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LUMINESCENT DENDRIMERS

In this review we discuss the main photophysical processes occurring within a class of supramolecular systems called dendrimers. In particular, the attention is focused on examples of luminescent dendrimers studied in our laboratory capable of (a) performing excimer and/or exciplex emission, (b) exploiting energy transfer for harvesting light, (c) undergoing electron transfer processes, (d) down and up converting light frequency, (e) playing the role of ligands for luminescent and non-luminescent metal ions, and (f) performing as photoswitchable hosts for luminescent dyes.

endrimers [1] constitute a class of macromolecules that exhibit a defined structure and 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 (Fig. 1). Moreover, thanks to their three-dimensional structure, internal dynamic cavities are present, where ions or molecules can be hosted. It is thus possible to construct large nanoobjects capable of performing complex func-

tionalities that derive from the integration of the specific properties of the constituent moieties. Nowadays both chemistry and physics of dendritic molecules are rapidly expanding for fundamental research as well as for technological applications [2].

Dendrimers are ideal scaffold to organize many luminescent units in a restricted space according to a predetermined pattern. Because of their proximity, the various functional groups of a dendrimer may easily interact with one another, or with molecules hosted in the dendritic cavities or associated to the dendrimer surface [3].

In this review article we briefly summarize some fundamental concepts

concerning excited state deactivation processes in luminescent dendrimers and then we focus on dendrimers as (i) ligands of metal ions, (ii) light-harvesting antennae, (iii) systems for energy up-conversion, and (iv) photoswitchable hosts. Illustration of these processes, which are often interconnected one another, will offer us the opportunity to discuss some important topics like (a) multiple luminescence, (b) quenching and sensitization of species encapsulated by dendrimers, (c) sensing metal ions with signal amplification, and (d) photocontrolled uptake and release of guest molecules by dendrimers. We will discuss some prototypical examples taken from the work performed in our laboratory to illustrate the above mentioned functionalities.

Deactivation processes of luminescent excited states of dendrimers

Deactivation of the luminescent excited state of a chromophore A can take place by intrinsic deactivations, i.e. by radiative, non-radiative, or photochemical pathways. In this case, the excited state lifetime τ can be expressed in terms of the kinetic constants of the various processes:

$$\tau = 1/(k_r + k_{nr} + k_p) \tag{1}$$

where $k_{\rm r},\,k_{\rm nr},$ and $k_{\rm p}$ are the rate constants of the radiative, non-radiative, and photochemical pathways, respectively.

When the chromophore A is inserted in a dendritic structure, interaction with other groups of the same dendrimer can take place. Energy and electron transfer processes can occur between functional groups incorporated in a dendrimer and, in this case, they take place by first order kinetics. They must compete, of course, with the intrinsic excited state decay, $1/\tau$ of A. For example, in a species consisting of A and B component units, excitation of A (eq. 2) may be followed by energy (eq. 3) or electron (eqs. 4 and 5) transfer to B [4]:

$A-B + h\nu \rightarrow A-B \tag{2}$	2)
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$$^{*}A - B \rightarrow A - ^{*}B \tag{3}$$

$$^{*}A - B \rightarrow A^{-} - B^{-} \tag{4}$$

$$^{*}A - B \rightarrow A^{-} - B^{+} \tag{5}$$

In the case of energy transfer (eq. 3), the quantum yield of the sensitized emission of B, Φ_{sens} , is given by the product of the efficiency η_{et} of energy transfer from *A to B and the emission quantum yield of B upon direct excitation of this component, Φ_{*B} ,

$$\Phi_{\text{sens}} = \eta_{\text{et}} \Phi_{^{\star}\text{B}} \tag{6}$$

$$\eta_{\text{et}} = k_{\text{et}} / (k_{\text{et}} + 1/\tau + k_{\text{d}}) \tag{7}$$

where k_{et} is the first order rate constant for energy transfer from *A to B (eq. 3), τ is the intrinsic lifetime of the relevant excited state of A involved in the process (eq. 1), and k_d is the rate constant of other deactivation processes that compete with energy transfer (e.g., elec-

tron transfer, eqs. 4 and 5).

