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Review

Metal ion complexes of cyclam-cored dendrimers for molecular photonics

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ABSTRACT

Because of its ability to form stable complexes with a wide variety of metal ions, cyclam (1,4,8,11-tetraazacyclotetradecane) is one of the most studied ligands in coordination chemistry. Functionalizing the cyclam unit with photoactive dendrons open a door to construct giant homo- and heteroleptic metal complexes that display interesting spectroscopic properties, particularly as far as luminescence is concerned. Light is a tool both to study metal coordination processes, and to act as input or output in order to achieve the desired function.

This paper reviews some results obtained with metal complexes of cyclam-based dendrimers capable of acting as: (i) sensor, (ii) logic gates, and (iii) molecular antennae.

1. Introduction

1,4,8,11-Tetraazacyclotetradecane (cyclam) is one of the most extensively investigated ligands in coordination chemistry [1]. Its flexibility enables the complexation of a wide variety of metal ions. 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^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+} with very large stability constants [1]. Furthermore, cyclam and its derivatives have been studied in medical applications [2], as carrier of metal ions in antitumor treatments [3], as imaging contrast agents for magnetic resonance imaging (MRI) [4], and positron emission tomography (PET) [5], as anti-HIV agents [6], and, most recently, as neuroprotective or neurorescue agents to cure Alzheimer's disease [7].

Cyclam is commercially available, and its nitrogen atoms can be easily linked to functional units, thus paving the way to a large variety of derivatives. For example, dendrons, even of different types, can be appended to the cyclam core. The synthesis of cyclam-cored dendrimers proceeds via a convergent approach, i.e. by coupling dendrons, containing proper functional units at the apical position, to the nitrogen atoms of the cyclam core [8]. The synthesis of cyclam-cored dendrimers containing dendrons of two different types has recently been reported by proper protection/deprotection of the nitrogen atoms of the core [9]. Coupling cyclam and dendrimer chemistry is very interesting from both a fundamental and applications point of view. Dendrimers [10,11] constitute a class of multibranched molecules that can–by design–exhibit a high degree of order, but also a high degree of complexity. From a topological viewpoint, dendrimers contain three different regions: core, branches, and surface. A most important feature of dendrimer chemistry is the possibility to insert selected chemical units in predetermined sites of the dendritic architecture. Moreover, thanks to their three-dimensional structure, internal

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dynamic cavities are present, where ions or molecules can be hosted. It is thus possible to construct large nanoobjects capable of performing complex functionality that derives from the integration of the specific properties of the constituent moieties.

Cyclam-cored dendrimers have a coordination site at their core, so that metal ion complexes with defined stoichiometry can be formed, on the contrary of the most widely investigated dendritic metal complexes in which coordination takes place by multiple identical units that are part of the dendrimer branches (e.g., amine, imine or amide groups) or appended at the dendrimer periphery (e.g., terpyridine, cathecolamide ligands) [12].

Luminescence is another interesting property that can be implemented in dendritic architectures. A large number of chromophores can be arranged according to predetermined patterns in a restricted space. In the case of dendritic ligands for metal ions [12,13], luminescence can be exploited for a variety of purposes that include investigation of metal complex structure [14], light harvesting [15], and reversible metal complex assembly [16].

The present paper is focused on the light signal manipulation performed by metal ion complexes of luminescent cyclam-cored dendrimers, with particular references to transition metal and lanthanide ions. Three main topics dealing with molecular photonics will be discussed with selected examples, most of them derived from the work carried out in our laboratory: (a) sensors, (b) logic gates, and (c) molecular antennae.

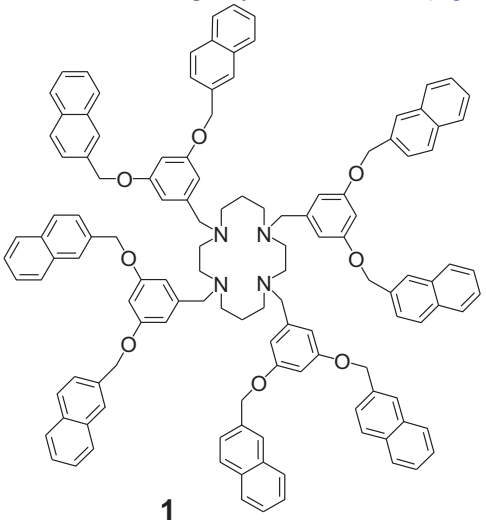
2. Luminescent sensors

A very interesting feature of luminescent dendritic ligands is the possibility to perform as sensors of metal ions with signal amplification. The advantage of using a dendrimer for sensory applications is related to the fact that a single analyte can interact with a great number of units changing their properties, which results in signal amplification. In the case of luminescent sensors, recognition can affect the intensity, the position of the emission band, the lifetime of the corresponding excited state or the fluorescence anisotropy. For example, *one* analyte can revive the luminescence of *all* the peripheral luminescent units appended at the dendrimer periphery (Fig. 1a). This is a significant advance compared to a conventional luminescent sensor, in which the ratio between luminescent units and analyte is 1:1 (Fig. 1b). This behaviour is made possible by the well-ordered and flexible dendritic structure in which any excited fluorophore can "feel" the presence of the coordinated metal ion. Signal amplification effects have already been obtained with polymeric chains of sensors [17], and nanoparticles [18]. Because of their molecularly defined and tailor-made structure, dendrimers are more promising species for this kind of application [11f,19].

Depending on the nature of the metal ions and luminescent units present in the dendritic ligands, two cases can be distinguished: (a) luminescence is revived upon metal binding (*turn-on sensing*); (b) luminescence is turned off by metal complexation (*turn-off sensing*). The former is more promising for applications because the detection limit is lower; in this case the recognition process is based on the shutting down of a quenching process active for the unbound dendritic ligand. Therefore, the detected metal ions are those which do not possess low-lying excited states, and do not show oxidation or reduction processes at easily accessible potentials, so that they cannot be involved in photoinduced energy/electron transfer processes with the dendritic luminescent units.

2.1. Turn-on sensing

Dendrimers **1** and **2** consist of a cyclam core appended with four dimethoxybenzene and eight naphthyl units, and twelve dimethoxybenzene and sixteen naphthyl units, respectively [20]. In CH_3CN/CH_2Cl_2 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 (λ_{max} = 335 nm), naphthyl excimers ($\lambda_{max} \approx 390$ nm), and naphthyl-amine exciplexes (λ_{max} = 460 nm) (for dendrimer **2** solid line in Fig. 2a). The naphthyl localized emission is much lower (<10%) than that of a naphthalene isoabsorbing solution at the excitation wavelength because the radiative decay is in competition with the formation of an intramolecular naphthyl excimer and exciplex between the excited naphthyl unit and amine (Fig. 2b).



