Luminescent dendrimers as ligands for metal ions

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Abstract

Suitably designed luminescent dendrimers can play a role of ligands for luminescent and non-luminescent metal ions. This combination leads to species capable of exhibiting interesting and unusual properties, including (i) shielding excited states from quenching processes, (ii) light harvesting, (iii) conversion of incident UV light into visible or infrared emission, and (iv) metal ions sensing with signal amplification.
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1. Introduction

Dendrimers [1,2] constitute a new class of well-defined macromolecules exhibiting a tree-like architecture of nanodimension first derived by the "cascade molecule" approach [3]. Dendrimers are currently attracting great attention due to their unusual chemical and physical properties and the wide range of potential applications.

Dendrimer chemistry was initially developed in the field of organic chemistry. More recently, a number of dendrimers based on, or containing metal ions have been prepared and investigated. The study of these novel hybrid-species has considerably expanded the scope of metal coordination chemistry.

Metal complexes can exhibit valuable properties such as absorption of visible light, luminescence, and reduction and oxidation levels at accessible potentials. There-fore, coordination of metal ions by dendritic ligands can lead to complexes capable of performing valuable functions [4–7].

From a structural viewpoint, metal-containing dendrimers can be classified in several ways, e.g., as follows (for an alternative classification, see [8]).

(1) *Dendrimers built around a metal complex as a core.* These compounds can be considered metal complexes of ligands carrying dendritic substituents (Fig. 1(a)). The most commonly used metal containing cores are porphyrin complexes [9,10], poly-pyridine complexes [11], and ferrocene-type compounds [12].
(2) *Dendrimers containing metal complexes as branching centers.* In these compounds (Fig. 1(b)) metal complexes may play the role of connectors along the branches of a dendritic structure, as in the case of $[Ru(tpy)_2]^{2+}$ (tpy = 2,2′:6′,2″-terpyridine) [13].
(3) *Dendrimers containing metal complexes as peripheral units.* These compounds (Fig. 1(c)) belong to the class of dendrimers functionalized on the surface.

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Interesting examples are dendrimers coated with up to 48 Ru(Cp)(CO)$_2$R [14], 64 ferrocenyl units [15], or 3072 AuCl [16].

(4) *Dendrimers that can coordinate metal ions by ligand units that are present in the branches.* This is the case (Fig. 1(d)) of dendrimers whose branches contain many potential ligand units such as amines or amides. 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.

(5) *Dendrimers with a core which is able to coordinate a metal ion.* Examples of this kind (Fig. 1(e)) are the recently reported dendrimers built around a 1,4,8,11-tetraazacyclotetradecane (cyclam) core [17].

There are, of course, metal-containing dendrimers that belong to other categories [18] or to more than one of those mentioned above. For example, there are several examples of dendrimers built around a metal complex as a core and containing metal complexes as branching centers and as peripheral units (Fig. 1(f)). These compounds represent the extension of the old concept of polynuclear complex [19]. They are based on ligands capable of coordinating, and therefore bridging, two (or more) metal ions. Besides the metal ions and the bridging ligands, they contain normal (i.e., non-bridging) ligands at the periphery of the structure. Compounds made of 22 Ru polypyridine moieties [20], and

189 Pt [21] and 47 Pd [22] 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 has lead to a great variety of novel compounds.

The aim of this paper is limited to review some recent developments concerning luminescent dendrimers that can play the role of ligands for luminescent and non-luminescent metal ions. The reported examples, belonging to classes (a), (d), and (e), schematized in Fig. 1, are mostly taken from the joint work of our laboratories and concern transition metal or lanthanide ions.

