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Coordination Chemistry Reviews 251 (2007) 525–535
COORDINATION CHEMISTRY REVIEWS
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Review

Electronic spectroscopy of metal complexes with dendritic ligands

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Received 10 January 2006; accepted 9 April 2006
Available online 25 April 2006

Contents

Abstract

Combinations of suitably chosen metal ions and dendritic ligands may lead to giant metal complexes that display interesting spectroscopic properties, particularly as far as luminescence is concerned. This paper reviews some recent results obtained with metal complexes of dendrimers capable of exhibiting: (i) metal-centered, (ii) metal-to-ligand charge-transfer, or (iii) ligand-centered luminescence. The study of the luminescent properties reveals that these compounds can be useful for several purposes, including light harvesting, sensing with signal amplification, and conversion of the absorbed light into emitted light of quite different wavelength (e.g., UV light into IR light).

Keywords: Dendrimers; Light-energy conversion; Light-harvesting antennas; Luminescence; Luminescent sensors; Metal complexes; Metal ions

1. Introduction

For the sake of simplicity, electronic transitions in metal complexes are usually classified on the basis of the predominant localization, on the metal or on the ligand(s), of the molecular orbitals involved in the transition [1]. This assumption leads to the well-known classification of the electronic excited states of metal complexes into three types, namely metal-centered (MC), ligand-centered (LC), and charge-transfer (CT). The CT excited states can be further classified as ligand-to-metal charge-transfer (LMCT) and metal-to-ligand charge-transfer (MLCT).

Metal complexes may range from very simple to extremely complicated species. If we consider only mononuclear compounds, their complexity depends, of course, on the nature of the ligand(s). The electronic spectroscopy of metal complexes in the last 50 years has developed through several phases. Beginning with the pioneering work of Jørgensen [2], and Ballhausen [3], investigations were first focused on MC (also called ligand field) excited states of complexes containing simple ligands (e.g., H_2O, NH_3, Cl^-, CN^-) [4]. Such studies were essentially devoted to the elucidation of the electronic absorption spectra, except for Cr(III) [5] and lanthanide [6] complexes which display emission bands originating from intraconfigurational MC excited states. When the ligands used for building up novel metal complexes began to be large molecular species, the interest of spectroscopists moved from MC to CT and LC excited states. In particular, with the advent on the scene of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) and related systems [7], much attention was dedicated to MLCT and LC excited states, with increasing emphasis on emission spectra and related pho-

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doi:10.1016/j.ccr.2006.04.007

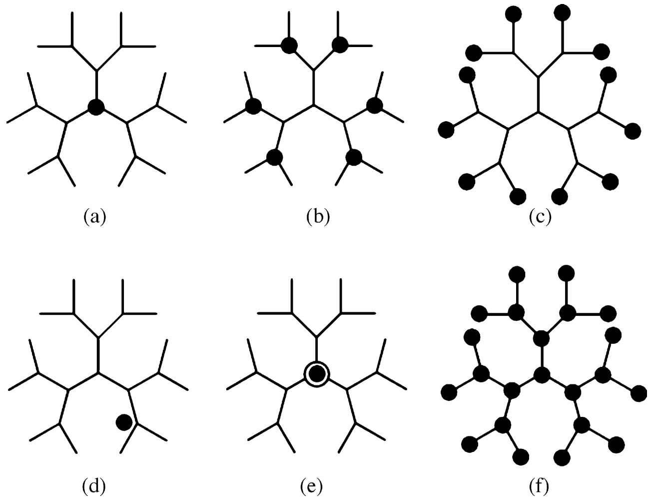


Fig. 1. Different kinds of metal-containing dendrimers: (a) dendrimers built around a metal complex as a core; (b) dendrimers containing metal complexes as branching centers; (c) dendrimers containing metal complexes as peripheral units; (d) dendrimers that can coordinate metal ions by ligand units that are present in the branches; (e) dendrimers with a core which is able to coordinate a metal ion; (f) dendrimers built around a metal complex as a core and containing metal complexes as branching centers and as peripheral units.

tophysical properties (e.g., excited state lifetimes and emission quantum yields) [8]. Recently, the development of dendrimer chemistry has allowed the design of giant multichromophoric ligands yielding metal complexes capable of exhibiting intercomponent energy or electron transfer processes among their own subunits, including the metal ion [9]. The study of the photophysical properties of these systems has opened the way to a variety of light induced processes.

Dendrimers [10,11] constitute a new class of well-defined macromolecules exhibiting a tree-like architecture of nanodimension, first derived by the "cascade molecule" approach [12]. Dendrimers are currently attracting great attention due to their peculiar chemical and physical properties and the wide range of potential applications. The metal complexes of dendrimers can be classified as follows (Fig. 1) [13]:

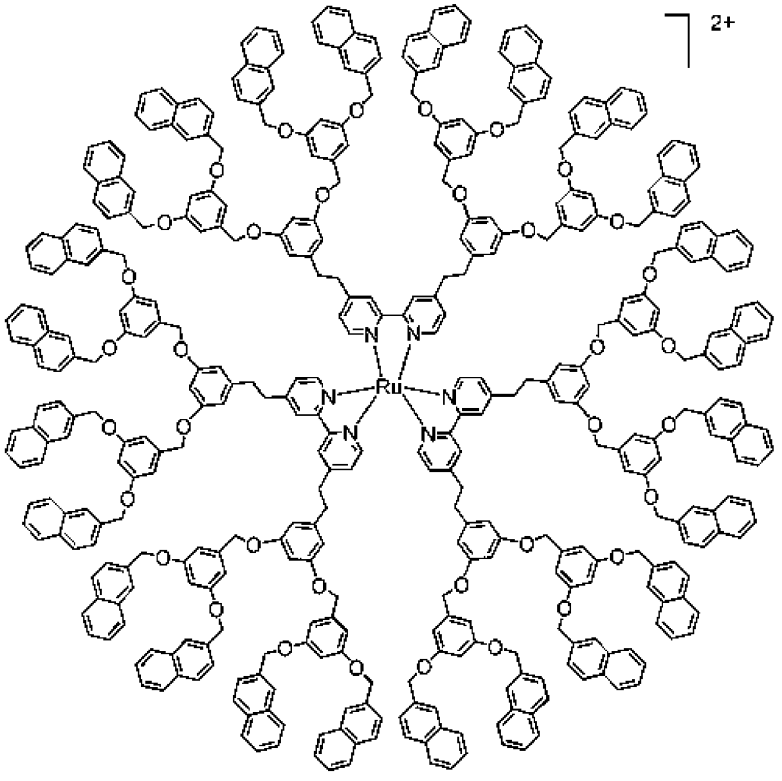
(a) *Dendrimers built around a metal complex as a core*. These compounds can be considered metal complexes of ligands carrying dendritic substituents (Fig. 1a). The most commonly used metal containing cores are porphyrin complexes [14], polypyridine complexes [15], and ferrocene-type compounds [16].
(b) *Dendrimers containing metal complexes as branching centers*. In these compounds (Fig. 1b) metal complexes, often of polydentate ligands (e.g., 2,3-bis(2-pyridyl)pyrazine, 2,3-dpp) [17] play the role of connectors along the branches of a dendritic structure.
(c) *Dendrimers containing metal complexes as peripheral units*. These compounds (Fig. 1c) derive from dendrimers functionalized on the surface with ligand moieties. Interesting examples are dendrimers coated with up to 48 $Ru(Cp)(CO)_2R$ [18] and 243 ferrocenyl units [19].
(d) *Dendrimers that can coordinate metal ions with ligand units that are present in the branches*. This is the case (Fig. 1d), for example, of dendrimers whose branches contain many potential ligands such as amines [20] or amides [21] or imines [22] units. In large dendrimers of this type, the exact coordination sites are difficult to localize and, sometimes, also the number of coordinated metal ions is difficult to establish.
(e) *Dendrimers with a core which is able to coordinate a metal ion*. Examples of this kind (Fig. 1e) are the recently reported dendrimers built around a 1,4,8,11-tetraazacyclotetradecane (cyclam) core [23].

There are, of course, metal-containing dendrimers that belong to more than one of the above mentioned categories. For example, there are several dendrimers built around a metal complex as a core and containing metal complexes as branching centers and as peripheral units [24] (Fig. 1f). These compounds represent the extension of the old concept of polynuclear complex [25]. Compounds made of 22 Ru polypyridine moieties [26], and 189 Pt [27] and 47 Pd [28] cyclometalated units have been synthesized.