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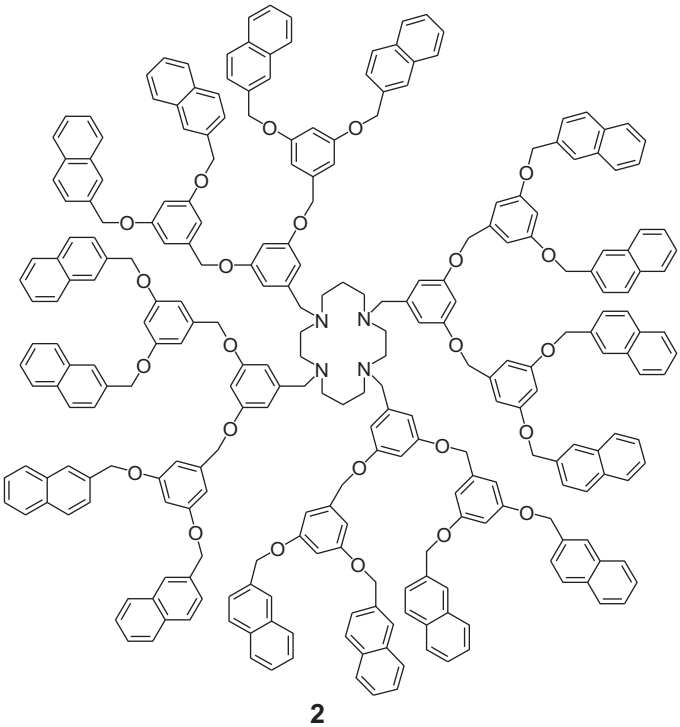

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Extensive investigation has been performed on the interaction of dendrimers **1** and **2** with metal ions [21]. Complexation with Zn^{2+}, a d^{10} metal ion which does not have any low lying excited states and does not show any redox processes at an easy accessible potential, engages the nitrogen lone pairs and thereby prevents exciplex formation, with a resulting intense naphthyl fluorescence (for dendrimer **2** dashed line in Fig. 2a). This strong fluorescent signal is quite suitable for monitoring the formation of

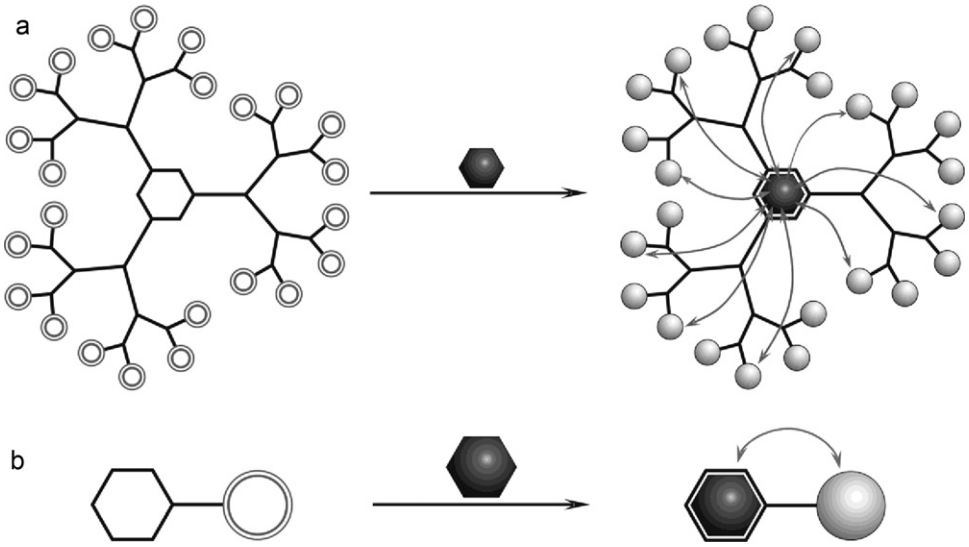


Fig. 1. Schematic representation of (a) a luminescent dendritic sensor with signal amplification and (b) a conventional luminescent sensor. The curved arrows represent interaction processes.

complexes in dendrimer/metal titration experiments. Surprisingly, both dendrimer **1** and **2** give rise to complexes with 2:1 ligand to 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 **2**, at low metal ion concentration only the species $[Zn(\mathbf{2})_2]^{2+}$ is present with a high formation constant ($>10^{13}\,M^{-2}$). The unexpected $[Zn(\mathbf{2})_2]^{2+}$ species shows that the dendrimer branches do not hinder coordination of cyclam to Zn^{2+} with respect to coordination of solvent molecules or counter ions. To account for the coordination number ($\leq$6) of Zn^{2+}, the two cyclam cores 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 (Fig. 3).

In the $[Zn(\mathbf{2})_2]^{2+}$ species, a single Zn^{2+} ion is able to revive the luminescence of all the 32 naphthyl units present in the two dendritic structure. This result shows that dendrimers can be profitably used as supramolecular fluorescent sensors for metal ions, as shown in Fig. 1a. In this case, the sensor fluorescence is switched on upon metal ion coordination, and low Zn^{2+} concentrations ($\approx$0.1 μM) can be easily detected.

The kinetics of complex formation with Zn^{2+} can be followed by monitoring the change in the fluorescence intensity [21b]. In the case of **1**, 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 **2**, 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.

A step further in cyclam-based dendritic ligands for metal ions is constituted by dendrimer 3, 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 [22]. Its photophysical properties are qualitatively similar to that observed for 1. For example, the emission spectrum indicates the presence of naphthyl localized excited states (λ_{max} = 335 nm),

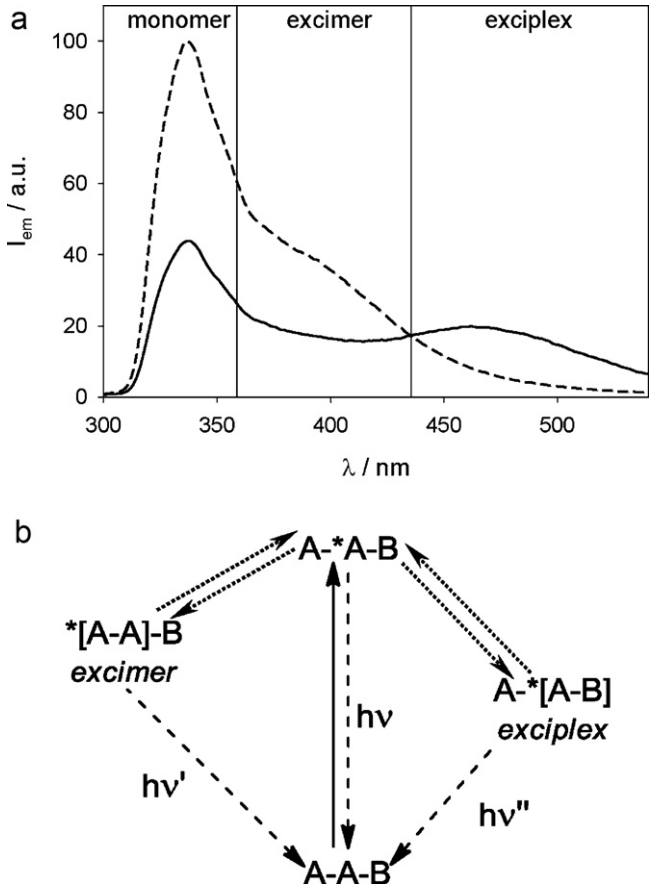


Fig. 2. (a) Emission spectra of dendrimer **2** in acetonitrile/dichloromethane 1:1 (v/v) solution before (solid line) and after (dashed line) addition of 1 eq. of $Zn(CF_3SO_3)_2$. (b) Energy level diagram showing the three types of emissions that can result from monomer, excimer and exciplex species. A stands for naphthalene and B for a cyclam nitrogen in the case of dendrimer **2**.