2. Dendrons as ligands

The first dendrimer in which purely organic branches have been convergently attached to a metal-based core is compound 1^{2+} [23]. The photophysical properties of this Ru-complex are very similar to those of its [Ru(bpy)$_2$ (phen)]$^{2+}$ core (bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline). The slight perturbation caused by the dendritic branches cannot be ascribed to their structure, but only to the electron-donating character of the benzyloxy groups. The expected energy transfer from the benzyloxy groups to the central core could not be investigated because the absorption bands of the organic chromophores of the branches are hidden by the more intense bands of the polypyridine ligands.
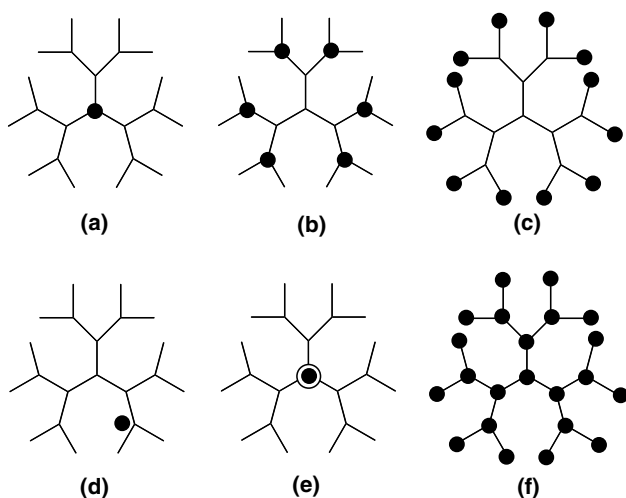

(a)   (b)   (c)

(d)   (e)   (f)

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 unit.


1^{2+}
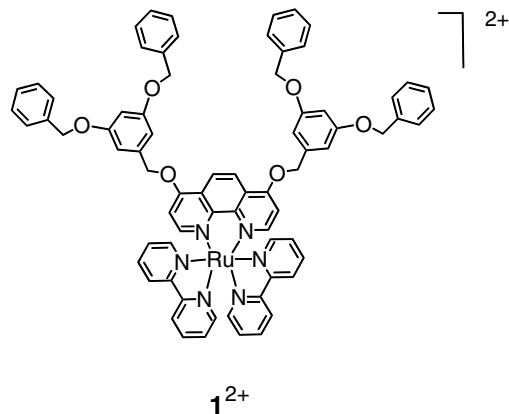
More complex dendritic ligands have been obtained by attaching branches in the 4,4′-positions of bpy. The largest dendritic bipyridine ligand contained 18 peripheral methylester units. Four Ru(II) dendritic complexes have then been synthesized (see e.g., 2^{2+}) [24]. Their absorption and emission spectra are very similar to those of the unsubstituted parent Ru(II)–bipyridine complexes, but in aerated solution the dendritic com-

plexes exhibit a more intense emission and a longer excited state lifetime than $[Ru(bpy)_3]^{2+}$. This result was attributed to a shielding effect of the dendrimer branches on the Ru–bipyridine core towards quenching by molecular oxygen. For the largest dendritic complex, that contains 54 peripheral methylester units, the excited state lifetime in aerated acetonitrile solution is longer than 1 μs, and the rate constant for dioxygen quenching is 12 times smaller than for $[Ru(bpy)_3]^{2+}$.

