DENDRIMERS, LUMINESCENT

1. Introduction

Luminescence can be defined as the emission of light [intended in the broader sense of ultraviolet (uv), visible (vis), or near-infrared (ir) radiation] by electronic excited states of atoms or molecules. Luminescence is an important phenomenon from a basic viewpoint (eg, for monitoring excited-state behavior) (1) as well as for practical applications (lasers, displays, sensors, etc) (2–5).

Luminescent units can be incorporated in different regions of a dendritic structure and can also be noncovalently hosted in the cavities of a dendrimer or associated at a dendrimer surface as schematically shown in Figure 1 (6).

Coupling luminescence with dendrimer chemistry (7) can lead to systems capable of performing very interesting functions (8–12) such as (a) light harvesting, (b) changing the “color” of light, (c) sensing with signal amplification, (d) quenching and sensitization processes, (e) shielding effects. Luminescence can also be used for elucidating dendritic structures and superstructures, and for investigating dendrimer rotation in solution. In this article, we will deal with luminescent dendrimers in the bulk of a solution. Dendrimer luminescence at the single molecule level (see, eg, 13) will not be covered.

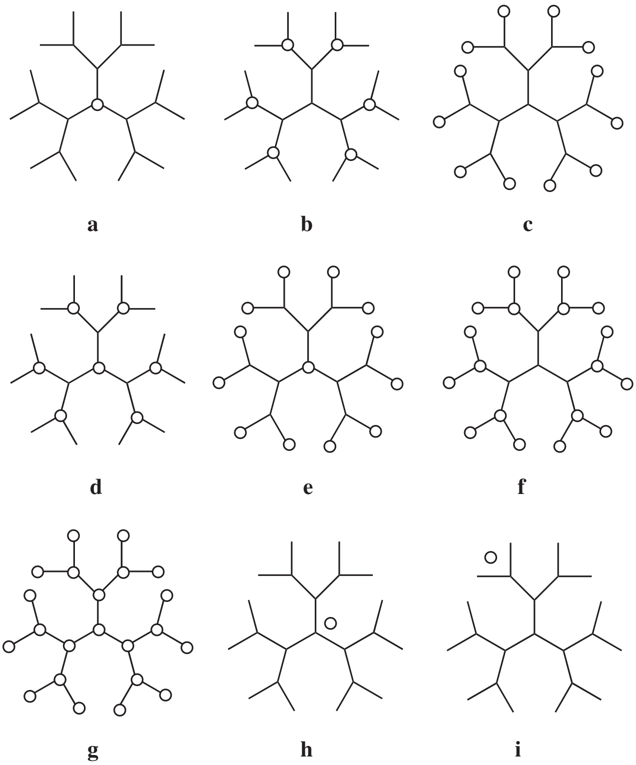


Fig. 1. Schematic illustration of the possible location of photoactive units, represented by circles, covalently linked (types **a**–**g**) or associated (types **h**–**i**) to a dendrimer.

2. Luminescence

Before illustrating examples of luminescent processes in dendrimers, it is worthwhile recalling a few elemental principles of molecular luminescence. Interested readers can refer to several books for deeper discussions (1,2,14,15). A necessary, but not sufficient, condition to obtain light emission from a molecule is the population of electronic excited states. When this result is achieved by light absorption, the light emission that follows is called luminescence (strictly speaking, *photo*luminescence). When the population of excited states (and the consequent light emission) is obtained by suitable chemical or electrochemical reactions, the terms *chemi*luminescence and *electro*chemiluminescence are used. In most cases, the ground state of a molecule is a singlet state (S_0), and the excited states are either singlets (S_1, S_2, etc) or triplets (T_1, T_2, etc). A schematic energy level diagram is shown in Figure 2. For the sake of simplicity, it is assumed that the molecule does not undergo photochemical reactions.