Energy transfer requires electronic interactions and therefore its rate decreases with increasing distance, r. Depending on the electronic interaction mechanism, the distance dependence may follow a 1/r⁶ (resonance, also called Förster-type, mechanism) or e^{-r} (exchange, also called Dexter-type, mechanism) [4]. In both cases, energy transfer is favoured when the emission spectrum of the donor overlaps the absorption spectrum of the acceptor [5].

Quenching of an excited state by electron transfer needs electronic interaction between the two partners and obeys the same rules as electron transfer between ground state molecules (Marcus equation and related quantum mechanical elaborations [4]), taking into account that the excited state energy can be used, to a first approximation, as an extra free energy contribution for the occurrence of both oxidation and reduction processes [5].

In most cases, quenching of an excited state (for example, by energy transfer) takes place by a weak electronic interaction. When the excited state and the quencher undergo a relatively strong electronic interaction, new chemical species, which are called excimers (from *exci*ted dimers) or exciplexes (from *exci*ted complexes), depending on whether the two interacting units have the same or different chemical nature, respectively. Excimers and exciplexes sometimes (but not always) can give luminescence, which is displaced to lower energy (longer wavelengths) compared with the "monomer" emission, and usually corresponds to a broad and rather weak band. In dendrimers containing a variety of components both exciplex and excimer formation can take place. In such a case, as many as three different types of luminescence can be observed, namely "monomer" emission, exciplex emission, and excimer emission (see below).

Dendrimers as ligands and sensors of metal ions

If dendrimers contain both luminescent units and coordination sites, they can perform as luminescent ligands for metal ions [6]. Coupling luminescence with metal coordination can indeed be exploited for a variety of purposes, that include investigation of dendrimer structures [7], encapsulated metal nanoparticles [8], stepwise complexation [9], and reversible metal complex assembly [10].

In most cases, metal ion coordination by a dendrimer takes place by multiple identical coordinating units that are present along the dendrimer branches or appended at the dendrimer periphery, thus resulting in metal complexes of variable stoichiometry and unknown structures. Luminescent dendrimers with a well defined metal-coordinating site have been reported so far, and the most used coordination site is 1,4,8,11-tetraazacyclotetradecane (cyclam).

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 and change their properties, which results in signal amplifi-



cation. In the case of luminescent dendrimers, *one* analyte can quench the luminescence of *all* the peripheral luminescent units appended at the dendrimer periphery (Fig. 2a). This is a significant advance compared to a conventional luminescent sensor, in which the ratio between quenched units and analyte is 1:1 (Fig. 2b). 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 [11], and nanoparticles [12]. Because of their well defined and fully programmable structures, dendrimers are more promising species for this kind of application [13].

Dendrimers containing multiple coordinating sites

The dendrimers of the poly(propylene amine) family can be easily functionalized in the periphery with luminescent units. Compound 1 (Scheme 1) represents the fourth generation dendrimer and contains 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 (λ_{max} =252 and 339 nm; ϵ_{max} ≈ 12,000 and 3,900 L mol⁻¹ cm⁻¹, respectively, for each dansyl unit) and a strong fluorescence band in the visible region (λ_{max} =500 nm; Φ_{em} =0.46, τ =16 ns) [14]. 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 Co²⁺ ions (as nitrate salt) has been carefully studied [15]. 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 Co²⁺ ions; (ii) in the case of the dendrimers, the absorption spectra are unaffected, but a strong quenching of the fluorescence of the periph-



eral 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 by addition of a competitive ligand; (v) a strong amplification of the fluorescence quenching signal is observed with increasing dendrimer generation. When a Co^{2+} ion enters dendrimer **1**, 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 was illustrated in Fig. 2.

Dendrimers containing a single coordinating unit

Cyclam is one of the most extensively investigated ligands in coordination chemistry [16]. Both cyclam and its 1,4,8,11-tetramethyl derivative in aqueous solution can be protonated and can coordinate metal ions such as Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Hg^{2+} with high stability constants.

Dendrimer **2** (Scheme 2) consists of a cyclam core appended with twelve dimethoxybenzene and sixteen naphthyl units. In acetonitriledichloromethane 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 (λ_{max} =337 nm), naphthyl excimers (λ_{max} ca. 390 nm), and naphthyl-amine exciplexes (λ_{max} =480 nm) [17].