2²⁺　　R = CH₃
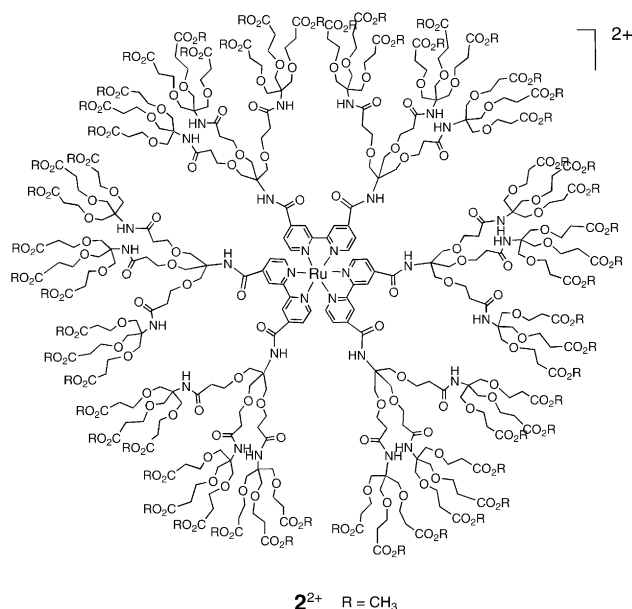
First and second generation dendrimers built around a $[Ru(bpy)_3]^{2+}$ core and bearing 12 and 24 naphthyl units (compound **3²⁺**) in the periphery, respectively, were synthesized [25]. The metallodendrimers were obtained by complexation of ruthenium trichloride with bipyridine ligands carrying dendritic wedges in the 4,4′-positions. Since the chromophoric groups present in the dendritic complexes are separated by aliphatic spacers, interchromophoric interactions are weak and the absorption spectra of the metallodendrimers are essentially equal to the summation of the spectra of the chromophoric groups which are present in their structures. The "free" wedges show an intense emission band in the region of the naphthyl-type units. Such a band, however, is almost completely absent in the emission spectrum of the metallodendrimers, which exhibit the visible emission band characteristic of their $[Ru(bpy)_3]^{2+}$-type core, regardless of the excitation wavelength. These results show that a very efficient energy-transfer process takes place from the potentially fluorescent excited states of the aromatic units of the wedges to the metal-based dendritic core (antenna effect). Once again, the dendrimer branches protect the Ru-bpy based core from dioxygen quenching.

3²⁺
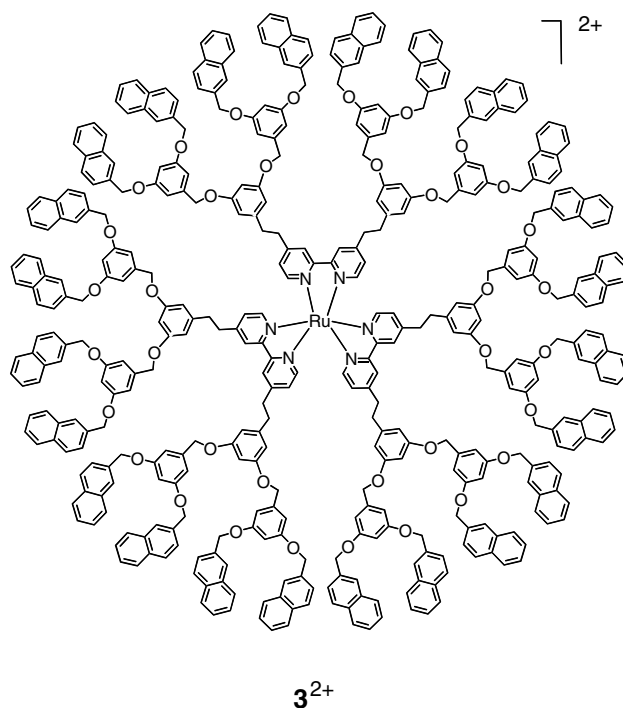
Six dendrimers built around a $[Ru(bpy)_3]^{2+}$-type core and bearing up to 24 4′-*tert*-butylphenyloxy (dendrimer **4²⁺**) or 48 benzyl units in the periphery have also been prepared by complexation of ruthenium trichloride or $Ru(bpy)_2Cl_2$ with bipyridine ligands carrying dendritic wedges in the 4,4′-positions [26]. All the examined compounds show the characteristic luminescence of the $[Ru(bpy)_3]^{2+}$-type core and the luminescent excited state is again protected by the dendritic branches towards quenching by dioxygen. For three compounds containing the 4′-*tert*-butylphenyloxy peripheral units, the electrochemical behavior and the excited state quenching via electron transfer were studied in acetonitrile solution. The core of dendrimer **4²⁺** showed an electrochemical behavior typical of encapsulated electroactive units. The reaction of the luminescent excited state of the $[Ru(bpy)_3]^{2+}$-type core with three electron-transfer quenchers (namely, methylviologen dication, tetrathiafulvalene, and anthraquinone-2,6-disulfonate anion) takes place by a dynamic mechanism in all cases. The value of the quenching rate constant decreases with increasing number and size of the dendritic branches. For dendrimer **4²⁺**, the rate constant of the reaction with methylviologen was more than one order of magnitude smaller than that of the "naked" $[Ru(bpy)_3]^{2+}$ complex.