In principle, transitions between states having the same spin value are allowed, whereas those between states of different spin are forbidden. Therefore, the absorption bands observed in the uv-vis spectrum of molecules usually

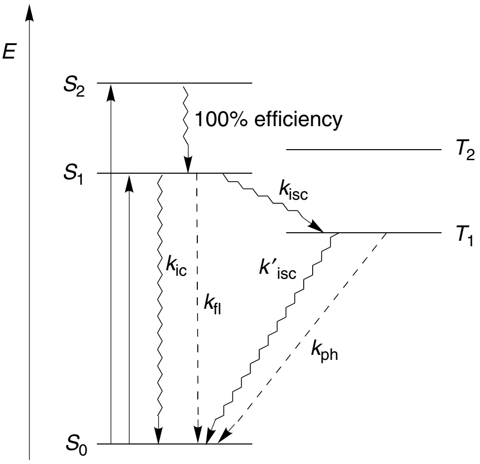


Fig. 2. Schematic energy level diagram for a generic molecule.

correspond to $S_0 \rightarrow S_n$ transitions. Excited states are unstable species that undergo fast deactivation by intrinsic (first-order kinetics) photophysical processes. When a molecule is excited to upper singlet excited states, it usually undergoes a fast and 100% efficient radiationless deactivation (internal conversion, ic) to the lowest excited singlet, S_1. Such an excited state undergoes deactivation via three competing photophysical processes: (1) nonradiative decay to the ground state (internal conversion, rate constant k_{ic}); (2) radiative decay to the ground state (luminescence, that in the specific case of a spin-allowed process is called *fluorescence*, rate constant k_{fl}); (3) conversion to the lowest triplet state T_1 (intersystem crossing, rate constant k_{isc}). In its turn, T_1 can undergo deactivation to the ground state S_0 via a nonradiative process (intersystem crossing, rate constant k'_{isc}) or a radiative process (luminescence, which in the specific case of a spin-forbidden transition is called *phosphorescence*, rate constant k_{ph}). Thermally activated back-conversion $T_1 \rightarrow S_1$ and triplet–triplet annihilation with formation of S_1 and S_0 can also occur, giving rise to delayed fluorescence. When the molecule contains heavy atoms, the formally forbidden (and, therefore, slow) intersystem crossing and phosphorescence processes become faster.

The lifetime (τ) of an excited state is given by the reciprocal of the summation of the first-order deactivation rate constants:

$$\tau(S_1) = 1/(k_{\mathrm{ic}} + k_{\mathrm{fl}} + k_{\mathrm{isc}}) \tag{1}$$

$$\tau(T_1) = 1/(k'_{\mathrm{isc}} + k_{\mathrm{ph}}) \tag{2}$$

The orders of magnitude of $\tau(S_1)$ and $\tau(T_1)$ are $\sim 10^{-9}$–10^{-7} s and 10^{-3}–10^{0} s, respectively.

The quantum yields of fluorescence (Φ_{fl}), defined as the ratio between the number of photons emitted by S_1 and the number of absorbed photons, and phosphorescence (Φ_{ph}), defined as the ratio between the number of photons emitted by T_1 and the number of absorbed photons, can have values between 0 and 1. When light excitation is performed in the absorption band corresponding to the S_1 excited state or in absorption bands corresponding to upper S_n excited states that undergo 100% efficient internal conversion to S_1, the fluorescence and phosphorescence quantum yield are given by the following expressions (Fig. 2):

$$\Phi_{\text{fl}} = k_{\text{fl}}/(k_{\text{ic}} + k_{\text{fl}} + k_{\text{isc}}) = k_{\text{fl}}\tau(S_1) \tag{3}$$

$$\Phi_{\text{ph}} = [k_{\text{isc}}/(k_{\text{ic}} + k_{\text{fl}} + k_{\text{isc}})] \cdot k_{\text{ph}}/(k'_{\text{isc}} + k_{\text{ph}}) = \eta_{\text{isc}}k_{\text{ph}}\tau(T_1) \tag{4}$$