Extensive investigations have been performed on the interaction of dendrimer **2** with metal ions [18]. Coordination of Zn^{2+} , a metal ion that is difficult to oxidize and reduce and that exhibits a d¹⁰ electronic configuration, leads to complexes that cannot exhibit electronic 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, dendrimer **2** gives rise to complexes with 2:1 dendrimer/metal stoichiometry at low Zn²⁺ concentration, as evidenced by both fluorescence and ¹H-NMR titrations with a high formation constant (log β >13). The unexpected [Zn(**2**)₂]²⁺ species shows that the dendrimer branches do not hinder coordination of cyclam to Zn²⁺ with respect to coordination of solvent molecules or counter ions. Furthermore, the two cyclam cores, to account for the coordination number (\leq 6) of Zn²⁺, are likely forced to adopt a structure in which not all of the four N atoms are available for Zn²⁺ coordination, thereby favouring a 2:1 stoichiometry.

In the $[Zn(2)_2]^{2+}$ 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. 2. In this case, the sensor fluorescence is switched on upon metal ion coordination, and low Zn^{2+} concentrations (ca. 1 μ M) can be easily detected.

Light-harvesting 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



absorption energy transfer

Fig. 3 - Schematic representation of antenna effect in a dendrimer

acceptor component (Fig. 3). 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 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). The quantum yield of the sensitized emission of the acceptor is represented by eq. 6. Clearly, the quantum yield of the sensitized emission obtained upon direct excitation of the chromophore. Another essential property of the light absorbing units of an antenna system is their chemical and photochemical stability.

In the last ten years, much attention has been devoted to the design and synthesis of dendrimers [19] capable of playing the role of antennas in artificial systems for the 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.

Light-harvesting dendrimers containing organic chromophores

Dendrimer **3** consists of a hexaamine core surrounded by 8 dansyl-, 24 dimethoxybenzene-, and 32 naphthalene-type units (Fig. 4) [20]. In dichloromethane solution, **3** exhibits the characteristic absorption bands of the component units and a strong dansyl-type fluorescence. Energy transfer from the peripheral dimethoxybenzene and naphthalene units to the fluorescent dansyl units occur with >90%



photoinduced energy transfer processes

efficiency. It can be used as a phase transfer agent in liquid-liquid extraction experiments. Indeed, it is soluble only in an organic phase (dichloromethane solution) and can extract eosin molecules, soluble only in an aqueous phase, by encapsulating them in its internal region. By looking at the absorption band of the eosin molecule in the organic and water phase, the average number of eosin per dendrimer can be estimated. In the case of dendrimer 3, the maximum dye loading is one eosin per dendrimer (Fig. 4). When the dendrimer hosts a molecule of the fluorescent eosin dye, the dansyl fluorescence is guenched and sensitization of the fluorescence of the eosin guest can be observed. Quantitative measurements showed that the encapsulated eosin molecule collects electronic energy from all the 64 chromophoric units of the dendrimer with an efficiency >80%. Both intramolecular (i.e., within dendrimer) and intermolecular (i.e., dendrimer host → eosin guest) energy-transfer processes occur very efficiently by a resonance mechanism because of the strong overlap between the emission and absorption spectra of the relevant donor/acceptor units.

Light-harvesting dendrimer containing a luminescent metal ion

Lanthanide ions show very long lived luminescence which is a quite useful property for several applications [21]. Because of the forbidden nature of their electronic transitions, however, lanthanide ions exhibit very weak absorption 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) [22].

Complexation of dendritic ligand ${\bf 2}$ with lanthanide ions (Nd³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Dy³⁺) [18b] leads to results qualitatively similar to those

obtained upon Zn²⁺ complexation (see above). However, the complex stoichiometry is different: at low metal ion concentration only the $[M(2)_3]^{3+}$ species is present (log $\beta_{1:3}$ =20.3), 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. Clearly, 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 **2** no sensitized emission from the lanthanide ion was observed.