Frechét-type dendrons bearing a carboxylate-core can self-assemble around Er^{3+}, Tb^{3+}, or Eu^{3+} ions leading to the formation of dendrimers (see e.g., **5**) [27]. Experiments carried out in toluene solution showed that UV excitation of the chromophoric groups contained in the branches caused the sensitized emission of the lanthanide ion, 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 Eu^{3+} can quench the donor excited state by electron-transfer [28].

4²⁺

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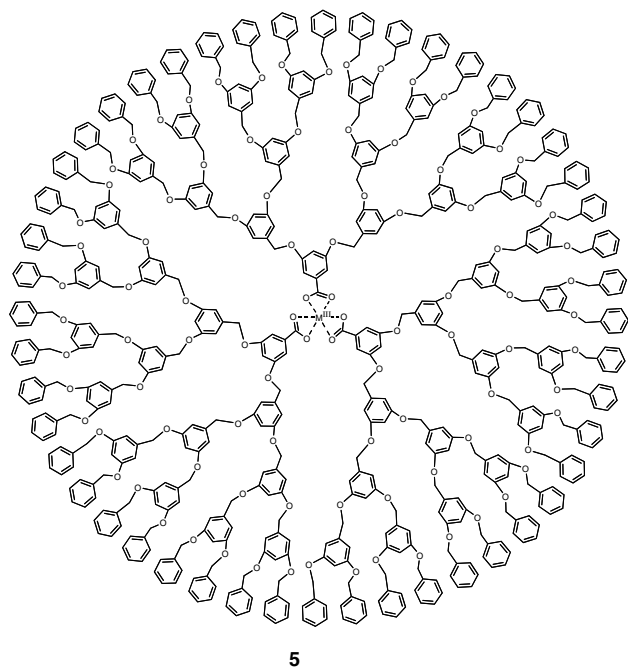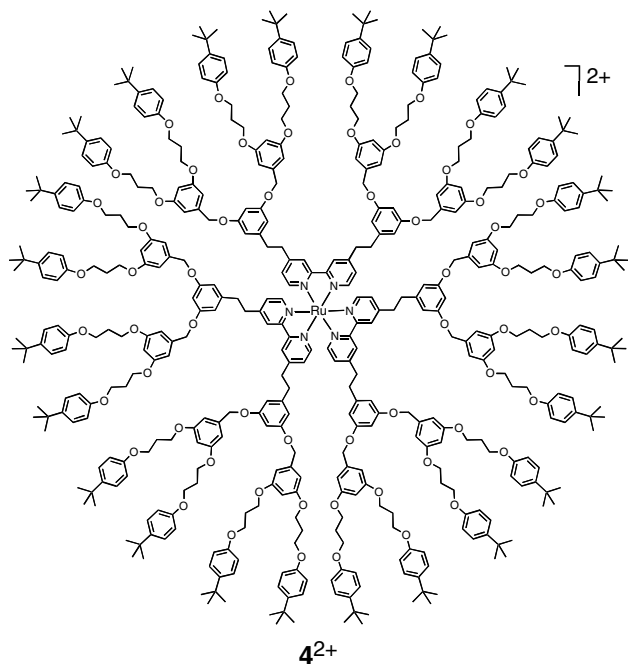
3. Dendrimers of the poly(propylene amine) family