where η_{isc} is the intersystem crossing efficiency. Deactivation of an excited state can occur not only by the above mentioned intrinsic (first-order) decay processes, but also by interactions with other species (quenching processes, second-order kinetics). The two most important types of quenching processes are those involving energy (eq. 6) or electron (eqs. 7 and 8) transfer (*A and *B stand for excited states of molecules A and B)(1):

$$A + h\nu \longrightarrow {}^*\text{A} \tag{5}$$

$$^*\text{A} + \text{B} \longrightarrow \text{A} + {}^*\text{B} \tag{6}$$

$$^*\text{A} + \text{B} \longrightarrow \text{A}^+ + \text{B}^- \tag{7}$$

$$^*\text{A} + \text{B} \longrightarrow \text{A}^- + \text{B}^+ \tag{8}$$

The disappearance of the excited state *A causes, of course, the disappearance (quenching) of the luminescence of the species A. It should be noted that in the case of energy transfer (eq. 6) an excited state of B, *B, is formed, so that the luminescence of species B can appear (sensitized luminescence). Energy and electron-transfer processes can occur not only between distinct molecules in an encounter, but also between nearby molecular components in a supramolecular structure (eqs. 10–12), eg, between functional groups incorporated in a dendrimer (15):

$$\text{A—B} + h\nu \longrightarrow {}^*\text{A—B} \tag{9}$$

$$^*\text{A—B} \longrightarrow \text{A—}^*\text{B} \tag{10}$$

$$^*\text{A—B} \longrightarrow \text{A}^+\text{—B}^- \tag{11}$$

$$^*\text{A—B} \longrightarrow \text{A}^-\text{—B}^+ \tag{12}$$

Energy and electron-transfer processes in supramolecular structures take place by first-order kinetics. They must compete, of course, with the intrinsic excited-state decay, $1/\tau$ (eqs. 1 and 2, Fig. 3).

Because of their proximity, the various functional groups of a dendrimer may easily interact with one another. Interaction can also occur between dendrimer units and molecules hosted in the dendritic cavities or associated to the dendrimer surface. In the context of this work, particularly interesting is the case in which a dendrimer light absorption by a component A is followed by energy transfer to a luminescent component B (eqs. 9 and 10) . The quantum yield of the sensitized emission of B, Φ_{sens}, is given by the product of the emission

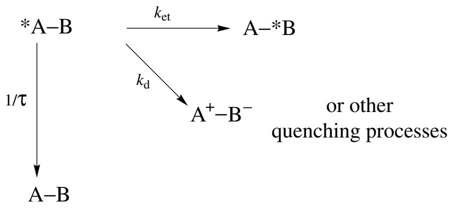


Fig. 3. Schematic deactivation processes of an excited state in a supramolecular species.

quantum yield of B upon direct excitation of this component, Φ_{*B}, and the efficiency η_{et} of energy transfer from *A to B

$$\Phi_{sens} = \eta_{et}\Phi_{*B} \tag{13}$$

$$\eta_{et} = k_{et}/(k_{et} + 1/\tau + k_d) \tag{14}$$

where k_{et} is the first-order rate constant for energy transfer from *A to B (eq. 10), τ is the intrinsic lifetime of the relevant [$\tau(S_1)$ or $\tau(T_1)$, eqs. 1 and 2] excited state of A involved in the process, and k_d is the rate constant of other deactivation processes (eg, electron transfer, eq. 11 and 12) that compete with energy transfer. 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 $1/r^6$ (resonance, also called Förster-type, mechanism) or e^{-r} (exchange, also called Dexter-type, mechanism) (1). In both cases, energy transfer is favored when the emission spectrum of the donor overlaps the absorption spectrum of the acceptor.

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 (16)], 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.

In most cases, quenching of an excited state (eg, by energy transfer) takes place by a weak interaction. It may happen, however, that the excited state and the quencher undergo a strong interaction yielding a new chemical species, which is called an excimer (from excited dimer)) or exciplex (from excited complex) depending on whether the two interacting units have the same or different chemical nature. It is important to notice that excimer and exciplex formation is a reversible process and that both excimers and exciplexes sometimes (but not always!) can give luminescence. Compared with the "monomer" emission, the emission of an excimer or exciplex is always displaced to lower energy (longer wavelengths) and usually corresponds to a broad and rather weak band.