To overcome this problem a supramolecular approach has been followed [23]. It was known that complexes of Ru²⁺ 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 [24, 25]. [Ru(bpy)₂(CN)₂] can coordinate Nd³⁺, as demonstrated by the quenching of the Ru²⁺ complex emission, and the sensitization of Nd³⁺ emission. Titration of a 1:1 mixture of dendrimer **2** and [Ru(bpy)₂(CN)₂] in acetonitrile:dichloromethane 1:1 (v/v) with Nd(CF₃SO₃)₃ brings about the formation of a three-component system {**2**·Nd³⁺·[Ru(bpy)₂(CN)₂]} (Fig. 5). Sensitization of the Nd³⁺ emission upon dendrimer excitation in the three-component system is mediated by the [Ru(bpy)₂(CN)₂] component. Indeed, a photoinduced energy transfer from the the naphthyl groups to the [Ru(bpy)₂(CN)₂] takes place with 60% efficiency, and then the Ru²⁺ complex sensitize Nd³⁺ emission with 90% efficiency.

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 spectral region because of 12 dimethoxybenzene and 16 naphthyl units, but it is unable to sensitize the emission of a Nd³⁺ ion



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placed in its cyclam core. The $[Ru(bpy)_2(CN)_2]$ complex can coordinate (by the cyanide ligands) and sensitize the emission of Nd³⁺ ions. Self-assembly of the three species leads to a quite unusual Nd³⁺ complex which exploits a dendrimer and a Ru²⁺ complex as ligands. Such a system behaves as an antenna that can harvest UV to VIS light absorbed by both the Ru²⁺ complex and the dendrimer and emits in the NIR region with line-like bands. In principle, the emission wavelength can be tuned by replacing Nd³⁺ with other lanthanide ions possessing low-lying excited states.

Dendrimers for energy up-conversion

Dendrimer **4** consists of a benzophenone core and branches that contain eight naphthalene units at the periphery (Fig. 6) [26]. In this dendrimer, excitation of the peripheral naphthalene units is followed by fast singlet-singlet energy transfer to the benzophenone core, but on a longer time scale a back energy transfer process takes place from the triplet state of the benzophenone core to the triplet state of the benzophenone units. Selective excitation of the benzophenone unit is followed by intersystem crossing and triplet-triplet energy transfer to the peripheral naphthalene

units (Fig. 6). This sequence of processes, which is made possible by the preorganization of photoactive units in a dendrimer structure, can be exploited for several purposes. In hydrogen donating solvents, the benzophenone core is protected from degradation by the presence of the naphthalene units. In solutions containing Tb(CF₃SO₃)₃, sensitization of the green Tb³⁺ luminescence is observed on excitation of both the peripheral naphthalene units and the benzophenone core.

processes

This dendrimer can also be useful for energy-up conversion applications because the lowest energy absorption band involves the benzophenone chromophore which is characterized by very close lying S_1 and T_1 excited states (Fig. 6) with a practically unitary efficiency of intersystem crossing $S_1 \rightarrow T_1$. Furthermore, the naphthalene chromophores have S_1 and T_1 excited states separated by a wide energy gap, as usually observed for π,π^* transitions and the naphthalene T₁ excited state can be populated by energy transfer from the corresponding benzophenone T₁ excited state. Therefore, upon excitation of the benzophenone $S_1(n,\pi^*)$ absorption band (355 nm) with a laser source, fast and 100% efficient intersystem crossing takes place, followed by triplet-triplet energy transfer from the $T_1(n,\pi^*)$ excited state of the core to the $T_1(\pi,\pi^*)$ excited state of the naphthalene units in the branches, and then by triplet-triplet annihilation of naphthalene excited states which leads to population of naphthalene S₁ excited state. Therefore, upon excitation at 355 nm (green line in Fig. 6) emission at 335 nm (blue line in Fig. 6) by the naphthalene peripheral chromophores is observed by an energy up-conversion mechanism.

Energy up-conversion based on sensitized triplet-triplet annihilation is a promisinig technology for wavelength shifting. Indeed, it is based



on sequential, highly allowed, one-photon absorptions, thereby permitting the use of low-power noncoherent excitation sources.

The advantage of the present example compared to other systems based on diffusion controlled quenching/sensitization processes [27] relies on the fact that it can operate in solid and rigid matrix where diffusion is completely shut down since the involved chromophores are linked inside a dendritic structure. Future studies will be aimed at improving efficiency and designing new dendrimers to shift the emission into the visible spectral region.