The dendrimers of the poly(propylene amine) family can be easily functionalized in the periphery with luminescent units. Each dendrimer nD, where the generation number n goes from 1 to 5, comprises $2^{(n+1)}$ dansyl functions in the periphery and $2^{(n+1)}-2$ tertiary amine units in the interior. Compound **6** represents the fourth genera-

tion dendrimer 4D containing 30 tertiary amine units and 32 dansyl functions. The dansyl units behave independently from one another so that the dendrimers display light absorption and emission properties characteristic of dansyl, 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) and a strong fluorescence band in the visible region $\lambda_{max} = 500$ nm; $\Phi_{em} = 0.46$, $\tau = 16$ ns) [29]. Because of the presence of the aliphatic amine in their interior these dendrimers can be used as ligands for transition metal ions. The interaction with Co^{2+} ions (as nitrate salt) has been carefully studied [30]. For comparison purposes, the behavior of a monodansyl reference compound has also been investigated. 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. This result shows that dendrimers 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 **6**, the fluorescence of all the 32 dansyl units is quenched, with a 32 time increase in sensitivity with respect to a normal dansyl sensor. This concept is illustrated in Fig. 2.

6
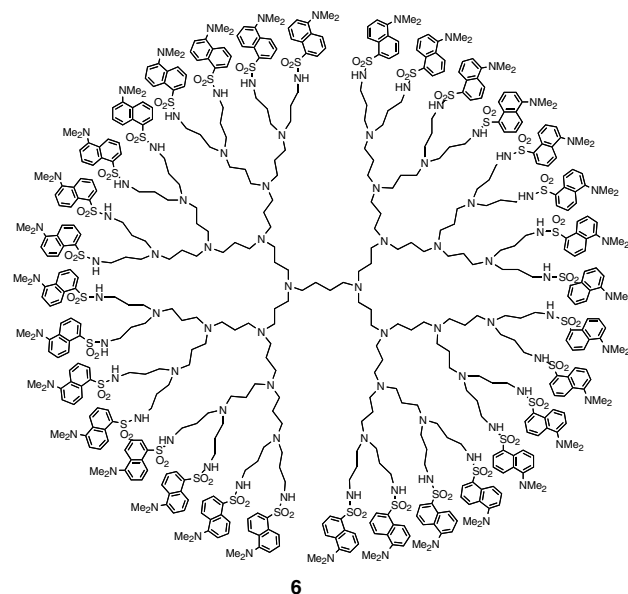
4. Dendrimers with amide units in the branches

Lanthanide ions are known to show very long lived luminescence which is a quite useful property for several applications (e.g., sensors [31] and fluoroimmunoassay [32]). 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 this 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) [33]. Such a process can involve either direct energy transfer from the singlet excited state of the chromophoric group with quenching of the chromophore fluorescence [34,35], 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 [33].

Amide groups are known to be good ligands for lanthanide ions [33b]. Dendrimer **7**, 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. 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) solutions, the absorption spectrum and the fluorescence properties of the dendrimer are those expected for a species containing 24 non-interacting dansyl units [36].