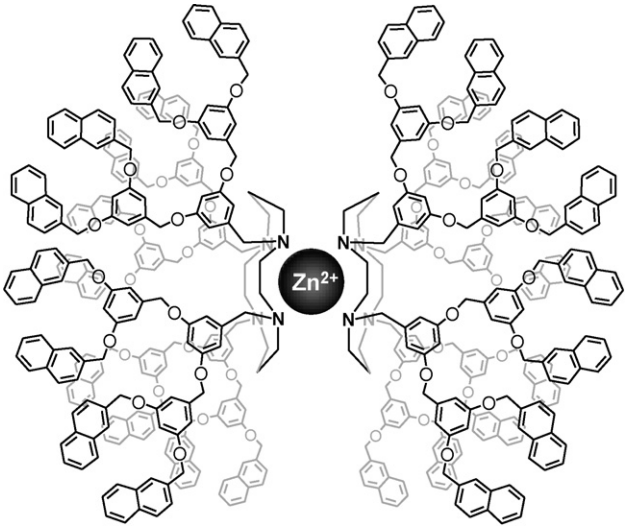
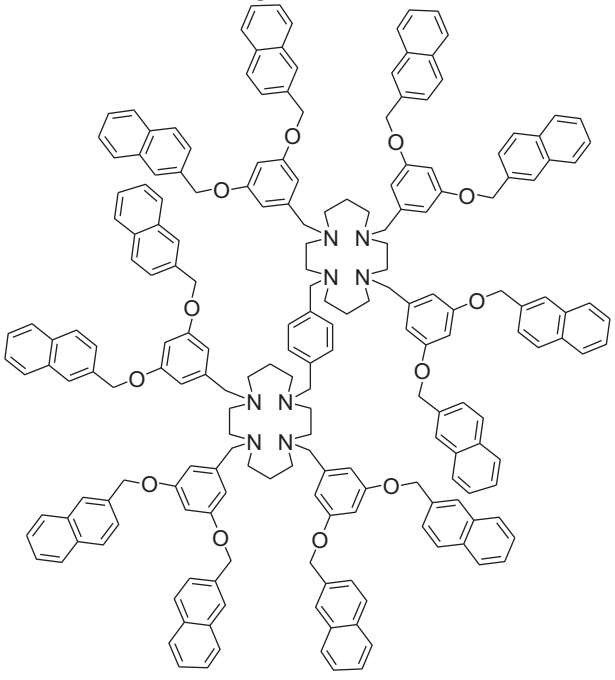


Fig. 3. Schematic representation of the $[Zn(\mathbf{2})_2]^{2+}$ species. In this figure dendrimer branches are extending outward.

naphthyl excimers ($\lambda_{max} \approx 390$ nm), and naphthyl-amine exciplexes ($\lambda_{max} = 460$ nm).

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, $[Zn(\mathbf{3})]^{2+}$, is first formed and then replaced by a 1:2 species, $[Zn_2(\mathbf{3})]^{4+}$ ($\log \beta_{1:1} = 9.7$ and $\log \beta_{1:2} = 16.1$ for these two species, respectively). In the 1:1 complex $[Zn(\mathbf{3})]^{2+}$, the metal ion is likely sandwiched between the two cyclam units. As previously observed in the case of dendritic ligands 1 and 2, 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 $[Zn(\mathbf{3})]^{2+}$ to $[Zn_2(\mathbf{3})]^{4+}$ 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.



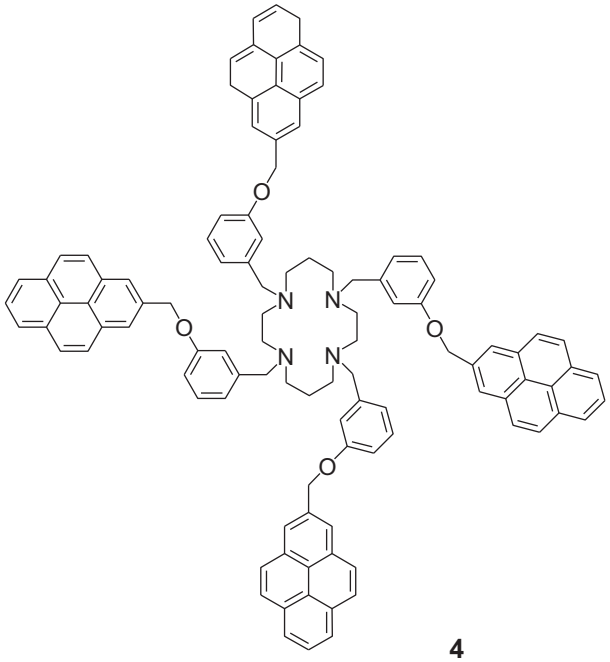
3

2.2. Turn-off sensing

The dendrimers **1** and **2** discussed above can efficiently bind also Ni^{2+}, Co^{2+}, and Cu^{2+}. However, changes in the luminescence properties are completely different from those reported before upon addition of Zn^{2+} because the dendritic naphthyl units can be involved in photoinduced energy and/or electron transfer processes with these metal ions.

Upon titration of dendrimer **2** in CH_3CN/CH_2Cl_2 1:1 (v/v) solution with nitrate salts of Ni^{2+}, Co^{2+}, and Cu^{2+}, the intensity and shape of the naphthyl luminescence bands are strongly affected [21d]. Complexation with these metal ions, in contrast to the previously investigated Zn^{2+} complexes, has a double-faced effect: on one hand, it can increase naphthyl localized emission and suppress exciplex emission, engaging nitrogen lone pairs of cyclam; on the other hand, it can quench this fluorescence by offering additional deactivation pathways to the naphthyl singlet excited state via energy or electron transfer processes. Complexation with Cu^{2+} causes not only changes in the relative intensities of the fluorescence bands, but also the appearance of a new and broad tail in the 300–400 nm region of the absorption spectrum, assigned to ligand-to-metal charge-transfer (LMCT) transitions (a similar absorption band was observed also in the case of mere cyclam). Analysis of the titration curves showed clear evidence for formation not only of 1:1 species, but also 2:1 ligand to metal species.

Dendrimers **4** and **5** contain a cyclam core and 4 or 8 pyrenyl units at the periphery [23]. In CH_2Cl_2 solution they show the expected absorption spectra on the basis of their model compounds. As far as emission spectra are concerned, stronger excimer emission intensities are observed compared to the corresponding dendrons at similar concentrations. Upon addition of Cu^{2+}, as triflate salt, dramatic fluorescence changes are observed, indicative of the formation of a 1:1 complex with a binding constant much lower than that observed for the unsubstituted cyclam, indicating a steric effect of the dendrons. Along the same trend, a higher complexation constant is observed for Cu^{2+} complexed by **4** than by **5**. The strong changes observed in pyrenyl excimer fluorescence upon addition of Cu^{2+} are explained in terms of photoinduced electron transfer. At variance with the previously reported examples, however, this process is not reversible and leads to decomposition products, so that the present dendrimers are not good candidates for ion sensing.