From the above mentioned examples it is clear that the combination of the chemistry of metal complexes with the chemistry of dendrimers can lead to a great variety of novel compounds. The aim of this paper is limited to review the photophysical properties of selected metal complexes of dendrimers, mainly investigated in our laboratories, with particular reference to classes a, d and e schematized in Fig. 1.

2. Dendrimers with a metal complex as a core

Dendrimer $\mathbf{1}^{2+}$ is a classical example of a dendrimer built around a metal complex core. In this compound the 2,2′-bipyridine ligands of the $[Ru(bpy)_3]^{2+}$-type core carry branches containing 1,3-dimethoxybenzene and 2-naphthyl chromophoric units separated by aliphatic connectors [29]. Since the interchromophoric interactions are weak, the absorption spectrum of $\mathbf{1}^{2+}$ is substantially equal to the summation of the spectra of the $[Ru(bpy)_3]^{2+}$ core, which is characterized by a broad spin allowed Ru → bpy MLCT band around 450 nm [30], and of the chromophoric groups contained in the branches, which show very intense bands in the near UV region.



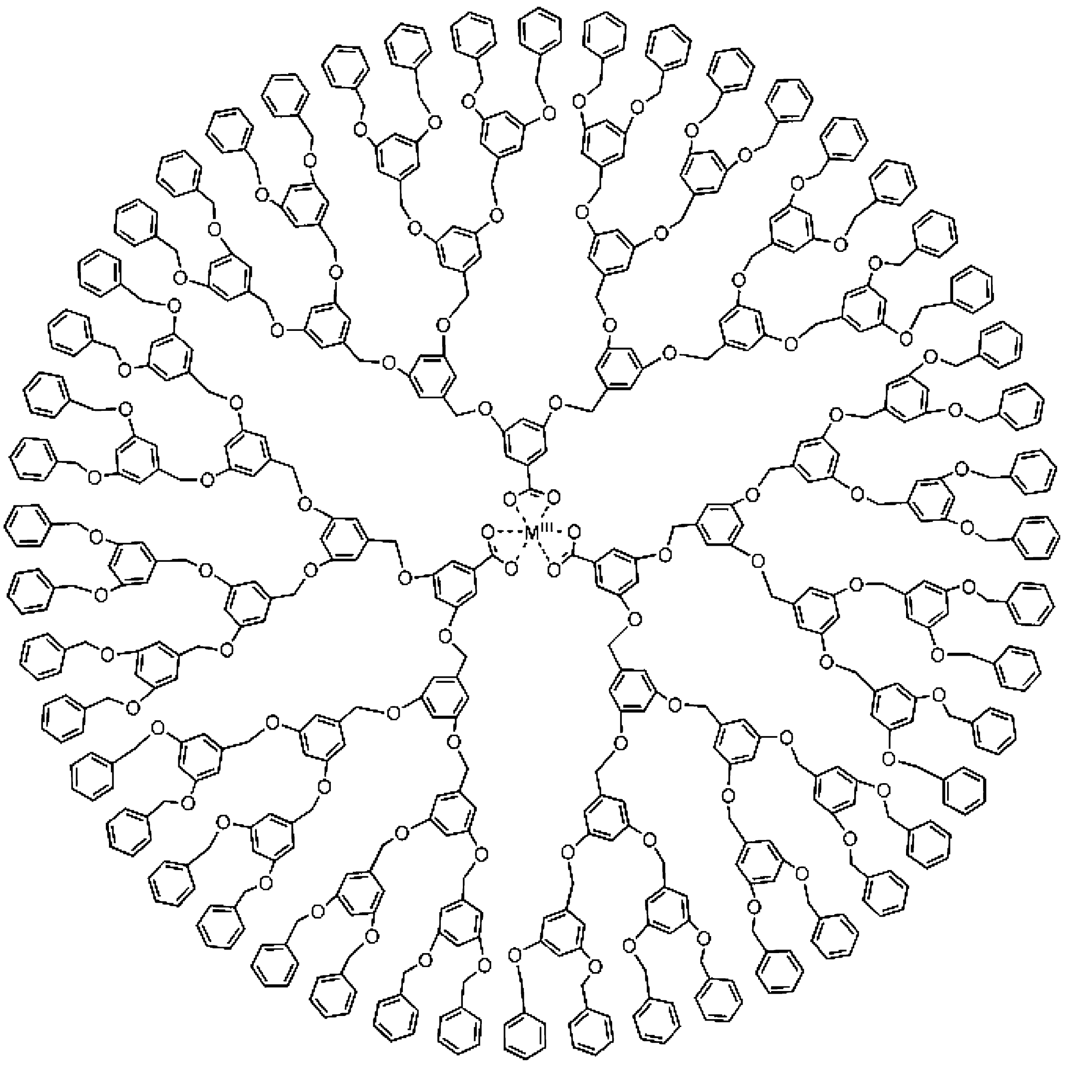
1^{2+}

It should be noted that the 1,3-dimethoxybenzene and 2-naphthyl chromophoric units contained in the branches of the dendrimer are not involved in metal coordination. In some way, they belong to a second coordination sphere covalently linked to the bpy ligands that constitute the first coordination sphere of the metal ion. If $\mathbf{1}^{2+}$ is considered a large metal complex molecule, the absorption and emission bands of the 1,3-dimethoxybenzene and 2-naphthyl chromophoric units can formally be classified as LC. However, $\mathbf{1}^{2+}$ can be more properly viewed as a supramolecular (multicomponent) species [31]. In such species, each chromophoric unit displays its own absorption spectrum since there is no appreciable interactions among them in the ground state, but in the excited state even weak interactions can cause intercomponent energy or electron transfer processes. This kind of reasoning can also be applied to the other systems discussed in this paper.

The lowest excited state of dendrimer $\mathbf{1}^{2+}$ is a core-centered ^{3}MLCT level; because of the presence of the heavy metal atom, this level is populated with unitary efficiency from the upper lying ^{1}MLCT excited state. All the three types of chromophoric groups present in the dendrimer, namely, $[\mathrm{Ru(bpy)_3}]^{2+}$, dimethoxybenzene, and naphthalene, are potentially luminescent species. In dendrimer $\mathbf{1}^{2+}$, however, the UV fluorescence of the dimethoxybenzene- and naphthyl-type units is almost completely quenched with concomitant sensitization of the orange $[\mathrm{Ru(bpy)_3}]^{2+}$ phosphorescence ($\lambda_{\max} = 610\,\mathrm{nm}$). These results show that energy-transfer processes with very high efficiency (ca. 90%) take place from the very short lived (nanosecond time scale) potentially fluorescent excited states of the aromatic units of the wedges to the relatively long lived (microsecond time scale) ^{3}MLCT level of metal-based dendritic core. Dendrimer $\mathbf{1}^{2+}$ is therefore an example of a light-harvesting antenna system, as well as of a species capable of changing the color of the incident light. It should also be noted that in aerated solution the phosphorescence intensity of the $[\mathrm{Ru(bpy)_3}]^{2+}$ dendritic core is more than twice intense as that of the “free” $[\mathrm{Ru(bpy)_3}]^{2+}$ parent compound because the dendrimer branches protect the core from dioxygen quenching [32].

Suitably designed dendritic ligands can be used to coordinate lanthanide metal ions. Most lanthanide ions show very long lived luminescence, which is a quite useful property for several applications (e.g., sensors [33] and fluoroimmunoassay [34]). Because of the forbidden nature of their electronic transitions, however, lanthanide ions exhibit very weak absorptions bands, which is a severe drawback for applications based on luminescence. In order to overcome the above difficulty, lanthanide ions are usually coordinated to ligands containing organic chromophores whose excitation, followed by energy transfer, causes the sensitized luminescence of the metal ion (antenna effect) [35]. Such a process can involve either direct energy transfer from the singlet excited state of the chromophoric group with quenching of the chromophore fluorescence [42,36], or, most frequently, via $S_1 \rightarrow T_1$ intersystem crossing followed by energy transfer from the T_1 excited state of the chromophoric unit to the lanthanide ion [35]. Dendrons bearing a carboxylate unit in their focal point can assemble around Er^{3+}, Tb^{3+}, or Eu^{3+} ions in the same way as do simple carboxylate groups (see, e.g., **2**)

[37]. In the resulting complexes, the MC (intraconfigurational) absorption bands are very weak (for more details, see Section 4) and the LMCT bands are also very weak (and lie at very high energy in the case of Er^{3+} and Tb^{3+} which are difficult to reduce). Therefore, the absorption spectrum is dominated by the strong LC bands of the dendritic ligands, which appear in the near UV region. Experiments carried out in toluene solution showed that excitation with light absorbed by such LC bands causes the sensitized emission of the lanthanide ions, presumably by an energy-transfer Förster mechanism. The much lower sensitization effect found for Eu^{3+} compared with Tb^{3+} was ascribed to a weaker spectral overlap, but it could be related to the fact that since Eu^{3+} can be easily reduced, in the Eu^{3+} complex a non-emissive LMCT level can be close to (or even lower than) the luminescent MC excited state. For more details on the quenching and sensitization processes involving lanthanide ions, see Section 4.