Dendrimers as photoswitchable hosts

It is well known that azobenzene-type compounds undergo an efficient and fully reversible photoisomerization reaction [28]. For this reason, they have been extensively used to construct photoswitchable devices [29]. It is also known that they are reversibly switched from the trans to the cis form by UV light and can then be converted back to the trans form by heating or by visible light. Isomerization of azobenzene units involves a large structural rearrangement since in going from the *trans* to the *cis* isomer the distance between the para carbon atoms of azobenzene decrease from 9 to 5.5 Å and the dipole moment increases from zero (since the trans form is planar and symmetric) to 3.0 D. Dendrimers containing azobenzene groups [30] in the core, branching points or periphery can modify their structure and flexibility according to the isomerization state of the azobenzene units. In particular, structural changes in the peripheral units of a dendrimer can change the surface properties and cause rearrangements in the internal cavities. For all these reasons, dendrimers bearing azobenzene groups in the periphery could play the



the release of two eosin molecules with formation of a photostable **D**(15t17c)⊃6eosin species ($\Phi = 0.15$). On the other hand, cis→trans thermal reaction is noticeably slowed down by the presence of eosin in the dendritic structure and the kinetics of eosin uptake or release is much faster in the case of the all trans dendrimer. Therefore, the isomerization state of the peripheral azobenzene units controls, to some degree, the permeability of the dendrimer cavities to eosin and, viceversa, eosin molecules hosted in the dendrimer cavities affect the velocity of thermal isomerization process of its peripheral azobenzene units. The results obtained suggest that a more extensive study of dendrimers with isomerizable azobenezene units in the periphery may lead to photocontrollable membranes and drug deliverv systems.

role of photoswitchable hosts.

Dendrimer **D**(32t) is a fluorescent and photoreactive fourth generation dendrimer of the poly(propylene amine) family functionalized with 32 naphthyl and 32 *trans*-azobenzene units (Fig. 7). The fluorescence of the naphthalene units is partially quenched by the tertiary amines (via electron transfer) as well as by the *trans*- and *cis*azobenzene units (via energy transfer) [31]. **D**(32t) can be converted to **D**(4t28c) upon irradiation with 365 nm light in dichloromethane solution with photoreaction quantum yield ($\Phi = 0.12$) very similar to that reported for azobenzene. **D**(4t28c) at 313 K, undergoes a thermal back reaction to **D**(32t) with rate constant *k*=7.0x10⁻⁵ s⁻¹.

This dendrimer can host eosin molecules in dichloromethane solution, extracting them from a water solution at pH=7 [32], as previously described for dendrimer **3**. The hosting capacity of the two isomeric forms of the dendrimer is not much different: 8 and 6 eosin molecules for **D**(32t) and D(4t28c), respectively. *Trans*—*cis* isomerization quantum yield is not significantly affected by eosin encapsulation: irradiation at 365 nm of the **D**(32t)⊃8eosin species at 298 K leads to

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Conclusions

The above discussed examples show that coupling luminescence with dendrimer chemistry can lead to very interesting results. Interaction of excited state units of a dendrimer with other units of the same dendrimer or with encapsulated species (e.g., metal ions and dye molecules) can affect the luminescence properties in several ways, thereby generating systems capable of harvesting light, displaying multiple light emission, down and up converting light frequency, sensing metal ions with signal amplification, sensitizing light emission and photochemical reactions, acting as photoswitchable hosts. These results may find future applications in the field of solar cells, light emitting diodes (LED), and photocontrolled drug-delivery systems.

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Dendrimeri luminescenti

In questa review vengono illustrati alcuni concetti fondamentali sui processi fotofisici che riguardano una particolare classe di supramolecole chiamate dendrimeri. In particolare, si descrivono alcuni studi effettuati nel nostro laboratorio che dimostrano l'utilizzo dei dendrimeri come (i) leganti e sensori di ioni metallici, (ii) antenne per il convogliamento dell'energia, (iii) sistemi per l'up-conversion dell'energia e (iv) recettori fotoisomerizzabili per il rilascio controllato di specie chimiche.