Excimers are usually obtained when an excited state of an aromatic molecule interacts with the ground state of a molecule of the same type. For example, between excited and ground state of anthracene units. Exciplexes are obtained when an electron donor (acceptor) excited state interacts with an electron acceptor (donor) ground-state molecule. For example, between excited states of aromatic molecules (electron acceptors) and amines. In dendrimers containing a variety of components, both exciplex and excimer formation can take place (see eg, 17,18). In such a case, as many as three different types of luminescence can be observed, namely, "monomer" emission, exciplex emission, and excimer emission. This happens, eg, in dendrimers with cyclam core and naphthalene units in the branches (19).

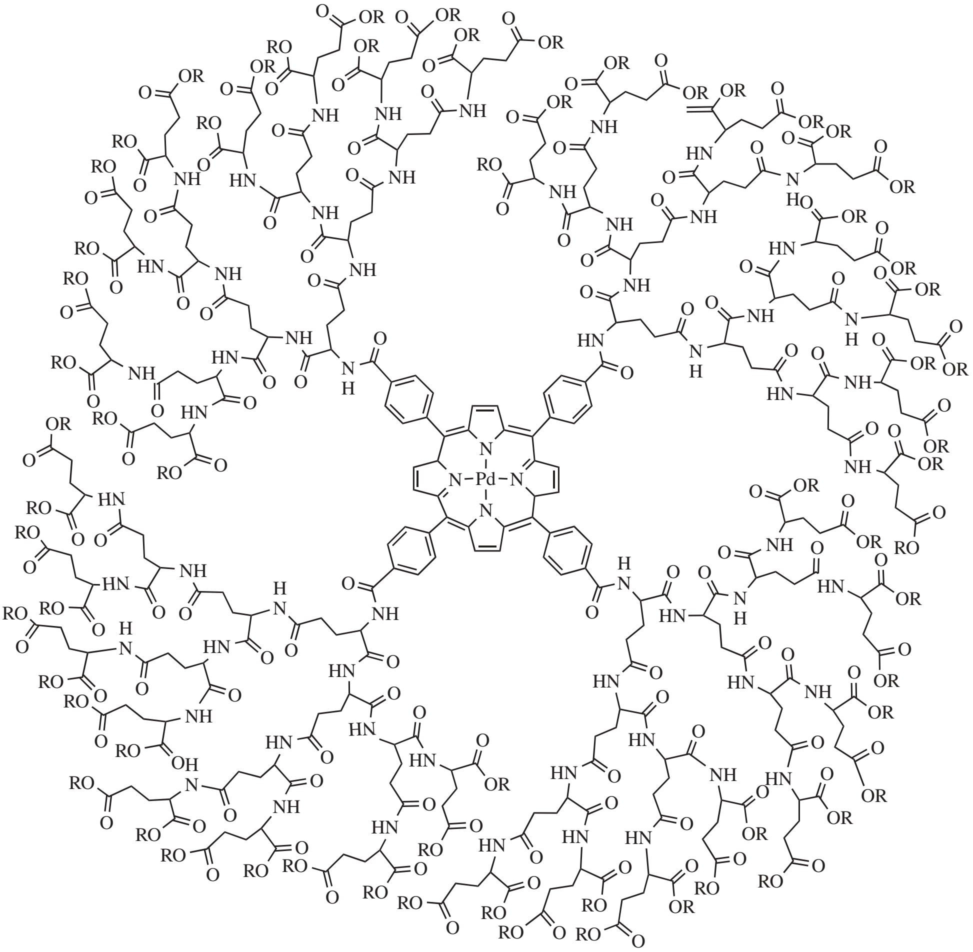
The equilibria between monomer, exciplex, and excimer can be displaced by changing temperature (in fact, exciplex or excimer emission can be used to measure temperature) and solvent polarity (20). When an exciplex is based on the presence of amines, it will be destroyed by addition of an acid (19).