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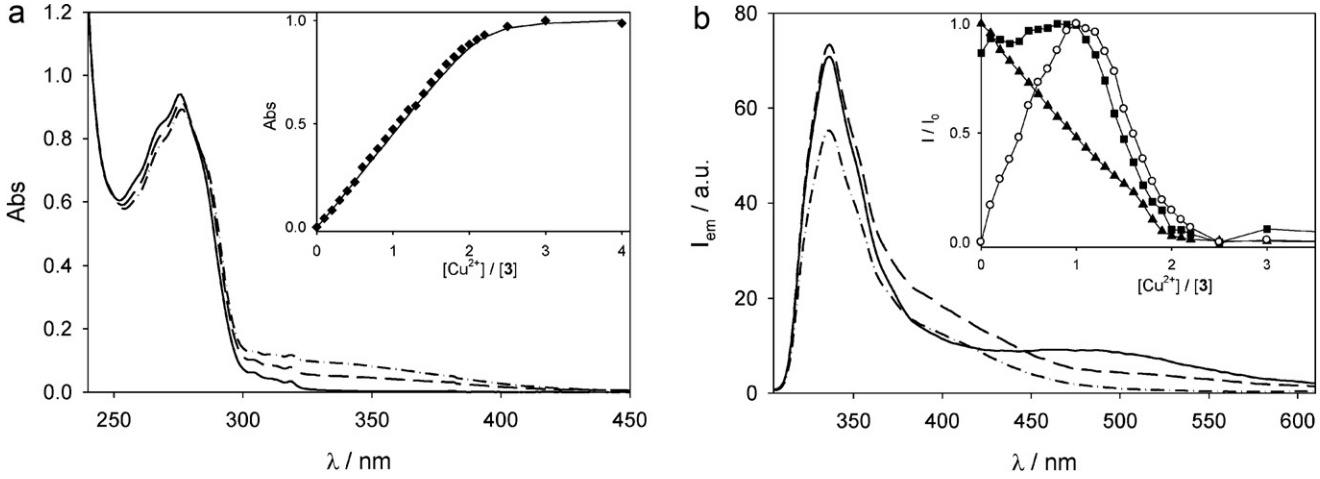
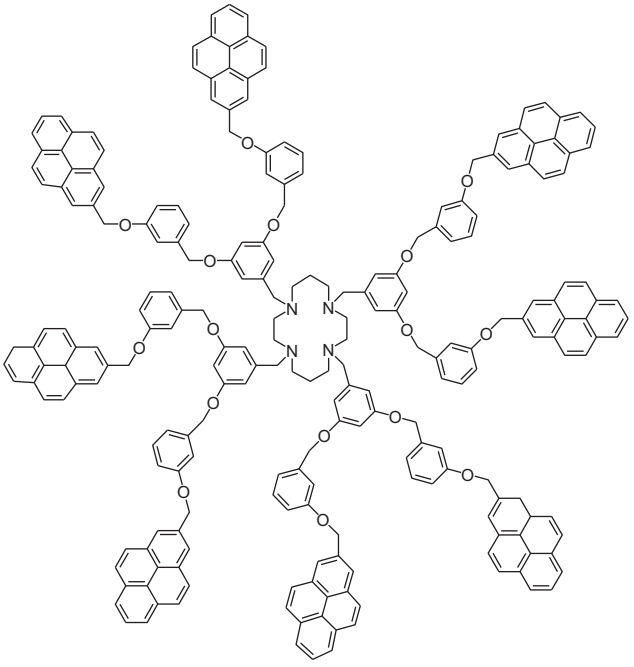


Fig. 4. (a) Absorption and (b) emission (λ_{ex} = 275 nm) spectra of **3** in CH_3CN/CH_2Cl_2 1:1 (v/v) solution before (full line) and after the addition of one (dashed line) and two (dotted-dashed lines) equivalents of $Cu(CF_3SO_3)_2$. Insets show the normalized (a) absorption and (b) emission changes at 319 nm (♦), 336 nm (■), 390 nm (○), and 510 nm (▲). The emission intensity at 390 nm has been corrected by taking into account the contribution of the naphthyl localized fluorescence.



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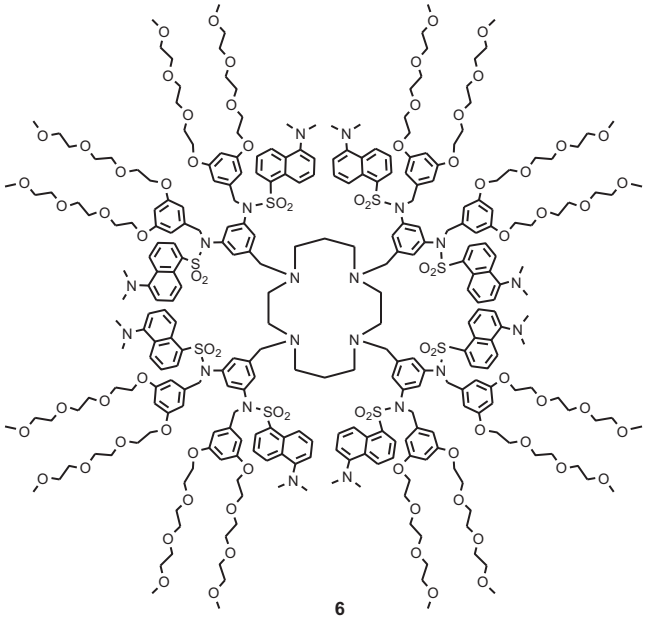
In the case of dendrimer **3** containing two cyclam units linked by a benzyl spacer as a core, titration with $Cu(CF_3SO_3)_2$ leads to strong changes both in absorption and emission spectra [8]. The absorption spectrum (Fig. 4a) showed the appearance of a broad tail in the 300–400 nm region, assigned to LMCT transitions as for dendrimer **2**. The absorbance values increase almost linearly up to the addition of 2 equivalents of metal ion per dendrimer. Therefore, upon addition of $Cu(CF_3SO_3)_2$ to **3**, both the cyclam units of the dendrimer coordinate a Cu^{2+} ion ($\log \beta_{1:2}$ = 11.9). More details were obtained from the changes observed in the emission spectrum (Fig. 4b), 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 spectroscopic changes upon addition of Cu^{2+} indicates the formation of a 1:1 complex, $[Cu(\mathbf{3})]^{2+}$, then replaced by a 1:2 species, $[Cu_2(\mathbf{3})]^{4+}$.

Another example of this class is represented by dendrimer **6** in which the cyclam core is appended with four benzyl substituents that carry, in the 3 and 5 positions, a dansyl amide derivative in which the sulfonamide hydrogen is replaced by a benzyl unit that carries, in the 3 and 5 position, a oligoethylene glycol chain [24]. All together, the dendrimer contains 16 potentially luminescent moieties (8 dansyl- and 8 dimethoxybenzene-type units) and three distinct types of multivalent sites that, in principle, can be protonated or coordinated to metal ions (the cyclam nitrogen atoms, the amine moieties of the 8 dansyl units, and the 16 oligoethylene glycol chains). The absorption spectrum of dendrimer **6** in acetonitrile is that expected on the basis of the model compounds apart from a small red-shift of the lowest energy dansyl absorption band, indicating that in the dendrimer the dansyl units indeed feel a less polar environment because of the oligoethylene glycol chains. As far the emission spectra are concerned, the dansyl units maintain their strong fluorescence, slightly red shifted (λ_{max} = 532 nm, Φ = 0.27, and τ = 15 ns, compared to the dansyl model compound under the same experimental conditions: λ_{max} = 522 nm, Φ = 0.30, and τ = 13 ns), and no dimethoxybenzene emission is present due to a quenching process by the nearby dansyl units.