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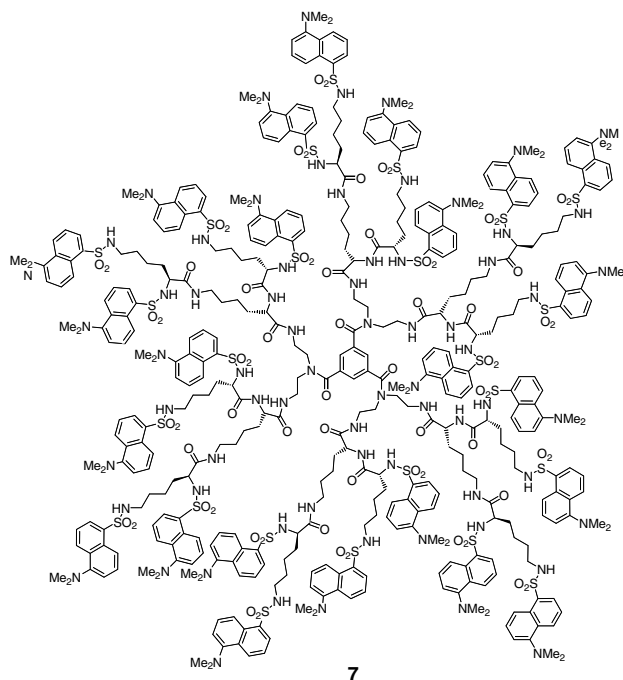
Addition of lanthanide ions to dendrimer solutions showed that [35]: (a) the absorption spectrum of the dendrimer is almost unaffected; (b) the fluorescence of the dansyl units is quenched; (c) the quenching effect is very large for Nd^{3+} and Eu^{3+}, moderate for Er^{3+} and Yb^{3+}, small for Tb^{3+}, 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
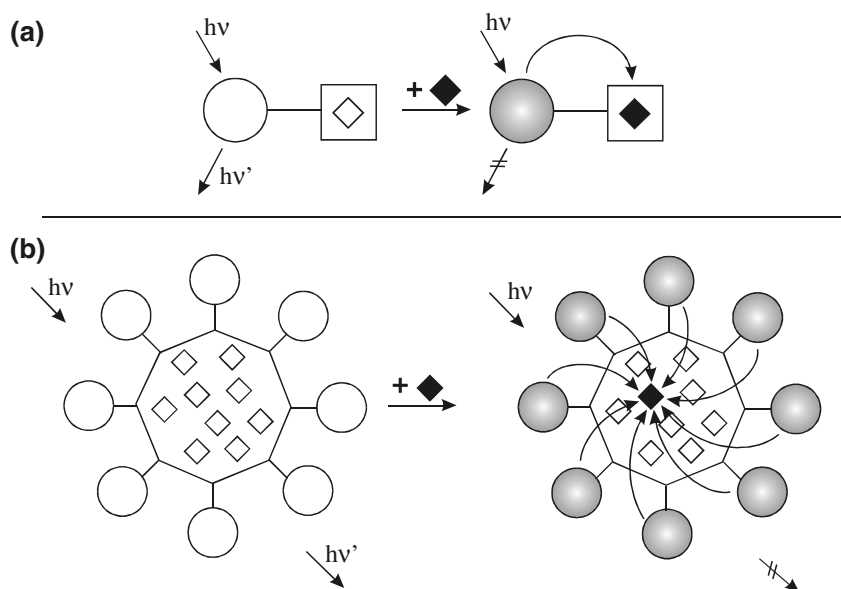