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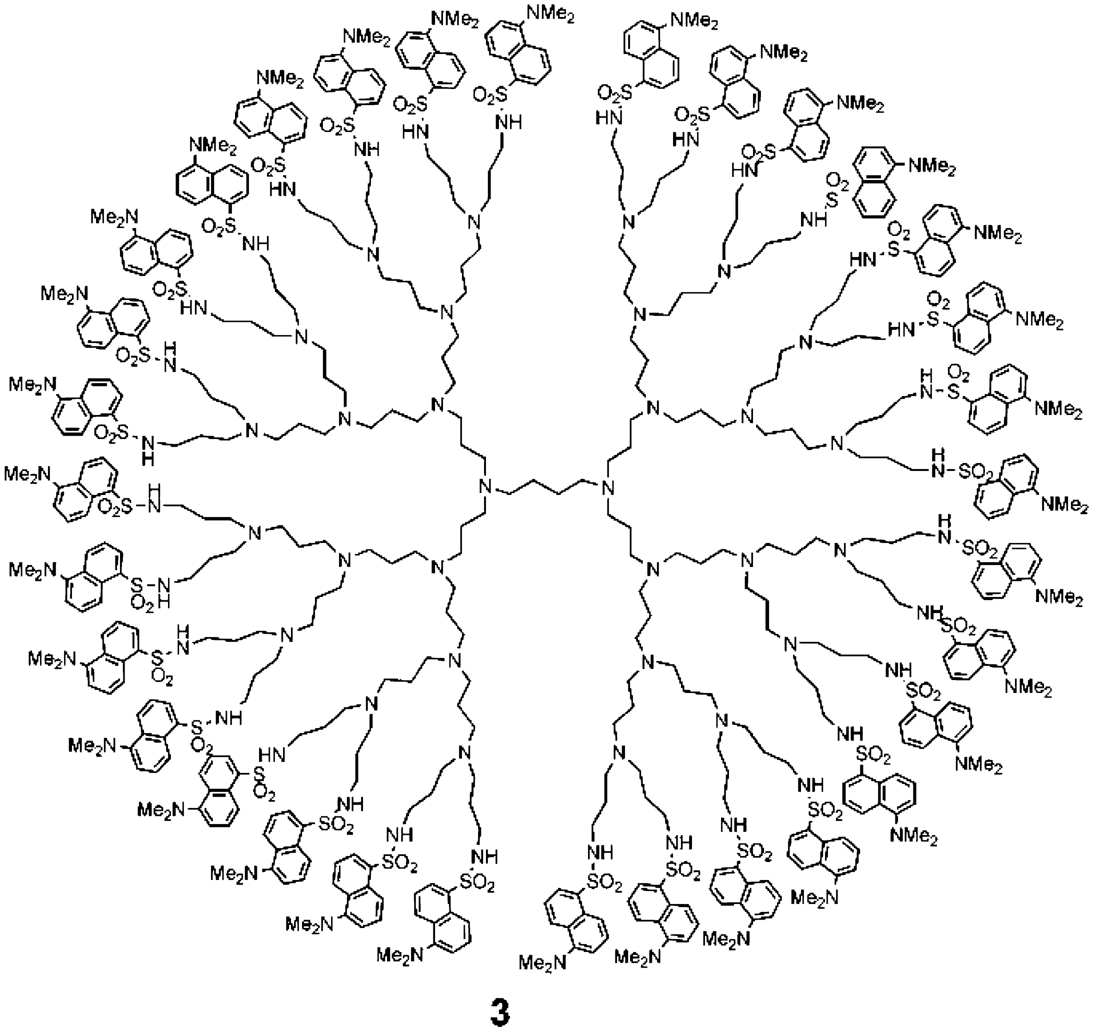
3. Dendrimers with amine coordinating units

Dendrimers of the poly(propylene amine) family can be easily functionalized in the periphery with luminescent units such as dansyl [38]. The resulting dendrimers *n*D, where the generation number *n* goes from 1 to 5, comprise $2^{(n+1)}$ dansyl functions in the periphery and $2^{(n+1)}$-2 tertiary amine units in the interior. Compound **3** is the fourth generation dendrimer 4D that contains 30 tertiary amine units and 32 dansyl functions. The dansyl units behave independently from one another so that these dendrimers display light absorption and emission properties characteristic of the dansyl chromophoric group, i.e. intense absorption bands in the near UV spectral region ($\lambda_{max} = 252$ and 339 nm; $\varepsilon_{max} \approx 12{,}000$ and $3900\,L\,mol^{-1}\,cm^{-1}$, respectively, for each dansyl unit in acetonitrile/dichloromethane 1:1 v/v solution) and a strong fluorescence band in the visible region (λ_{max} = 500 nm; Φ_{em} = 0.46, τ = 16 ns in acetonitrile/dichloromethane 1:1 v/v solution). Because of the presence of the aliphatic amine groups in their interior, these dendrimers can be used as ligands for transition metal ions. It should be noted that the dansyl units are not involved in metal coordination, so that, as we have seen in Section 2, they may be considered as components of a second coordination sphere covalently linked to the amine ligands that constitute the first coordination sphere of the metal ions. Therefore, the absorption and emission bands of dansyl can be classified as LC but, as discussed above, it is convenient to consider the metal complexes of **3** and of the related dendrimers as supramolecular species where the component chromophoric units do not interact in the ground state but excited state interactions can lead to intercomponent energy and electron transfer processes.