6

Upon complexation of Co^{2+}, Ni^{2+}, and Cu^{2+}, three quenching mechanisms can be expected, namely (i) an effect of the positive charge of the metal ion on the dansyl emission transition moment, (ii) an energy transfer quenching since the investigated metal ions have low-lying excited states, and (iii) an electron transfer quenching for metal ions that can be easily reduced, as in the case of Cu^{2+}. Changes in absorption and emission spectra are quite complex, but some general conclusions can be drawn: (i) the first equivalent of metal ion is coordinated by the cyclam core; (ii) the interaction of the resulting cyclam complex with the appended dansyl units depends on the nature of the metal ion; (iii) coordination of metal ions by the dansyl units follows at high metal ion concentrations; (iv) the effect of the metal ion depends on the nature of the counter anion. This example demonstrates that dendrimers may exhibit complex functionality resulting from the integration of the specific properties of their component units. Therefore, such design is interesting for understanding relations between complex structure and multiple functionality. Moreover, anion sensing can be implemented in the present system, as demonstrated by the dependence of emission intensity by the nature of the counter ion.

3. Logic gates

Information processing is crucial in everyday life not only in the rapidly evolving fields of computer science and telecommunication, but also to sustain life. In living systems information is processed by biomolecules, so that chemical inputs result in output product molecules, electrical signals, changes in concentration of chemical species, or even light signals. For example, when *Vibrio* bacteria get together, their chemical conversations–quorum sensing–induce the expression of light-producing proteins [25]. Since the theoretical work by Aviram in 1988 [26] and the experimental one by de Silva in 1993 [27], information processing at the molecular level has been demonstrated. It rapidly developed as an alternative route to solid-state molecular electronics towards the design and construction of the lengthy sought chemical computer, but also towards intelligent medical diagnostic and "lab-on-a-molecule" system. Nowadays, computing is based on connections of a huge number of very simple, stable, and fast logic gates, which have electrical inputs and outputs. Molecules are usually much less stable, requires inputs and outputs of different kinds, so that they cannot be easily interconnected, and the operation times is usually much longer. On the other hand, molecules are very small (nanometer, or sub-nm scale) so that density of information storage can be very high, they can integrate highly complex function on a single platform [28], they can be reconfigured in situ by changing inputs and outputs, or by manipulating the substrate by an external input, and they can work in confined environment, like cells, and even in vivo, where silicon-based technology fails.

From simple switches, the chemical approach has been developed to produce more complex molecular systems capable of performing a variety of classical logic functions [29], including extensions to switches on surfaces and examples of half-adder, full-adder, keypad lock, multiplexer–demultiplexer, encoder/decoders. Fluorescence is an ideal output because of its ease of detection even at the single-molecule limit [30]. Another remarkable feature of fluorescent signals is that they do not need to be wired to operate. Light can indeed bridge the gap between the world of molecules and our macroscopic world.

Supramolecular systems offer a good platform to implement complex function on a single molecular architecture. We will present in the following an example based on a dendritic system. We have seen in the previous examples that cyclam cored dendrimers can coordinate metal ions, but they can also be assembled as a second coordination sphere around a suitable metal complex, as presented in the following. 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 emission spectra because of the occurrence of intercomponent energy or electron transfer processes.

An interesting example is represented by the $[Ru(bpy)(CN)_4]^{2-}$ complex and the above discussed dendrimer **2** [16a]. In CH_3CN/CH_2Cl_2 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 **2** 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 cyclam amine units. 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 [20]. The absorption and emission spectra of a 1:1 mixture of $[Ru(bpy)(CN)_4]^{2-}$ and 2 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 spectroscopic 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 **2** and that after addition of two equivalents of acid a $\{[Ru(bpy)(CN)_4]^{2-}\bullet(2H^+)\bullet\mathbf{2}\}$ adduct is formed, in which the two original species share two protons (Fig. 5). Interestingly, whereas the exciplex type band of **2** disappears upon adduct formation, as expected because of the protonation of the cyclam nitrogen atoms, 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. Quantitative measurements have shown that such an energy transfer process does take place with an efficiency of 85%. Therefore, dendrimer **2** plays the role of a light-harvesting second coordination sphere that transfers the collected energy to the $[Ru(bpy)(CN)_4]^{2-}$ complex. Moreover, the $\{[Ru(bpy)(CN)_4]^{2-}\bullet(2H^+)\bullet\mathbf{2}\}$ adduct can

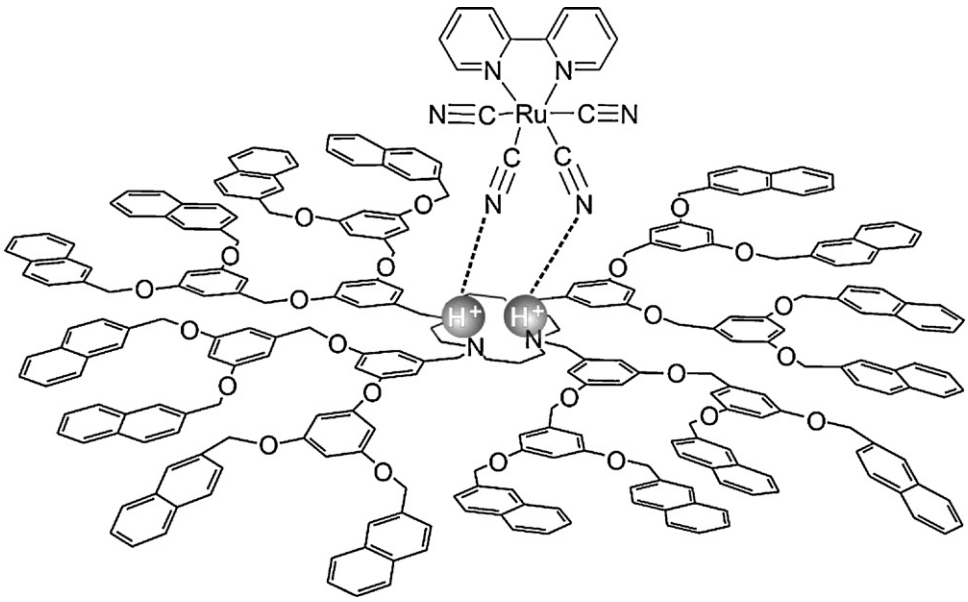


Fig. 5. Schematic representation of the $\{[Ru(bpy)(CN)_4]^{2-\bullet}(2H^+)^{\bullet}\mathbf{2}\}$ adduct.

Table 1
Truth table for a XOR logic gate.

$INPUT_1$ (acid)	$INPUT_2$ (base)	OUTPUT ($I_{335\ nm}$)
0	0	0
0	1	1
1	0	1
1	1	0

Table 2
Truth table for a XNOR logic gate.

$INPUT_1$ (acid)	$INPUT_2$ (base)	OUTPUT ($I_{680\ nm}$)
0	0	1
0	1	0
1	0	0
1	1	1

be disrupted not only, of course, by addition of a base (DABCO: 1,4-diazabicyclo[2.2.2]octane), yielding the starting species $[Ru(bpy)(CN)_4]^{2-}$ and **2**, but also by further addition of acid, with formation of $(\mathbf{2}^{\bullet}2H)^{2+}$ and protonated forms of $[Ru(bpy)(CN)_4]^{2-}$. Upon stimulation with two chemical inputs (acid and base) $\{[Ru(bpy)(CN)_4]^{2-\bullet}(2H^+)^{\bullet}\mathbf{2}\}$ 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 (see Tables 1 and 2, respectively) (Fig. 6).