Fig. 2. Schematic representation of (a) a conventional fluorescent sensor and (b) a fluorescent sensor with signal amplification. Open rhombi indicate coordination sites and black rhombi indicate metal ions. The curved arrows represent quenching processes. In the case of a dendrimer, the absorbed photon excites a single fluorophore component, that is quenched by the metal ion, regardless of its position [30].
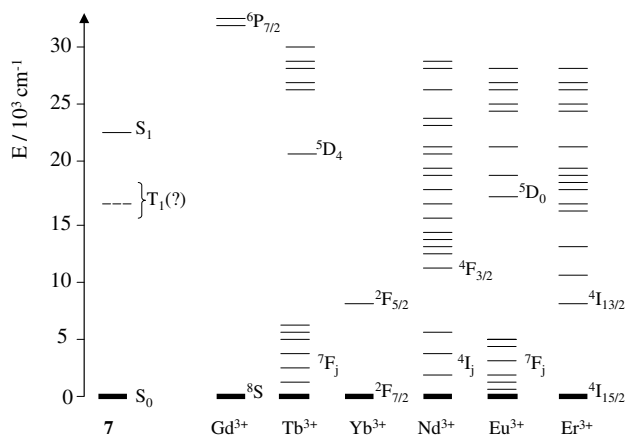
Fig. 3. Energy level diagrams for the dansyl units of dendrimer **7** and the investigated lanthanide ions. The position of the triplet excited state of **7** is uncertain because no phosphorescence can be observed [35].
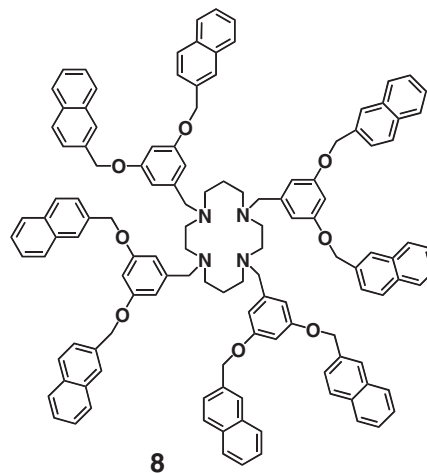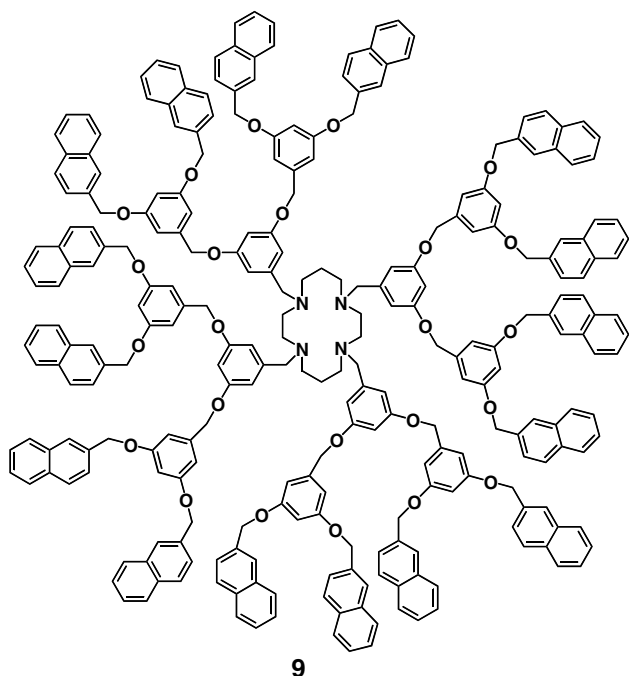
5. Dendrimers with a cyclam core

The 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 [37]. Both cyclam and its 1,4,8,11-tetramethyl derivative in aqueous solution can be mono and diprotonated and can coordinate metal ions such as Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) with very large stability constants [38]. Furthermore, cyclam and its derivatives have been studied in medical applications [39], as carrier of metal ions in antitumoral tests [40], imaging contrast agents [41], and, most recently, as anti-HIV agents [42].

Dendrimers **8** and **9** 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 their absorption spectra are dominated by naphthalene absorption bands and they 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) [17]. The tetraamine cyclam core undergoes only two protonation reactions, that not only prevents exciplex formation for electronic reasons, but also causes strong nuclear rearrangements in the cyclam structure which affect excimer formation between the peripheral naphthyl units of the dendrimers.

the results obtained on the basis of the energy levels (Fig. 3) and redox potentials of the dendrimer and of the metal ions have lead to the following conclusions: (i) at low metal ion concentrations, each dendrimer hosts only one metal ion; (ii) when the hosted metal ion is Nd^{3+} or Eu^{3+}, all the 24 dansyl unit of the dendrimer are quenched with unitary efficiency; (iii) 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+}); (iv) quenching by Eu^{3+} does not lead to any sensitized emission since the lowest excited state of the system is an 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, which originates from the quenching of the T_1 excited state of the protonated dansyl units; (v) in the case of Yb^{3+}, the sensitization of the near-infrared metal-centered emission occurs via the intermediate formation of an 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; (vi) 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; (vii) the very small quenching effect observed for Gd^{3+} is assigned to either induced intersystem crossing or, more likely, to charge perturbation of the S_1 dansyl excited state.