For the sake of space, our illustration will be limited to a few examples of luminescent dendrimers, namely (a) dendrimers with a luminescent core; (b) dendrimers with luminescent units in the periphery; (c) dendrimers whose luminescence is governed by energy transfer processes; (d) luminescent dendrimers hosting luminescent guests. Luminescent dendrimers exclusively made of transition metal complexes have already been reviewed (6) and will not be discussed in this article.

3. Dendrimers with a Luminescent Core

Luminescent metal complexes, particularly porphyrins, have extensively been used as cores to obtain large dendrimers (10). Even when the dendrons do not exhibit relevant light absorption and light emission properties, the luminescent properties of the dendrimer may differ from those of the naked core since the appended dendrons can shield the luminescent excited state of the core from quenching (eqs. 6–8) by dioxygen or other impurities.

An interesting example showing the complexity of such a core shielding effect is represented by Pd porphyrins surrounded by polyglutamic dendrons up to the fourth generation (**1**–**3**) (21). In deaerated solutions these dendrimers show a strong phosphorescence at 692 nm and single exponential decays in the range of 400–600 μs. In the presence of dioxygen a quenching process has been observed. In particular, while in air-equilibrated dimethylformamide (DMF) solutions the quenching rate constants are independent of the size and hydrophobicity of the dendrimer periphery, in air-equilibrated water solutions an increase in the dendrimer size causes a large decrease in the quenching rate constant. This peculiar behavior can be easily rationalized taking into account that in dipolar aprotic media, such as DMF, dendritic branches terminated by either carboxylic (1) or ester groups (**2**,**3**) are neutral and adopt a rather unfolded conformation, so that dioxygen access is not hindered. On the other hand, in water solutions, hydrophobic interactions lead the dendritic shell to shrink around the core. Therefore, upon increasing dendrimer generation, the Pd porphyrin is encapsulated by a more densely packed cage, partly preventing dioxygen quenching. The same family of polyglutamic dendrimers (up to the third generation) containing carboxylate groups at the periphery and a free-base porphyrin, instead of the Pd porphyrin, core shows strong changes of the absorption and emission properties of the porphyrin core upon protonation in water solution (22). The pK value corresponding to the first protonation gradually shifts towards alkaline pH values upon increasing generation. Indeed, a growing stabilization of the central positive charge is brought about by the increasing negative charge on the dendrimer periphery. Therefore, an electrostatic core shielding effect is active as long as dendritic branches are deprotonated. These dendrimers may find useful applications as pH sensors in biological systems because of (a) a pK value close to 7 for the first protonation, (b) unlimited water solubility, (c) high emission quantum yield, and (d) impermeability through biological membranes. A recent study (23) compares the shielding ability toward dioxygen quenching of the phosphorescent Pd porphyrin core present in dendrimer 1 by three different types of dendrons, namely, Fréchet poly(aryl ether)s, Newkome poly(ether amide)s, and polyglutamates. The changes of the dioxygen quenching constants are rather insignificant in DMF and tetrahydrofuran (THF) upon changing both the dendron type and the generation. However, in water solution the Fréchet dendrons are the most efficient in core shielding. In particular, a strong decline in quenching rate has been observed upon increasing the generation: A 24 times decrease takes place between generation 0 and 2, while addition of the next dendritic layer does not bring about any significant change.