Upon 270 nm excitation (90% of the light is absorbed by naphthyl units), a solution of the $\{[Ru(bpy)(CN)_4]^{2-\bullet}(2H^+)^{\bullet}\mathbf{2}\}$ adduct shows emission bands at 335 and 680 nm. The intensities of these two optical outputs change upon addition of base or acid (inputs) as shown in Fig. 7. In a binary logic scheme a threshold value must be fixed for the emission intensity, and in a positive logic convention, a 0 can be used to represent a signal that is below this threshold value and a 1 can be employed to indicate a signal that is above it. Considering the emission at 335 nm, and using a proper threshold value, we can write the truth table shown in Table 1, which shows that the system behaves as an XOR logic gate. Conversely established another proper threshold value for the emission intensity and monitoring the signal at 680 nm, the system behaves as an XNOR logic gate as confirmed by the truth table reported in Table 2.

4. Molecular antennae

An antenna for light harvesting is an organized multicomponent system in which many chromophoric molecular units absorb the incident light and then channel the excitation energy to a common acceptor component (Fig. 7). This implies the occurrence of a sequence of energy transfer steps along predetermined directions. In order to have a high light-harvesting efficiency, each energy

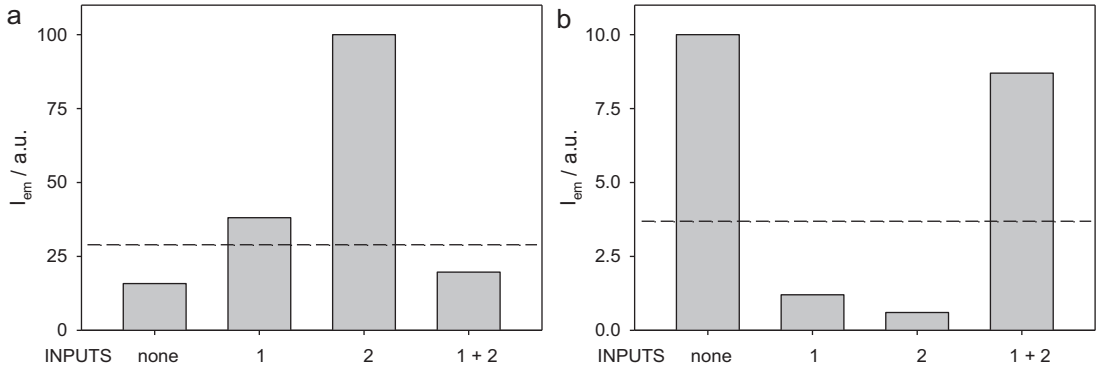


Fig. 6. Normalized emission intensities at (a) 335 nm and (b) 680 nm of $\{[Ru(bpy)(CN)_4]^{2-\bullet}(2H^+)^{\bullet}\mathbf{2}\}$, in CH_3CN/CH_2Cl_2 1:1 (v/v) solution. λ_{ex} = 270 nm; "INPUT 1" is DABCO, 30 equivalents; "INPUT 2" is triflic acid, 30 equivalents. Dashed line indicate a proper threshold value.

transfer step must successfully compete with the intrinsic decay of the excited state as well as with other excited state deactivation processes (e.g., electron transfer, exciplex and excimer formation). Another essential property of the light absorbing units is their chemical and photochemical stability.

In the last ten years, much attention has been devoted to the design and synthesis of dendrimers [11e,31] capable of playing the role of antennas in artificial systems for the challenge of photochemical conversion of solar energy.

Taking advantage of the dynamic cavities present in dendrimers, energy transfer from the numerous chromophoric units of a suitable dendrimer to a luminescent guest may be exploited to construct systems for light harvesting and for changing the light frequency. An advantage shown by such host–guest systems compared with dendrimers with a luminescent core is that the wavelength of the sensitized emission can be tuned by changing the luminescent guest hosted in the same dendrimer.

In the following, we will consider examples of two different types: (a) heteroleptic complexes in which energy transfer takes place from the multiple luminescent units of the dendrimers to a second coordinated ligand and the metal ion plays the role of a "glue"; (b) heteroleptic complexes of lanthanide metal ions in which lanthanide luminescence is sensitized by dendritic ligands.

4.1. Interligand energy transfer

We have seen above that a metal ion can assemble two dendrimers **2**. A step further in the complexity of the system is constituted by assembling around a metal ion a dendrimer together with another ligand. An example [32] is given by the assembly around a metal ion of dendrimer **2** and a molecular clip $\mathbf{C}^{2-}$ (Fig. 8) consisting of two anthracene sidewalls and a benzene bridge carrying two sulfate substituents on the para positions.

Upon addition of $Zn(CF_3SO_3)_2$ to an equimolar solution of dendrimer **5** and clip $\mathbf{C}^{2-}$, changes in the absorption and, particularly, in the emission spectra are registered. Upon excitation at 288 nm where most of the light is absorbed by the 16 naphthalene chromophores of **2**, a strong increase of the anthracene emission at 400 nm is registered together with changes in intensity of the naphthyl band at 335 nm. A closer look to the titration profiles shows that: (i) changes in absorption and emission bands of the clip are significant only after addition of ≈0.2 equivalents of Zn(II); (ii) changes in the naphthyl fluorescence at 335 nm are effective since the beginning with an increase up to ≈0.6 equivalents of Zn^{2+} and then a minimum at 1.1 equivalents of Zn^{2+}. These results can be interpreted by formation of a $[Zn(\mathbf{2})_2]^{2+}$ complex at low Zn^{2+} concentration since naphthyl based emission increases, while clip absorption and emission spectra are not affected. Indeed, as previously discussed, dendrimer **2** forms a very stable complex with 2:1 ligand to metal stoichiometry. Upon further addition of metal ion, the $[Zn(\mathbf{2})_2]^{2+}$ complex is disrupted and Zn^{2+} is coordinated by both **2** and $\mathbf{C}^{2-}$ forming a [**2**Zn**C**] complex, as demonstrated by the quenching of the naphthyl emission and the sensitization of the anthracene emission. This quenching/sensitization process has an efficiency higher than 95% and it cannot take place by dynamic mechanisms because of the short lifetime of the fluorescent naphthyl excited state of the dendrimer ($\tau < 10$ ns) and the low concentration of the clip acceptor. It is evident that the Zn^{2+} complexation drives the formation of a self-assembled light-harvesting antenna that is able to collect efficiently the UV light by the 16 naphthyl and 12 dimethoxybenzene units of the dendrimer **2** and transfer this excitation energy to the two anthracene chromophores of the clip **C** with very high efficiency. Upon addition of an excess of Zn^{2+} (≈80 equivalents), the fluorescence of both the dendrimer and the clip are those expected for the two separated $[Zn\mathbf{2}]^{2+}$ and [Zn**C**] complexes, demonstrating that the three-component system is destroyed.

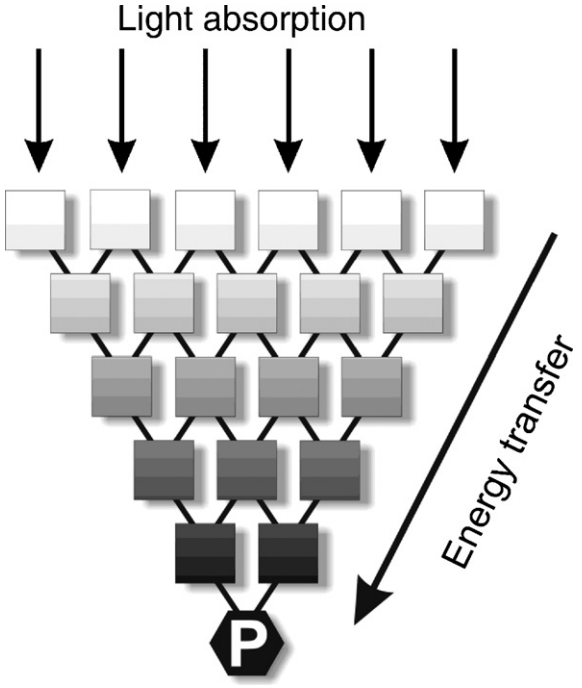


Fig. 7. Schematic representation of a light-harvesting antenna.