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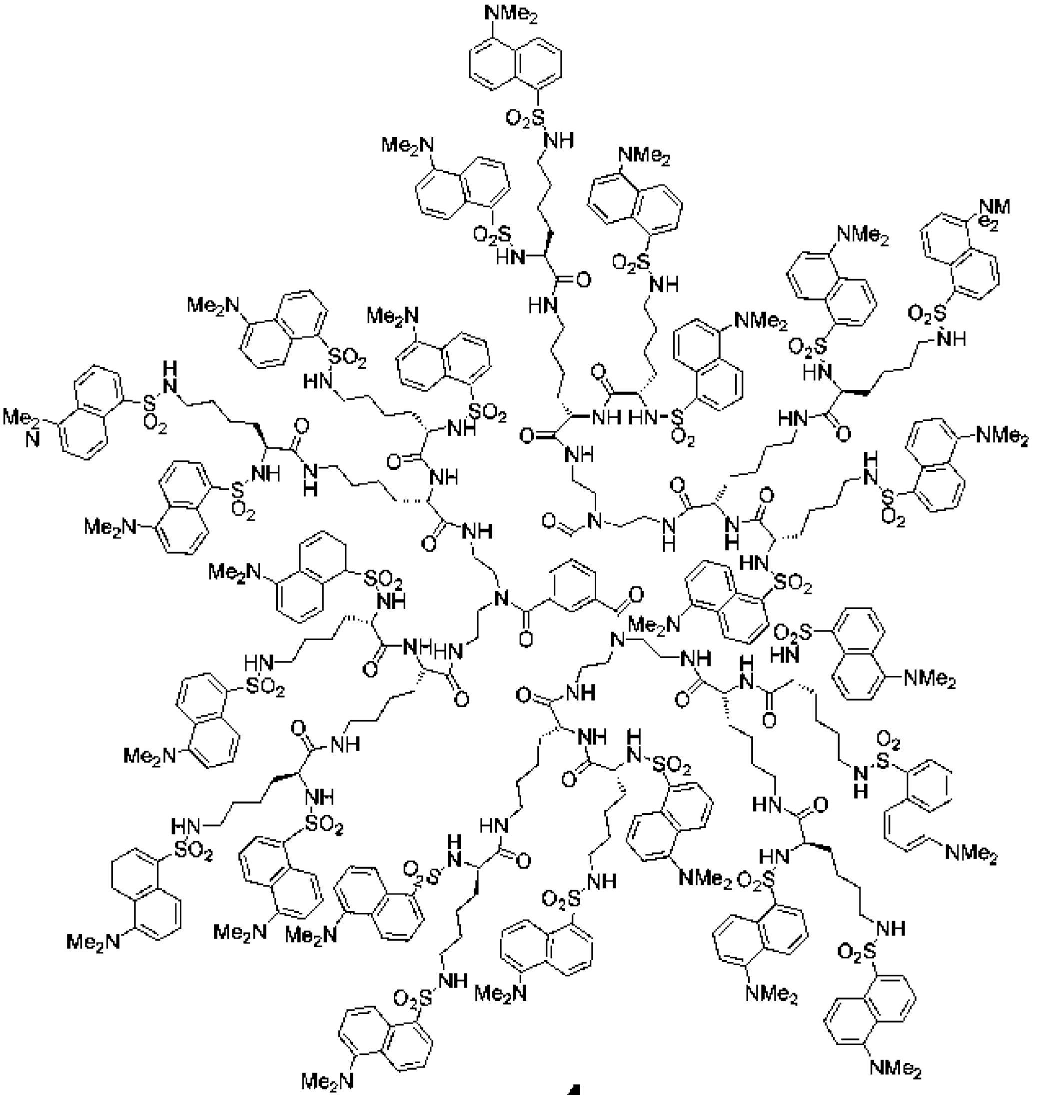
The titration of these dansyl functionalized dendrimers with Co^{2+} ions (as $Co(NO_3)_2 \cdot 6H_2O$) has been carefully investigated [20,39]. For comparison purposes, the behavior of a monodansyl reference compound has also been studied. The results obtained have shown that: (i) the absorption and fluorescence spectra of a monodansyl reference compound are not affected by addition of Co^{2+} ions; (ii) in the case of the dendrimers, the absorption spectra are unaffected, but a strong quenching of the fluorescence of the peripheral dansyl units is observed; (iii) the fluorescence quenching takes place by a static mechanism involving coordination of metal ions in the interior of the dendrimers; (iv) metal ion coordination by the dendrimers is a fully reversible process; (v) a strong amplification of the fluorescence quenching signal is observed with increasing dendrimer generation. The results obtained show that metal coordination involves the amine groups and that the poly(propylene amine) dendrimers functionalized with luminescent dansyl units can be profitably used as supramolecular fluorescent sensors for metal ions. The advantage of a dendrimer for this kind of application is related to the fact that a single analyte can interact with a great number of fluorescent units, which results in signal amplification. For example, when a Co^{2+} ion enters dendrimer **3**, the fluorescence of all the 32 dansyl units is quenched, with a 32 times increase in sensitivity with respect to a normal dansyl sensor. This concept is illustrated in Fig. 2.

4. Dendrimers with amide coordinating units

Dendrimer **4**, which is based on a benzene core branched in the 1, 3, and 5 positions, contains 18 amide groups in its branches and 24 chromophoric dansyl units in the periphery. It is well known that, in sufficiently basic solution, amide groups [40], including the dansylamide units [41] can undergo deprotonation and coordination of transition metal ions. As we have seen above, the dansyl units show strong absorption bands in the near UV spectral region and an intense fluorescence band in the visible region. In acetonitrile/dichloromethane (5:1 v/v) solution, the absorption spectrum and the fluorescence properties of the dendrimer are those expected for a species containing 24 non-interacting dansyl units [21b]. Upon addition of Co^{2+} or Ni^{2+} ions (as $M(NO_3)_2{\cdot}6H_2O$ salts) to a solution of **4** in the presence of a weak base, the absorption band of the dansyl units did not show any appreciable change, but a strong static quenching of the dansyl fluorescence was observed [21b]. These results indicate that the metal ions are coordinated by the aliphatic amide units and can quench the dansyl fluorescent excited state by energy or electron transfer. Under conditions in which each dendrimer can coordinate not more than a single metal ion, about nine out of 24 dansyl units are quenched. Apparently, contrary to what happens in the case of dendrimer **3** discussed above, the metal ion cannot interact with all the dansyl units present in a dendrimer because it is coordinated offset.



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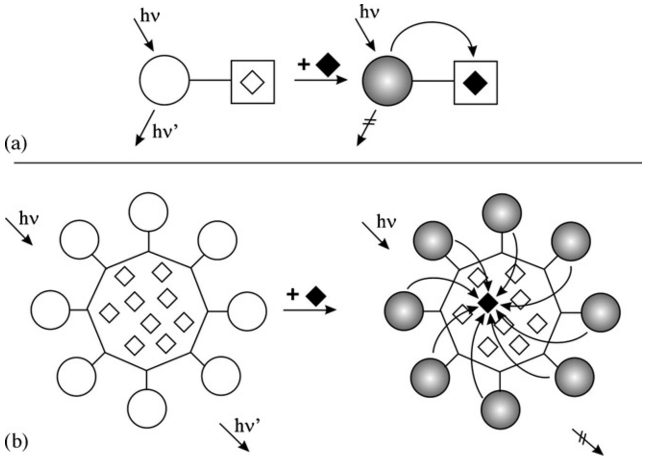


Fig. 2. Schematic representation of (a) a conventional fluorescent sensor and (b) a fluorescent sensor with signal amplification. Open rhombi indicate coordination sites and black rhombi indicate metal ions. The curved arrows represent quenching processes. In the case of a dendrimer, the absorbed photon excites a single fluorophore component, that is quenched by the metal ion, regardless of its position [39].

Investigations have then been extended [42] to lanthanide ions since amide groups are known to be good ligands for such metal ions even in the absence of base [21a].

Addition of lanthanide ions to solutions containing dendrimer **4** showed that [42]: (a) the absorption spectrum of the dendrimer is almost unaffected; (b) the fluorescence of the dansyl units is quenched; (c) the quenching effect is very large for Nd^{3+} and Eu^{3+}, moderate for Er^{3+} and Yb^{3+}, small for Tb^{3+}, and very small for Gd^{3+}; (d) in the case of Nd^{3+}, Er^{3+}, and Yb^{3+} the quenching of the dansyl fluorescence is accompanied by the sensitized near-infrared emission of the lanthanide ion. Interpretation of the results obtained on the basis of the energy levels (Fig. 3) and redox potentials of the dansyl unit and of the metal ions have led to the following conclusions: (i) at low metal ion concentrations, each dendrimer hosts only one metal ion; (ii) the very small quenching effect observed for Gd^{3+} is assigned to charge perturbation of the S_1 dansyl excited state, indicating that the effect on intersystem crossing is small, if any; (iii) when the hosted metal ion is Nd^{3+} or Eu^{3+}, all the 24 dansyl unit of the dendrimer are quenched with unitary efficiency; (iv) quenching by Nd^{3+} and Er^{3+} takes place by direct energy transfer from the fluorescent (S_1) excited state of dansyl to a manifold of Nd^{3+} energy levels, followed by sensitized near-infrared emission from the metal ion ($\lambda_{max} = 1064$ nm for Nd^{3+} and $\lambda_{max} = 1525$ for Er^{3+}); (v) quenching by Eu^{3+} does not lead to any sensitized emission since the lowest excited state of the system is a non-emissive electron-transfer excited state; upon protonation of the dansyl units, however, the electron-transfer excited state moves to very high energy and at 77 K a sensitized Eu^{3+} emission is observed. Since the sensitization is not accompanied by quenching of the protonated dansyl fluorescence, energy transfer originates from the T_1 excited state of the protonated dansyl units; (vi) in the case of Yb^{3+}, the sensitization of the near-infrared metal-centered emission occurs via the intermediate formation of a dansyl to Yb^{3+} electron-transfer excited state; at 77 K the electron-transfer excited state moves to higher energy, thus preventing the population of the Yb^{3+} emitting excited state; (vii) the small quenching effect observed for Tb^{3+} is partly caused by a direct energy transfer from the fluorescent (S_1) excited state of dansyl; on protonation of the dansyl units, a strong Tb^{3+} sensitized emission is observed at 77 K, originating from the T_1 excited state of the protonated dansyl units.