(**1**) R = H
(**2**) R = Et
(**3**) R = Bz

4. Dendrimers with Luminescent Units in the Periphery

The dendrimers of the poly(propylene amine) family do not exhibit any absorption band in the visible and near-uv spectral region and do not show any luminescence. These dendrimers, however, can be easily functionalized in the periphery with luminescent units. Compound **4** represents the fourth generation dendrimer 4D of the nD family where the generation number n goes from 1 to 5 (24). These dendrimers contain 2^{n+1} (ie, 64 for 5D) dansyl functions in the periphery and $(2^{n+1}-2)$ (ie, 62 for 5D) tertiary amine units in the interior. The dansyl units behave independently from one another so that the dendrimers display light absorption and emission properties characteristic of dansyl, ie, intense absorption bands in the near-uv spectral region $\lambda_{max} = 252$ and 339 nm; $\partial_{max} \approx 12{,}000$ and 3,900 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). Poly(propylene amine) dendrimers functionalized with dansyl units at the periphery like **4** can coordinate metal ions by the aliphatic amine units contained in the interior of the dendrimer and can thus be used as fluorescent sensors for metal ions (25). 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 in dendrimer **34**, the fluorescence of all the 32 dansyl units is quenched, with a 32 times increase in sensitivity with respect to a normal dansyl sensor. This concept is illustrated in Figure 4.

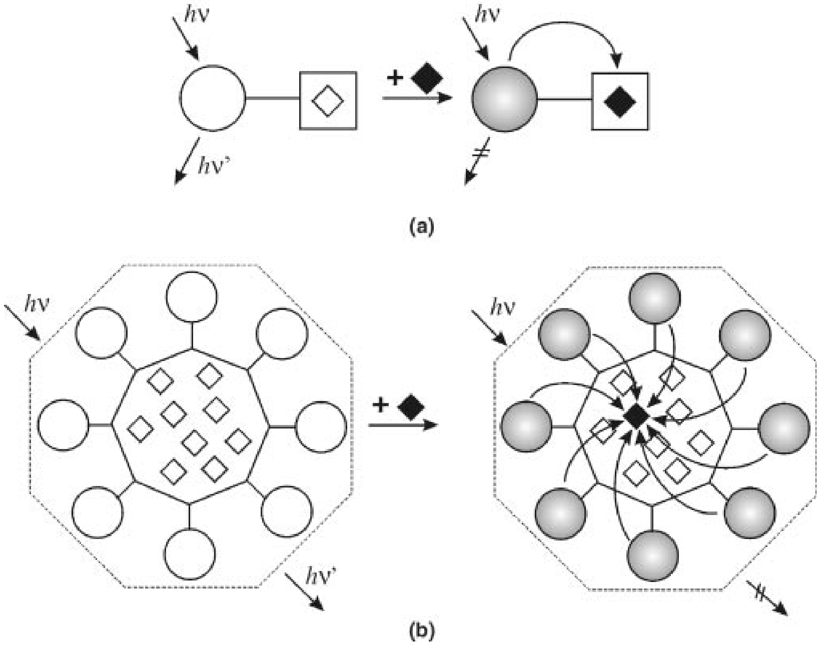
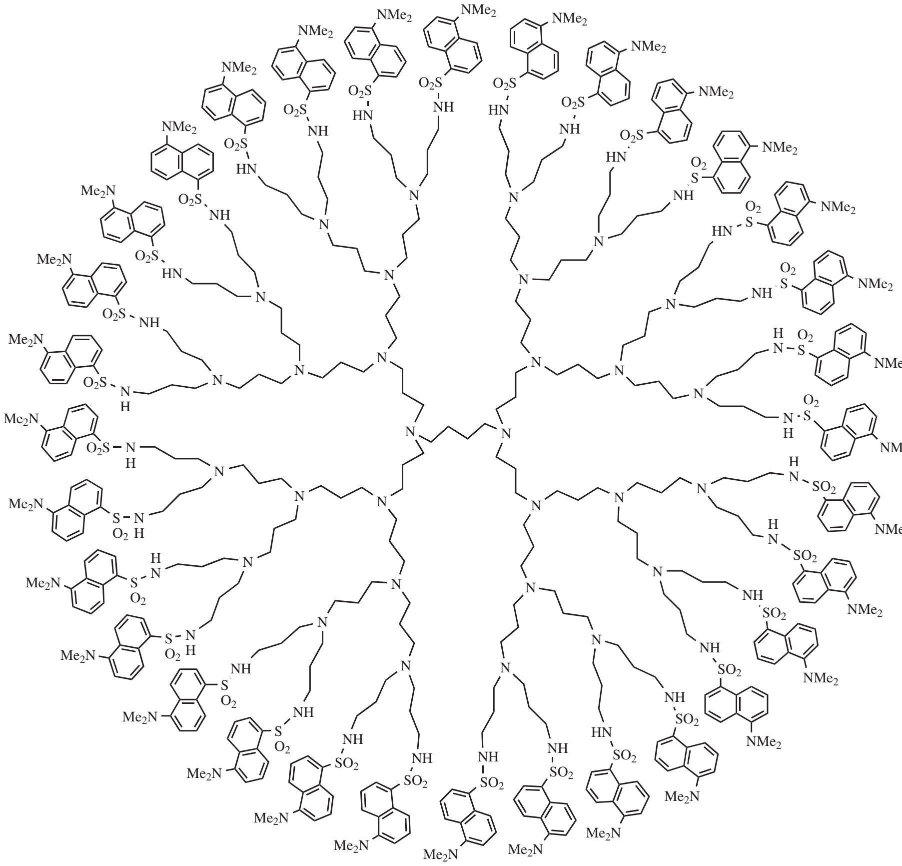