Another tool to investigate the formation of the [**2**Zn**C**] complex is represented by fluorescence anisotropy. [33] For a simple molecule randomly oriented in fluid solution, the value of anisotropy r is dependent on the angle between the absorption and emission transition moments, an intrinsic property of the fluorophore, and on the rate of the molecule rotation in solution. In principle, the formation of a complex can be followed by a decrease in fluorescence anisotropy (i.e. depolarization) since the complex rotation in solution is expected to be slower compared to that of the ligand because of the bigger dimension. The measured value r_{exp} is given by the following equation:

$$r_{exp} = F_L r_L + F_A r_A$$

where F_L and F_A are the fractional fluorescence intensities, and r_L, r_A are the fluorescence anisotropy of the ligand L and associated species A. For a supramolecular system containing multiple identical fluorophores, other channels of depolarization are represented by local movements of the fluorophore inside the multicomponent structure, and by energy migration between identical fluorophores.

In the case of the clip, two anthracene chromophores are linked by a quite rigid bridge, so that depolarization can only be caused by global rotation of the clip and by energy migration: the resulting value of steady-state anisotropy in CH_3CN/CH_2Cl_2 1:1 (v/v) solution at 298 K is very low (steady state anisotropy: $r_{ss} \approx 0.01$). Upon addition of 1 eq. of Zn^{2+} and formation of the [Zn**C**] complex, the value of r_{ss} does not show a significant variation, demonstrating that the resulting complex is still rotating very fast. On the other hand, upon addition of the dendrimer and formation of the [**2**Zn**C**] complex, a significant increase of the anthracene anisotropy is observed ($r_{ss} \approx 0.02$). Upon complexation of **2** the mass and dimension increase to a significant extent and rotation of the whole resulting complex is sufficiently slow that the measured steady state anisotropy doubles.

To the best of our knowledge, this is the first time in which the formation of a metal ion complex in solution is followed by fluorescence anisotropy. Indeed, this has been made possible in

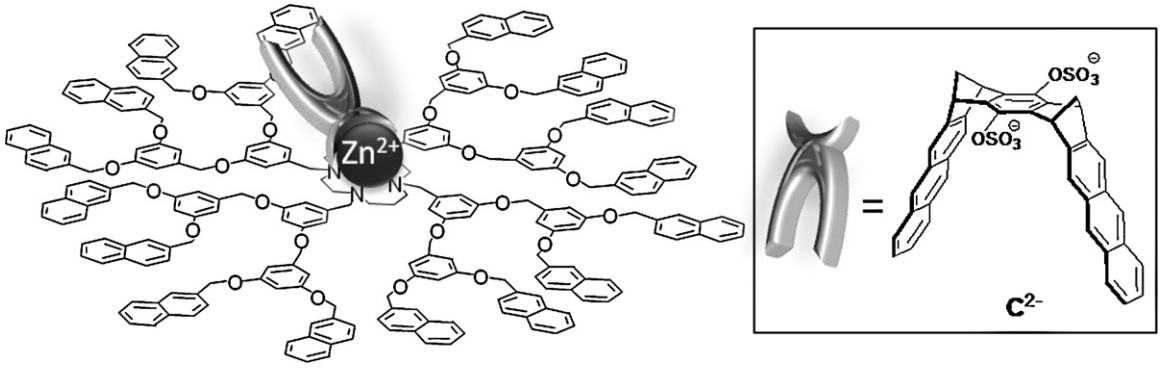


Fig. 8. Schematic representation of a metal complex constituted by dendrimer **2**, one Zn^{2+} ion, and a molecular clip $\mathbf{C}^{2-}$.

low viscosity solvents because of the profound change of mass and dimension between the [Zn**C**] complex and the [**2**Zn**C**] complex.

4.2. Sensitization of lanthanide metal ions

Trivalent lanthanide metal ions possess 4*f* open-shell electronic configurations with forbidden intra-configurational *f*–*f* transitions, which results in very low extinction coefficients (ε typically from *ca.* 1–10 M^{-1} cm^{-1}), characteristic narrow line-like emission bands, mostly in the visible and near infrared regions, and long-lived luminescence [34]. Because direct excitation of lanthanide ions is inefficient, coordinating chromophores are usually exploited to sensitize their luminescence (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 [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 [35,37]. Another drawback of lanthanide luminescence is non-radiative quenching of the emitting excited state by energy loss to high frequency vibrational modes of the solvent [34], a phenomenon that can at least in part be prevented by encapsulation of the metal ion [38]. The unique magnetic and photophysical properties of these metals have attracted great interest over the past few years, and useful applications can be envisaged in the field of medical diagnostics [39], as bio-sensors, for luminescent imaging [40], and in photonic applications [41], such as waveguide amplifiers, plastic lasers, and light-emitting diodes.

Complexation of dendritic ligands 1 and 2 with lanthanide ions (Nd^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}) [21c] leads to results qualitatively similar to those obtained upon Zn^{2+} complexation (see above): an increase of the monomer naphthalene emission band at 335 nm and a complete disappearance of the exciplex band at 460 nm. However, the complex stoichiometry is different. Emission data were best fitted considering the formation of 3:1 and 1:1 (ligand/metal) complexes ($\log \beta_{2:1} = 14.1$ and $\log \beta_{3:1} = 20.0$) in the case of 1 and a 3:1 (ligand/metal) complex ($\log \beta_{3:1} = 20.3$) for compound 2. Therefore, at low metal ion concentration only the $[M(\mathbf{2})_3]^{3+}$ species is present, as demonstrated also by NMR titration. It is likely that in this complex not all the 12 nitrogen atoms 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 nitrogen atoms 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 1 and 2 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 1 and 2 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 [42]. Apparently, the nature of the coordination sphere plays an important role concerning energy transfer efficiency.