8

9

Extensive investigation has been performed on the interaction of dendrimers **8** and **9** with metal ions [43,44]. Complexation with Zn^{2+} engages the nitrogen lone pairs and thereby prevents exciplex formation, with a resulting intense naphthyl fluorescence. This strong fluorescent signal is quite suitable for monitoring the formation of complexes in dendrimer/metal titration experiments. Surprisingly, both dendrimer **8** and **9** give rise to complexes with 2:1 ligand to metal stoichiometry at low Zn^{2+} concentration, as evidenced by both fluorescence and ^1H NMR titrations. In particular, in the case of the largest dendrimer **9**, at low metal ion concentration only the species $[Zn(9)_2]^{2+}$ is present with a high formation constant ($>10^{13}$ M^{-2}). The unexpected $[Zn(9)_2]^{2+}$ species shows that the dendrimer branches not only do not hinder, but in fact favor 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 favored. This seems to be the case for dendrimer **8**, but not for dendrimer

9. Therefore, in the $[Zn(9)_2]^{2+}$ species the dendrimer branches are likely extending outward. Furthermore, the two cyclam cores, to account for the coordination number ($\leqslant 6$) 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 favoring a 2:1 stoichiometry.

The kinetics of complex formation with Zn^{2+} can be followed by monitoring the change in the fluorescence intensity [43b]. In the case of **8**, the change in the fluorescence intensity with time indicates a biphasic kinetics with the incorporation rate constants $k_1 = 4.9 \times 10^5$ $M^{-1}s^{-1}$ followed by a first order process $k_2 = 0.40$ s^{-1}. The second-order process contributes to 95% of the total change in fluorescence. For the reaction of Zn^{2+} with **9**, the observed changes in the fluorescence intensity can be accounted for by only a second-order process alone, with $k_1 = 1.2 \times 10^5$ $M^{-1}s^{-1}$. The rate-limiting step does not correspond to the simple desolvation of Zn^{2+}. The observed decrease in the second-order rate constant upon increasing dendrimer generation can be accounted for by a decrease, on increasing size of the branches, of either cyclam flexibility, or accessibility to the dendrimer core due to efficient hydrophobic shielding. Incorporation of Zn^{2+} into dendrimers of different generations could indeed involve structural changes resulting in slow kinetics. Conformational changes in the dendron subunits are necessary for the closure of the chelate ring and it is likely that the reorganisation of the dendron subunits becomes slower on increasing dendrimer size because of steric congestions.

Complexation of dendritic ligands **8** and **9** with lanthanide ions ($M = Nd^{3+}$, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}) [44] leads 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/ligand) complexes ($\log\beta_{1:2} = 14.1$ and $\log\beta_{1:3} = 20.0$) in the case of **8** and a 1:3 (metal/ligand) complex ($\log\beta_{1:3} = 20.3$) for compound **9**. Therefore, at low metal ion concentration only the $[M(9)_3]^{3+}$ 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 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 **8** and **9** 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 **8** and **9** 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 [45]. Apparently, the nature of the coordination sphere plays an important role concerning energy transfer efficiency.

6. Conclusion

The above discussed examples show that the design of dendrimers capable of playing the role of ligands for metal ions can lead to novel classes of metal complexes where the properties of the dendrimer and metal ion moieties can be profitably combined to obtain interesting and useful light-related functions. It is likely that improving design of these types of dendrimers will lead to coordination compounds capable of performing even more sophisticated functions, such as energy up-conversion and electrochemiluminescence, besides those discussed in this paper.

Acknowledgement

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