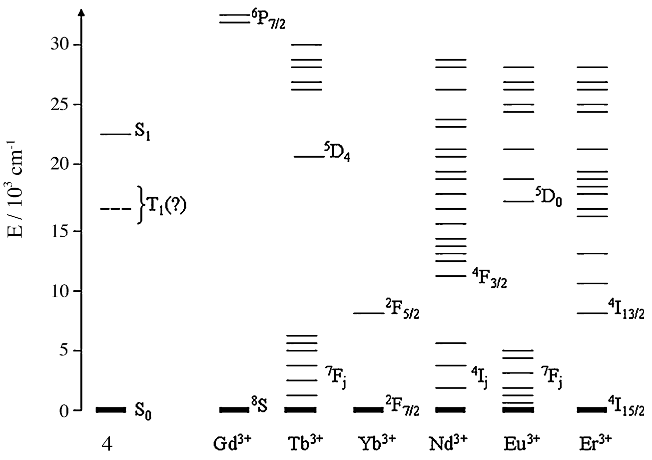


Fig. 3. Energy level diagrams for the dansyl units of dendrimer **4** and the investigated lanthanide ions. The position of the triplet excited state of **4** is uncertain because no phosphorescence can be observed [36].

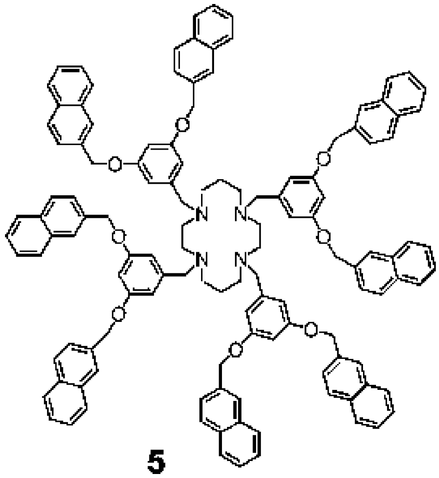
5. Dendrimers with a well defined coordinating site as a core

The above discussed dendrimers which contain amine or amide groups in their branches give rise to metal complexes of variable stoichiometry and unknown structures since they contain several more or less equivalent ligand units and not well defined coordination sites. A much better defined coordination arrangement is obtained when a dendrimer is constructed around a precise coordination site.

1,4,8,11-Tetraazacyclotetradecane (cyclam) is one of the most extensively investigated ligands in coordination chemistry [43]. Both cyclam and its 1,4,8,11-tetramethyl derivative in aqueous solution can be protonated and can coordinate metal ions such as Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) with high stability constants [44].

Dendrimers **5** and **6** consist of a cyclam core appended with four dimethoxybenzene and eight naphthyl units, and 12 dimethoxybenzene and 16 naphthyl units, respectively. In acetonitrile–dichloromethane 1:1 v/v solution the absorption spectra are dominated by naphthalene absorption bands and the dendrimers exhibit three types of emission bands, assigned to naphthyl localized excited states ($\lambda_{max} = 337$ nm), naphthyl excimers (λ_{max} ca. 390 nm), and naphthyl-amine exciplexes ($\lambda_{max} = 480$ nm) [45]. Upon titration with trifluoroacetic acid, the tetraamine cyclam core undergoes two successive protonation reactions, that not only prevent exciplex formation by engaging the nitrogen lone pairs, but also cause strong nuclear rearrangements in the cyclam structure which affect excimer formation between the peripheral naphthyl units of the dendrimers.

It should also be noted that the impossibility to form exciplexes results in a strong increase of the naphthyl localized emission.



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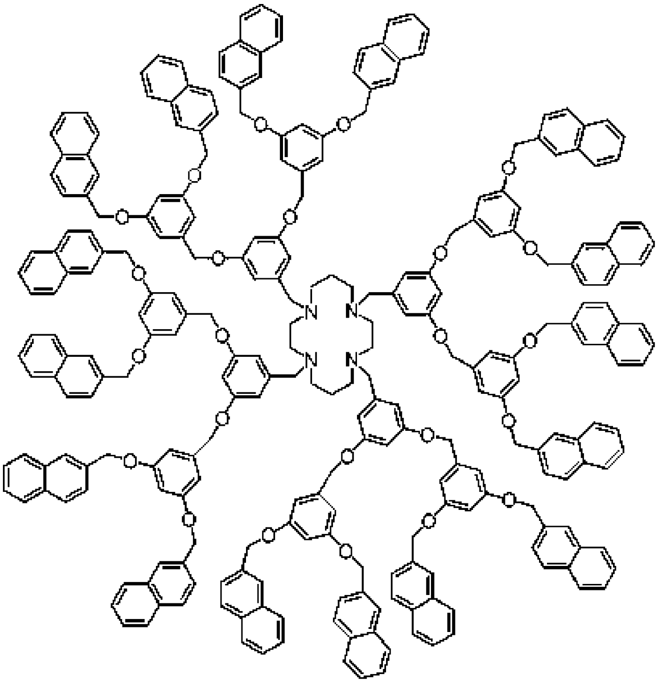


6

Extensive investigations have been performed on the interaction of dendrimers **5** and **6** with metal ions [23,46]. Coordination of Zn^{2+}, a metal ion that is difficult to oxidize and reduce and that exhibits a d^{10} electronic configuration, leads to complexes that cannot exhibit MC or CT excited states at low energy. Nevertheless, Zn^{2+} coordination by the dendrimer causes strong changes in the emission spectrum of the dendrimer since engagement of the nitrogen lone pairs in the coordination of the metal ion prevents exciplex formation, with a resulting increase of the naphthyl fluorescence. Such a fluorescent signal is quite suitable for monitoring the formation of the complexes in dendrimer/metal titration experiments. Surprisingly, both dendrimers **5** and **6** give rise to complexes with 2:1 dendrimer/metal stoichiometry at low Zn^{2+} concentration, as evidenced by both fluorescence and ^{1}H NMR titrations. In particular, in the case of the largest dendrimer **6**, at low metal ion concentration only the species $[Zn(\mathbf{6})_2]^{2+}$ is present with a high formation constant ($>10^{13}$ M^{-2}). The unexpected $[Zn(\mathbf{6})_2]^{2+}$ species shows that the dendrimer branches not only do not hinder, but in fact favour coordination of cyclam to Zn^{2+} with respect to coordination of solvent molecules or counter ions. Two limiting structures can be proposed for the 2:1 complexes: (i) an "inward" structure, stabilized by the intermeshing of the branches of the two coordinated dendrimers; (ii) an "outward" structure in which the branches of the two coordinated dendrimers do not interact but impose to the cyclam core a very specific coordination structure. Indeed, an "inward" structure for the 2:1 complex stabilized by branch intermeshing should increase the probability of excimer formation compared with the 1:1 species. In such a case, the intensity of the excimer band (λ_{max} ca. 390 nm) should grow more rapidly at the beginning of the titration, when formation of a 2:1 species is favoured. This seems to be the case for dendrimer **5**, but not for dendrimer **6**. Therefore, in the $[Zn(\mathbf{6})_2]^{2+}$ species the dendrimer branches are likely extending outward (Fig. 4). Furthermore, the two cyclam cores, to account for the coordination number (≤ 6) of Zn^{2+}, are likely forced to adopt a structure in which not all of the four N atoms are available for Zn^{2+} coordination, thereby favouring a 2:1 stoichiometry.

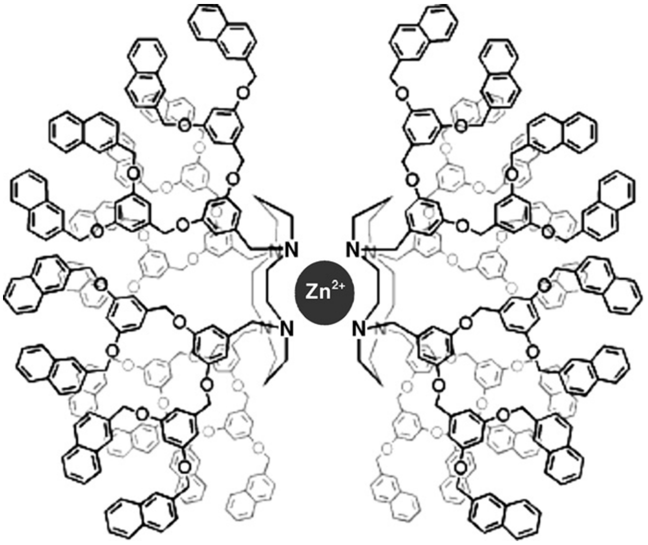
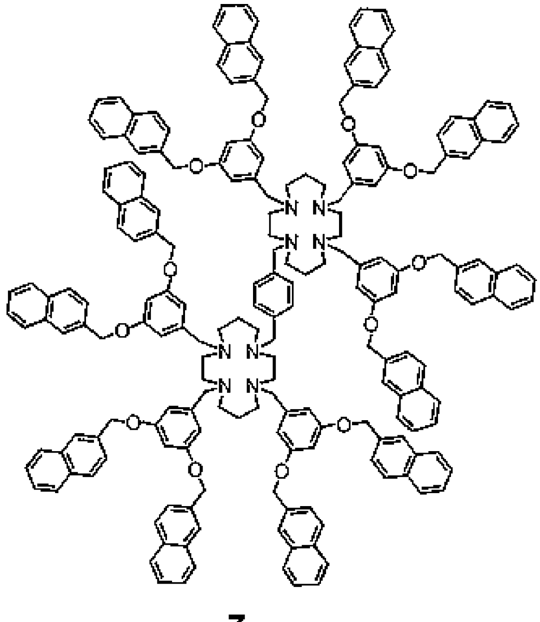


Fig. 4. Schematic representation of the $[Zn(\mathbf{6})_2]^{2+}$ species in which the dendrimer branches are extending outward.