To overcome this problem a supramolecular approach has been followed [43]. It was known that complexes of Ru^{2+} containing 2,2′-bipyridine (bpy) and cyanide ligands, i.e. $[Ru(bpy)_2(CN)_2]$ and $[Ru(bpy)(CN)_4]^{2-}$, are luminescent and can play the role of ligands giving rise to supercomplexes [44,45]. Titration of an CH_3CN/CH_2Cl_2 1:1 (v/v) solution of $[Ru(bpy)_2(CN)_2]$ with Nd^{3+} causes changes in the absorption spectrum and quenching of the Ru^{2+} complex emission, accompanied by sensitized Nd^{3+} emission, demonstrating the ability of $[Ru(bpy)_2(CN)_2]$ to complex the lanthanide metal ion. Titration of a 1:1 mixture of dendrimer **2** and $[Ru(bpy)_2(CN)_2]$ in CH_3CN/CH_2Cl_2 1:1 (v/v) with $Nd(CF_3SO_3)_3$ brings about changes in the absorption and emission spectra. The lowest energy absorption band is blue-shifted, as observed for the titration of $[Ru(bpy)_2(CN)_2]$ in the absence of dendrimer. Upon excitation at 260 nm, where most of the light is absorbed by dendrimer **2**, the intensity of the naphthyl monomer emission at 335 nm does not show a monotonous increase, as observed in the absence of the $[Ru(bpy)_2(CN)_2]$ complex, reaches a maximum at 0.5 equivalent and then decreases up to about 1.0 equivalent of Nd^{3+} to rise again for higher metal ion concentration. The emission intensity at 1.0 equivalent is lower than that observed in the absence of $[Ru(bpy)_2(CN)_2]$. These results show that a three-component system $\{\mathbf{2}^{\bullet}Nd^{3+}\bullet[Ru(bpy)_2(CN)_2]\}$ (Fig. 9) is formed in which the dendrimer emission is quenched. The three-component system can be disassembled by addition of an excess of each component, or of cyclam. The main photophysical processes of the $\{\mathbf{2}^{\bullet}Nd^{3+}\bullet[Ru(bpy)_2(CN)_2]\}$ adduct are summarized in Fig. 10, which shows the energy levels of the three components. In the two-component dendrimer-Nd^{3+} system, energy transfer from either the lowest singlet (S_1) or triplet (T_1) excited state of the naphthyl units of the dendrimer to the lanthanide ion does not occur. Sensitization of the Nd^{3+} emission upon dendrimer excitation in the three-component system is mediated by the $[Ru(bpy)_2(CN)_2]$ component. Comparison between the emission quantum yield of $[Ru(bpy)_2(CN)_2]$ upon excitation at 260 nm (dendrimer absorption) and 450 nm ($[Ru(bpy)_2(CN)_2]$ absorption) has allowed to estimate that the energy transfer efficiency from the S_1 excited state of the naphthyl groups to the ^{1}MLCT excited state of $[Ru(bpy)_2(CN)_2]$ is about 60% (Fig. 10). The energy transfer efficiency from the ^{3}MLCT excited state of $[Ru(bpy)_2(CN)_2]$ to Nd^{3+} can be assumed to be equal to the efficiency of the quenching of the $[Ru(bpy)_2(CN)_2]$ emission (≈90%) because quenching by electron transfer can be ruled out in view of the Nd^{3+} redox properties. No evidence of energy transfer

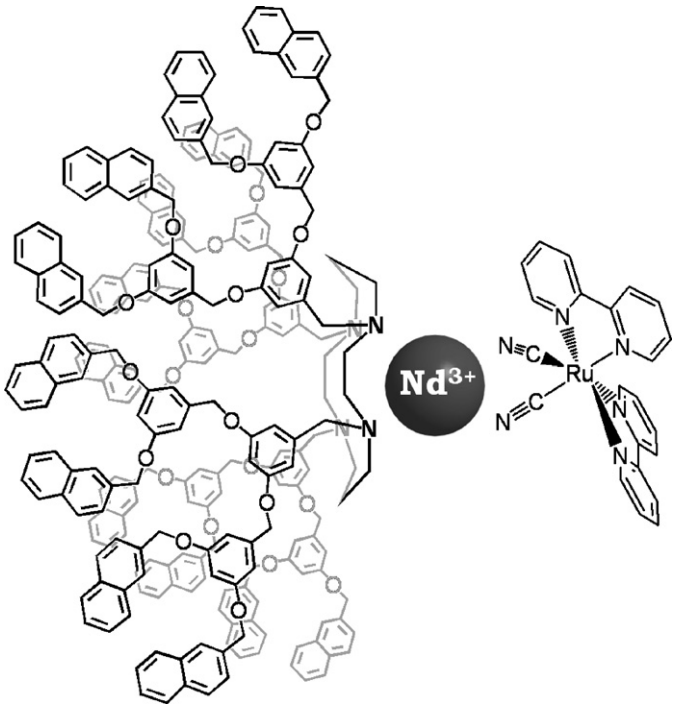


Fig. 9. Schematic representation of the self-assembled {**2**•Nd^{3+}•$[Ru(bpy)_2(CN)_2]$}.

in the adduct from the naphthyl-localized T_1 excited state of the dendrimer to the lowest ^{3}MLCT state of $[Ru(bpy)_2(CN)_2]$ has been found since no change in the T_1 lifetime at 77 K has been observed.

The three components of the self-assembled structure have complementary properties, so that new functions emerge from their assembly. Dendrimer **2** has a very high molar absorption coefficient in the UV spectroscopic region because of 12 dimethoxybenzene and 16 naphthyl units, but it is unable to sensitize the emission of a Nd^{3+} ion placed in its cyclam core. The $[Ru(bpy)_2(CN)_2]$ complex can coordinate (by the cyanide ligands) and sensitize the emission of Nd^{3+} ions. Self-assembly of the three species leads to a quite unusual Nd^{3+} complex which exploits a dendrimer and a Ru^{2+} complex as ligands. Such a system behaves as an antenna that can harvest UV to VIS light absorbed by both the

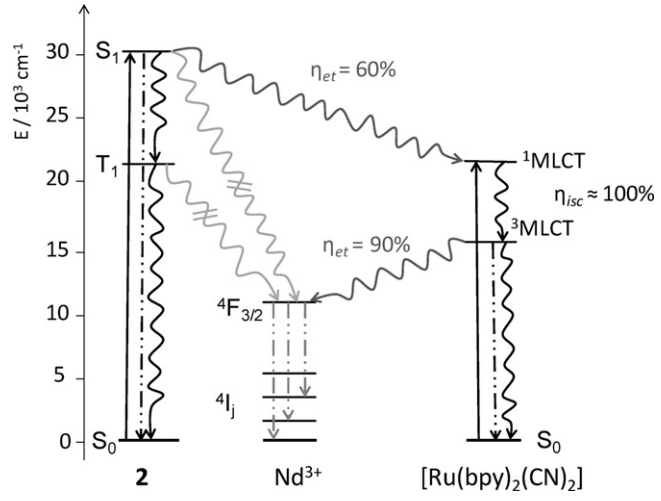


Fig. 10. Energy level diagram showing the excited states involved in the main photophysical processes (absorption: solid lines; radiative deactivation: dotted-dotted-dashed lines; non-radiative deactivation processes: wavy lines) of the {**2**•Nd^{3+}•$[Ru(bpy)_2(CN)_2]$} three-component system. Naphthyl excimer energy level has been omitted for clarity.

Ru^{2+} complex and the dendrimer and emit in the NIR region with line-like bands. In principle, the emission wavelength can be tuned by replacing Nd^{3+} with other lanthanide ions possessing low-lying excited states.

5. Conclusion

The introduction of dendrimers as ligands has greatly expanded the scope of metal coordination chemistry and, in particular, has revitalized the study of luminescent metal complexes. Metal complexes containing dendritic ligands have shown very complex luminescence properties. In particular, research on cyclam-cored dendrimers has led to supramolecular systems, capable of manipulating light signals towards applications in the fields of luminescent sensors, logic gates, and light-harvesting antenna. The role of light in the reported studies is: on one hand, to study metal–ligand coordination processes, on the other hand, to act as an input or output of the supramolecular platform in order to achieve the desired function.

Future perspectives are envisioned in the field of (i) dendrimers containing more than one cyclam linked by photoswitchable bridge in order to tune the coordination properties upon external photochemical inputs, and (ii) supramolecular adducts in which the metal ion acts as a glue of two different dendritic ligands in view of light-harvesting purposes. Indeed, 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, electrochemiluminescence, and light emitting diodes (LED), besides those discussed in this paper.

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