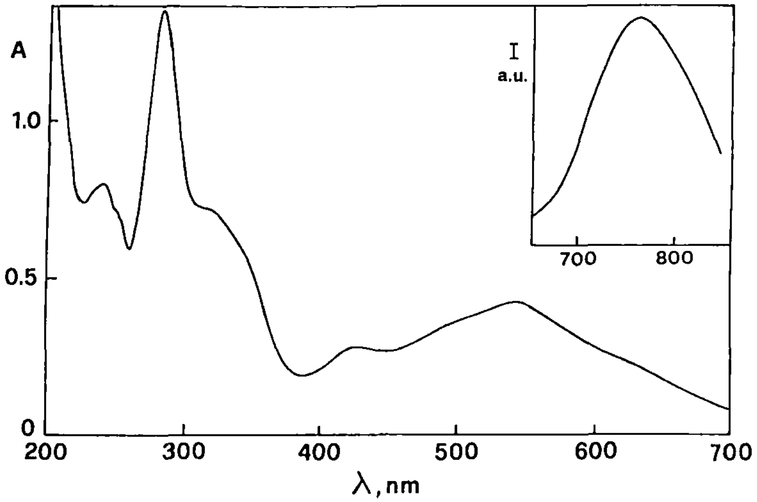


FIGURE 2. Absorption and (inset) luminescence spectra of the tridecanuclear compound in acetonitrile solution at room temperature.

On the basis of the above considerations and of the knowledge of the energy levels of the various metal-containing units, it has been possible to design polynuclear complexes where the electronic energy generated by light absorption can be channelled towards a desired direction along the supramolecular structure.[3j,5] This can be done by locating different building blocks in an appropriate sequence so as to have a driving force for energy transfer. A few examples are illustrated below.

In tetranuclear complexes, the energy migration pattern shown in Fig. 3a has been obtained by locating a low energy $Os(\mu\text{-}2,3\text{-}dpp)_3{}^{2+}$ component at the center and higher energy $Ru(bpy)_2(\mu\text{-}2,3\text{-}dpp)^{2+}$ components at the periphery. The demonstration of a 100% efficient energy migration from the periphery to the center is the complete quenching of the luminescence of the peripheral components and the 100% efficient sensitization of the luminescence of the central component, as indicated by the identity between absorption and corrected excitation spectra.[8] Tetranuclear complexes which exhibit other energy migration patterns have also been prepared.[8]

In decanuclear complexes, the energy migration pattern shown in Fig. 3b has been obtained by locating Os-based components in the center and in the periphery.[3j] The luminescent units of this complex are the peripheral ones and their emission takes place in the near IR (90 K: λ_{max} = 900 nm).[9] Several other decanuclear complexes with different energy migration patterns have been obtained .[3j]

In the 22-nuclear compound schematized in Fig. 3c, the lowest energy units are the peripheral $Ru(bpy)_2(\mu\text{-}2,3\text{-}dpp)^{2+}$ ones, which in fact collect the excitation energy of the other units and exhibit luminescence in the red spectral region (300 K: λ_{max} = 784 nm; 77 K: λ_{max} = 730 nm).[10]

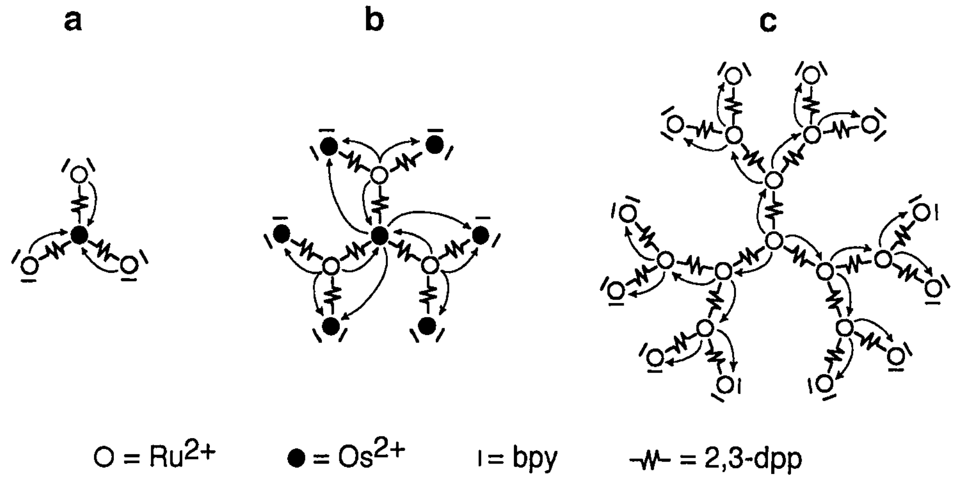


FIGURE 3 Energy migration patterns in selected polynuclear metal complexes. For details, see text.

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