Complexation of dendritic ligands **5** and **6** with lanthanide ions (Nd^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}) [46b] led to qualitatively similar results: an increase of the monomer naphthalene emission band at 337 nm and a complete disappearance of the exciplex band at 480 nm. However, the complex stoichiometry is different. Emission data were best fitted considering the formation of 1:3 and 1:2 (metal/dendrimer) complexes ($\log \beta_{1:2} = 14.1$ and $\log \beta_{1:3} = 20.0$) in the case of **5** and a 1:3 (metal/dendrimer) complex ($\log \beta_{1:3} = 20.3$) for compound **6**. Therefore, at low metal ion concentration only the $[M(\mathbf{6})_3]^{3+}$ species is present, as demonstrated also by NMR titration. It is likely that in this complex not all the 12 nitrogens of the three cyclam cores are engaged in metal ion coordination. However, upon metal coordination the exciplex emission band completely disappears, as it is was previously observed upon acid titration. Clearly, as is also shown by NMR results, the presence of the 3+ ion is "felt" by all the nitrogens of the three cyclam moieties, thereby raising the energy of the exciplex excited state above that of the naphthyl-based one. For all the lanthanide complexes of **5** and **6** no sensitized emission from the lanthanide ion was observed. Therefore, energy transfer from either the S_1 or T_1 excited state of the naphthyl units of **5** and **6** to the lanthanide ion is inefficient. By contrast, efficient energy transfer from naphthalene-like chromophores to Eu^{3+} has been reported in the case in which naphthalene is linked through an amide or carboxylate bond to the lanthanide [47]. Apparently, the nature of the first coordination sphere plays an important role concerning energy transfer efficiency.

A step further in cyclam-based dendritic ligands for metal ions is constituted by dendrimer **7**, containing two covalently linked cyclam units as a core, appended to six branches, each one of them consisting of a dimethoxybenzene and two naphthyl units [48]. Its photophysical properties are qualitatively similar to that observed for **5**. For example, the emission spectrum evidences the presence of naphthyl localized excited states (λ_{max} = 337 nm), naphthyl excimers (λ_{max} ca. 390 nm), and naphthyl-amine exciplexes (λ_{max} = 480 nm). Upon titration with trifluoroacetic acid, the two cyclams undergo protonation reactions, that, as previously discussed, not only prevent exciplex formation and, consequently, increase naphthyl localized emission, but also cause strong nuclear rearrangements in the cyclam structure which affect excimer formation between the peripheral naphthyl units of the dendrimers. At variance with dendrimers **5** and **6**, no further change in the emission spectrum was observed after addition of two equivalents of protons per dendrimer, i.e., after formation of a **7**($2H^+$) species. These results suggest that the two cyclam units of **7** do not behave independently and that in the **7**($2H^+$) species the two protons are likely shared by the two cyclam units in a sandwich-type structure.



7

Dendrimer's **7** ability to coordinate Zn(II) and Cu(II) in acetonitrile/dichloromethane 1:1 (v/v) solution has been carefully investigated [48].

Upon titration with $Zn(CF_3SO_3)_2$ no change was observed in the absorption spectrum, whereas strong changes were observed in the emission spectrum. Such changes, qualitatively similar to those caused by protonation, indicate that a 1:1 complex, $[Zn(\mathbf{7})]^{2+}$, is first formed and then replaced by a 2:1 species, $[Zn_2(\mathbf{7})]^{4+}$ ($\log \beta_{1:1} = 9.7$ and $\log \beta_{2:1} = 16.1$ for these two species, respectively). In the 1:1 complex $[Zn(\mathbf{7})]^{2+}$, the metal ion is likely sandwiched between the two cyclam units. As previously observed in the case of dendritic ligands **5** and **6**, apparently, the dendrimer branches favour coordination of cyclam units to metal ions with respect to solvent molecules and counter ions. Furthermore, the experimental observation that in going from $[Zn(\mathbf{7})]^{2+}$ to $[Zn_2(\mathbf{7})]^{4+}$ the intensity of the excimer band does not change suggests that in these sandwich-type complexes the dendrimer branches extends outward and maintain the same structure in both species.

Quite different results were obtained upon titration with $Cu(CF_3SO_3)_2$ both in absorption and emission spectra. The absorption spectrum showed the appearance of a broad tail in the 300–400 nm region, assigned to ligand-to-metal charge-transfer (LMCT) transitions (a similar absorption band was observed also in the case of mere cyclam). The absorbance values increase almost linearly up to the addition of 2 equivalents of metal ion per dendrimer. Therefore we can conclude that upon addition of $Cu(CF_3SO_3)_2$ to **7**, both the cyclam units of the dendrimer coordinate a Cu^{2+} ion ($\log \beta_{2:1} = 11.9$). More details were obtained from the changes observed in the emission spectrum, that can be summarized as follows: (i) the intensity of the naphthyl band is almost constant up to the addition of one equivalent of metal ion and then decreases slightly; (ii) the intensity of the exciplex band decreases linearly and disappears after addition of two equivalents of metal ions; (iii) the intensity of the excimer band increases at the beginning of the titration, and reaches a maximum value after addition of one equivalent of metal ion and then decreases. At variance with the case of H^+ or Zn^{2+}, the decrease in the intensity of the exciplex emission, caused by the engagement of the cyclam N atoms by protons or metal ions, is not accompanied by an increase in the intensity of the naphthyl localized emission. This result can be easily rationalized considering that coordination of Cu^{2+}, while preventing deactivation of the excited naphthyl units via exciplex formation, introduces another deactivation channel related to the presence of the low energy LMCT state. Furthermore, analysis of the emission spectral changes upon addition of Cu^{2+} evidences the formation of a 1:1 complex, $[Cu(\mathbf{7})]^{2+}$, then replaced by a 2:1 species, $[Cu_2(\mathbf{7})]^{4+}$.

6. Adducts between metal complexes and dendrimers

Suitably designed dendrimers can be assembled as a second coordination sphere around a suitable metal complex. In such a case, the absorption spectrum of the adduct is again expected to correspond to the summation of the spectra of the components of the adduct, whereas strong changes can be observed in the

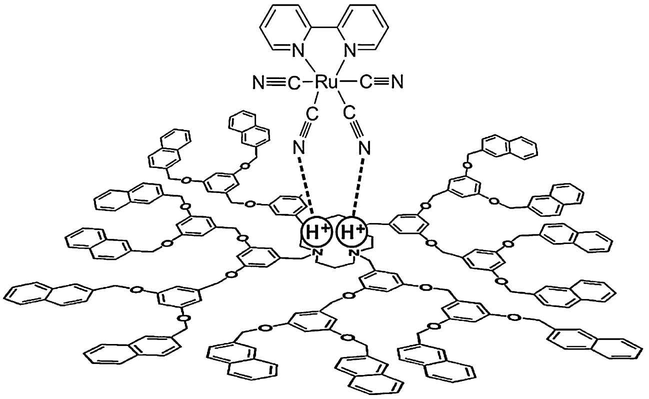


Fig. 5. Schematic representation of the $\{[Ru(bpy)(CN)_4]^{2-}\cdot(2H^+)\cdot\mathbf{6}\}$ adduct.

emission spectra because of the occurrence of intercomponent energy or electron transfer processes.

An interesting example involving the $[Ru(bpy)(CN)_4]^{2-}$ complex and the above discussed dendrimer **6** consisting of a cyclam core appended with 12 dimethoxybenzene and 16 naphthyl units [49]. In acetonitrile-dichloromethane 1:1 v/v solution, $[Ru(bpy)(CN)_4]^{2-}$ exhibits two moderately intense ^{1}MLCT absorption bands at 373 and 535 nm and a very weak ^{3}MLCT emission at 770 nm. Upon titration with trifluoroacetic acid, successive protonation of two CN^- ligands takes place with displacement of the absorption and emission bands to higher energies. As discussed above, dendrimer **6** displays a complex emission spectrum dominated by a naphthalene type fluorescence at 335 nm and a broad exciplex-type band at 460 nm originating from the interaction between the excited state of the naphthyl unit with the lone pairs of the 1,4,8,11-tetraazacyclotetradecane (cyclam) amine units. We have also seen in Section 5 that upon addition of trifluoroacetic acid, dual protonation of the cyclam core of the dendrimer takes place leading to the disappearance of the exciplex band and to the increase in intensity of the naphthyl localized band at 335 nm [45]. The absorption and emission spectra of a 1:1 mixture of $[Ru(bpy)(CN)_4]^{2-}$ and **6** consist of the absorption and emission bands of the isolated components, showing that there is no interaction between the two species. Titration of this mixture with trifluoroacetic acid, however, causes strong spectral changes with isosbestic points maintained up to the addition of two equivalents of acid. The results obtained show that protons promote association of $[Ru(bpy)(CN)_4]^{2-}$ and **6** and that after addition of two equivalents of acid a $\{[Ru(bpy)(CN)_4]^{2-}\cdot(2H^+)\cdot\mathbf{6}\}$ adduct is formed, in which the two original species share two protons. Interestingly, whereas the exciplex type band of **6** disappears upon adduct formation, as expected because of the protonation of the cyclam nitrogens, the intensity of the naphthyl band does not increase, as would be expected by disappearance of the exciplex, but decreases. This shows that a new deactivation channel, namely energy transfer to the lower lying excited state of the Ru complex, is available for the naphthyl excited state in the adduct (Fig. 5). Quantitative measurements have shown that such an energy-transfer process does take place with an efficiency of 85%. Therefore, dendrimer **6** plays the role of a light-harvesting second coordination sphere that transfers the collected energy to the $[Ru(bpy)(CN)_4]^{2-}$ complex. Such a system shows another interesting feature. The $\{[Ru(bpy)(CN)_4]^{2-}\cdot(2H^+)\cdot\mathbf{6}\}$ adduct can be disrupted not only, of course, by addition of a base (1,4-diazabicyclo[2.2.2]octane), yielding the starting species $[Ru(bpy)(CN)_4]^{2-}$ and **6**, but also by further addition of acid, with formation of $(\mathbf{6}\cdot 2H)^{2+}$ and protonated forms of $[Ru(bpy)(CN)_4]^{2-}$. It is shown that upon stimulation with two chemical inputs (acid and base) $\{[Ru(bpy)(CN)_4]^{2-}\cdot(2H^+)\cdot\mathbf{6}\}$ exhibits two distinct optical outputs (a naphthalene-based and a Ru(bpy)-based emissions) that behave according to an XOR and an XNOR logic, respectively.

7. Conclusion

The above discussed examples show that the giant complexes obtained upon metal ion coordination by dendrimers possessing luminescent and coordinating units can exhibit interesting spectroscopic properties that reflect the occurrence of intercomponent energy and electron transfer processes. It is likely that improving design of these types of dendritic ligands will lead to coordination compounds capable of performing even more sophisticated functions, such as energy up-conversion and electrochemiluminescence.

Acknowledgments

Financial support from FIRB (Manipolazione molecolare per macchine nanometriche) and University of Bologna (Funds for Selected Topics) is gratefully acknowledged.

References

[1] V. Balzani, V. Carassiti, Photochemistry of Coordination Compounds, Academic Press, London, 1970.
[2] C.K. Jørgensen, Absorption Spectra and Chemical Bonding in Complexes, Pergamon Press, Oxford, 1962.
[3] C.J. Ballhausen, Introduction to Ligand Field Theory, McGraw-Hill, New York, 1962.
[4] (a) A.B.P. Lever, Coord. Chem. Rev. 3 (1968) 119;
(b) A.B.P. Lever, Inorganic Electronic Spectroscopy, 2nd ed., Elsevier, Amsterdam, 1984.
[5] L.S. Forster, K. De Armond, J. Chem. Phys. 34 (1961) 2193.
[6] C.A. Parker, Photoluminescence of Solutions, Elsevier, Amsterdam, 1968.
[7] (a) G.A. Crosby, R.J. Watts, D.H.W. Carstens, Science 170 (1970) 1195;
(b) A.D. Gafney, A.W. Adamson, J. Am. Chem. Soc. 94 (1972) 8238;
(c) N. Sabbatini, V. Balzani, J. Am. Chem. Soc. 94 (1972) 7587.
[8] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, Coord. Chem. Rev. 84 (1988) 85.
[9] V. Balzani, P. Ceroni, M. Maestri, C. Saudan, V. Vicinelli, Top. Curr. Chem. 228 (2003) 159.
[10] (a) C.A. Schalley, F. Vögtle (Eds.), Top. Curr. Chem. 228 (2003);
(b) G.R. Newkome, C. Moorefield, F. Vögtle, Dendrimers and Dendrons: Concepts, Syntheses, Perspectives, VCH, Weinheim, 2001;
(c) J.M.J. Fréchet, D.A. Tomalia (Eds.), Dendrons and other Dendritic Polymers, Wiley, 2001.
[11] For some recent reviews, see:
(a) D.A. Tomalia, J.M.J. Fréchet (Eds.), Prog. Polym. Sci. 30 (3/4) (2005);
(b) T.G. Goodson III, Acc. Chem. Res. 38 (2005) 99;
(c) F.C. De Schryver, T. Vosch, M. Cotlet, M. Van der Auweraer, K. Müllen, J. Hofkens, Acc. Chem. Res. 38 (2005) 514;
(d) R.W.J. Scott, O.M. Wilson, R.M. Crooks, J. Phys. Chem. B 109 (2005) 692;

(e) D. Astruc, F. Lu, J.R. Aranzaes, Angew. Chem. Int. Ed. 44 (2005) 7852;
(f) P.A. Chase, R.J.M. Klein Gebbink, G. van Koten, J. Organomet. Chem. 689 (2004) 4016;
(g) W. Ong, M. Gomez-Kaifer, A.E. Kaifer, Chem. Commun. (2004) 1677;
(h) M. Ballauff, C.N. Likos, Angew. Chem. Int. Ed. 43 (2004) 2998;
(i) A.-M. Caminade, J.-P. Majoral, Acc. Chem. Res. 37 (2004) 341.
[12] E. Buhleier, W. Wehner, F. Vögtle, Synthesis (1978) 155.
[13] P. Ceroni, V. Vicinelli, M. Maestri, V. Balzani, S.-K. Lee, J. van Heyst, M. Gorka, F. Vögtle, J. Organomet. Chem. 689 (2004) 4375.
[14] For some recent examples, see:
(a) T. Imaoka, R. Tanaka, S. Arimoto, M. Sakai, M. Fujii, K. Yamamoto, J. Am. Chem. Soc. 127 (2005) 13896;
(b) R.P. Brinas, T. Troxler, R.M. Hochstrasser, S.A. Vinogradov, J. Am. Chem. Soc. 127 (2005) 11851;
(c) F. Loiseau, S. Campagna, A. Hameurlaine, W. Dehaen, J. Am. Chem. Soc. 127 (2005) 11352;
(d) Y.-J. Mo, D.-L. Jiang, M. Uyemura, T. Aida, T. Kitagawa, J. Am. Chem. Soc. 127 (2005) 10020;
(e) W.-S. Li, D.-L. Jiang, Y. Suna, T. Aida, J. Am. Chem. Soc. 127 (2005) 7700;
(f) X. Yan, T. Goodson III, T. Imaoka, K. Yamamoto, J. Phys. Chem. B 109 (2005) 9321;
(g) S.A. Chavan, W. Maes, L.E.M. Gevers, J. Wahlen, I.F.J. Vankelecom, P.A. Jacobs, W. Dehaen, D.E. De Vos, Chem. Eur. J. 11 (2005) 6754;
(h) J. Larsen, B. Brueggemann, T. Polivka, V. Sundström, E. Aakesson, J. Sly, M.J. Crossley, J. Phys. Chem. A 109 (2005) 10654.
[15] (a) F. Puntoriero, S. Serroni, M. Galletta, A. Juris, A. Licciardello, C. Chiorboli, S. Campagna, F. Scandola, Chem. Phys. Chem. 6 (2005) 129;
(b) N.D. McClenaghan, R. Passalacqua, F. Loiseau, S. Campagna, B. Verheyde, A. Hameurlaine, W. Dehaen, J. Am. Chem. Soc. 125 (2003) 5356.
[16] For some recent examples, see:
(a) D. Sobransingh, A.E. Kaifer, Chem. Commun. (2005) 5071;
(b) F.E. Appoh, D.S. Thomas, H.-B. Kraatz, Macromolecules 38 (2005) 7562.
[17] V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni, M. Venturi, Acc. Chem. Res. 31 (1998) 26.
[18] Y.-H. Liao, J.R. Moss, Organometallics 15 (1996) 4307.
[19] S. Nlate, J. Ruiz, V. Sartor, R. Navarro, J.-C. Blais, D. Astruc, Chem. Eur. J. 6 (2000) 2544.
[20] See, e.g.:
V. Balzani, P. Ceroni, V. Vicinelli, S. Gestermann, M. Gorka, C. Kauffmann, F. Vögtle, J. Am. Chem. Soc. 122 (2000) 10398.
[21] See, e.g.:
(a) J.P. Cross, M. Lauz, P.D. Badger, S. Petoud, J. Am. Chem. Soc. 126 (2004) 16278;
(b) V. Balzani, P. Ceroni, S. Gestermann, M. Gorka, C. Kauffmann, F. Vögtle, J. Chem. Soc., Dalton Trans. (2000) 3765.
[22] See, e.g.:
(a) T. Imaoka, R. Tanaka, S. Arimoto, M. Sakai, M. Fujii, K. Yamamoto, J. Am. Chem. Soc. 127 (2005) 13896.
[23] See, e.g.:
(a) C. Saudan, V. Balzani, M. Gorka, S.-K. Lee, M. Maestri, V. Vicinelli, F. Vögtle, J. Am. Chem. Soc. 125 (2003) 4424.
[24] A.-M. Caminade, J.-P. Majoral, Coord. Chem. Rev. 249 (2005) 1917.
[25] V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serroni, Chem. Rev. 96 (1996) 759.
[26] S. Serroni, G. Denti, S. Campagna, A. Juris, M. Ciano, V. Balzani, Angew. Chem. Int. Ed. Engl. 31 (1992) 1493.
[27] K. Onitsuka, A. Shimizu, S. Takahashi, Chem. Commun. (2003) 280.
[28] W.T.S. Huck, F.G.J.M. van Veggel, D.N. Reinhoudt, Angew. Chem. Int. Ed. Engl. 35 (1996) 1213.
[29] M. Pleovets, F. Vögtle, L. De Cola, V. Balzani, New J. Chem. 23 (1999) 63.
[30] V. Balzani, G. Bergamini, F. Marchioni, P. Ceroni, Coord. Chem. Rev., doi:10.1016/j.ccr.2005.11.013.
[31] (a) V. Balzani, A. Credi, M. Venturi, Chem. Eur. J. 8 (2002) 5524;
(b) V. Balzani, A. Credi, M. Venturi, Molecular Devices and Machines—A Journey in the Nano World, Wiley-VCH, Weinheim, 2003.
[32] F. Vögtle, M. Plevoets, M. Nieger, G.C. Azzellini, A. Credi, L. De Cola, V. De Marchis, M. Venturi, V. Balzani, J. Am. Chem. Soc. 121 (1999) 6290.
[33] (a) T. Gunnlaugsson, J.P. Leonard, Chem. Commun. (2003) 2424;
(b) T. Gunnlaugsson, J.P. Leonard, K. Sénéchal, A.J. Harte, J. Am. Chem. Soc. 125 (2003) 12062;
(c) P. Atkinson, Y. Bretonniere, D. Parker, Chem. Commun. (2004) 438.
[34] M.H.V. Wets, R.H. Woudenberg, P.G. Emmerink, R. van Gassel, J.W. Hofstraat, J.W. Verhoeven, Angew. Chem. Int. Ed. 39 (2000) 4542.
[35] (a) D. Parker, R.S. Dickins, H. Puschmann, C. Crossland, J.A.K. Howard, Chem. Rev. 102 (2002) 1977;
(b) N. Sabbatini, M. Guardigli, J.-M. Lehn, Coord. Chem. Rev. 123 (1993) 201.
[36] G.A. Hebbink, S.I. Klink, L. Grave, P.G.B. Oude Alink, F.C.J.M. van Veggel, Chem. Phys. Chem. 3 (2002) 1014.
[37] M. Kawa, J.M.J. Fréchet, Chem. Mater. 10 (1998) 286.
[38] F. Vögtle, S. Gestermann, C. Kauffmann, P. Ceroni, V. Vicinelli, L. De Cola, V. Balzani, J. Am. Chem. Soc. 121 (1999) 12161.
[39] V. Balzani, P. Ceroni, S. Gestermann, C. Kauffmann, M. Gorka, F. Vögtle, Chem. Commun. (2000) 853.
[40] (a) L. Fabbrizzi, F. Forlini, A. Perotti, B. Seghi, Inorg. Chem. 23 (1984) 807;
(b) L. Fabbrizzi, M. Licchelli, P. Pallavicini, A. Perotti, A. Taglietti, D. Sacchi, Chem. Eur. J. 2 (1996) 75;
(c) V. Amendola, L. Fabbrizzi, C. Mangano, P. Pallavicini, A. Perotti, A. Taglietti, J. Chem. Soc., Dalton Trans. (2000) 185.
[41] L. Prodi, F. Bolletta, M. Montalti, N. Zaccheroni, Eur. J. Inorg. Chem. (1999) 455.
[42] (a) F. Vögtle, M. Gorka, V. Vicinelli, P. Ceroni, M. Maestri, V. Balzani, Chem. Phys. Chem. 12 (2001) 769;
(b) V. Vicinelli, P. Ceroni, M. Maestri, V. Balzani, M. Gorka, F. Vögtle, J. Am. Chem. Soc. 124 (2002) 6461.
[43] (a) I. Lukeš, J. Kotek, P. Vojtíšek, P. Hermann, Coord. Chem. Rev. 216/217 (2001) 287;
(b) B.P. Hay, R.D. Hancock, Coord. Chem. Rev. 212 (2001) 61.
[44] (a) A. Bianchi, M. Micheloni, P. Paoletti, Coord. Chem. Rev. 110 (1991) 17;
(b) E. Kimura, Prog. Inorg. Chem. 41 (1994) 443;
(c) M. Meyer, V. Dahaoui-Gindrey, C. Lecomte, R. Guilard, Coord. Chem. Rev. 178 (1998) 1313;
(d) L. Fabbrizzi, M. Licchelli, P. Pallavicini, D. Sacchi, Supramol. Chem. 13 (2001) 569.
[45] C. Saudan, V. Balzani, P. Ceroni, M. Gorka, M. Maestri, V. Vicinelli, F. Vögtle, Tetrahedron 59 (2003) 3845.
[46] (a) C. Saudan, V. Balzani, M. Gorka, S.-K. Lee, J. van Heyst, M. Maestri, P. Ceroni, V. Vicinelli, F. Vögtle, Chem. Eur. J. 10 (2004) 899;
(b) C. Saudan, P. Ceroni, V. Vicinelli, M. Maestri, V. Balzani, M. Gorka, S.-K. Lee, J. van Heyst, F. Vögtle, Dalton Trans. (2004) 1597.
[47] (a) A. Beeby, D. Parker, J.A.G. Williams, J. Chem. Soc., Perkin Trans. 2 (1996) 1565;
(b) C.-H. Tung, L.-Z. Wu, J. Chem. Soc., Faraday Trans. 92 (1996) 1381;
(c) D. Parker, J.A.G. Williams, J. Chem. Soc., Perkin Trans. 2 (1995) 1305.
[48] G. Bergamini, P. Ceroni, V. Balzani, L. Cornelissen, J. van Heyst, S.-K. Lee, F. Vögtle, J. Mater. Chem. 15 (2005) 2959.
[49] G. Bergamini, C. Saudan, P. Ceroni, M. Maestri, V. Balzani, M. Gorka, S.-K. Lee, J. van Heyst, F. Vögtle, J. Am. Chem. Soc. 126 (2004) 16466.