Fig. 4. Schematic representation of (**a**) a conventional fluorescent sensor and (**b**) a fluorescent sensor with signal amplification. Open rhombi indicate coordination sites and black rhombi indicate metal ions. The curved arrows represent quenching processes. In the case of a dendrimer, the absorbed photon excites a single fluorophore component, that is quenched by the metal ion, regardless of its position.



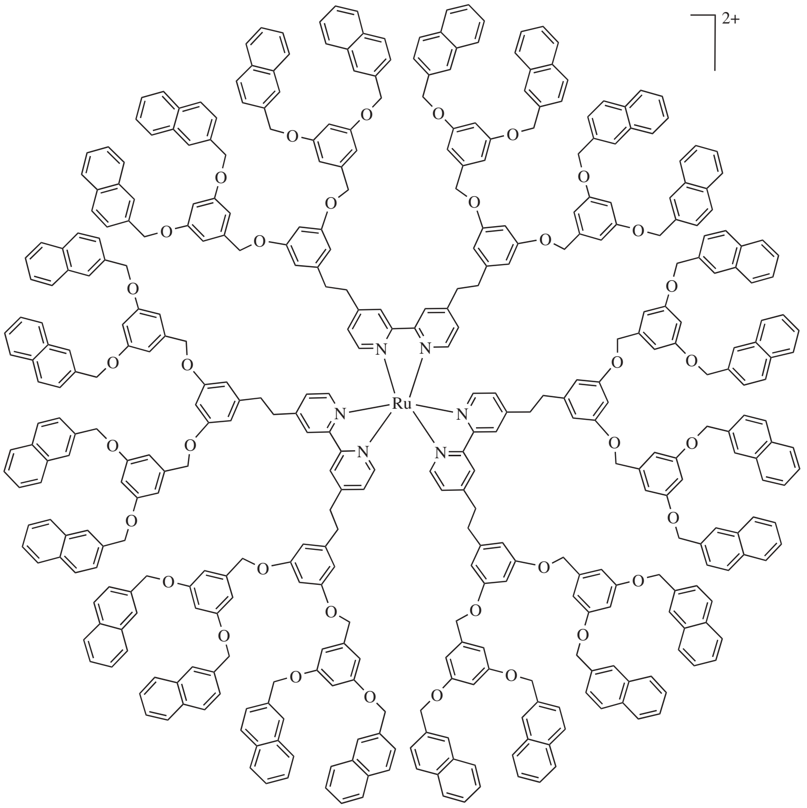
(**4**)

5. Dendrimers whose Luminescence is Governed by Energy-Transfer Processes

In dendrimer $\mathbf{5}^{2+}$ the 2,2′-bipyridine (bpy) ligands of the $[\mathrm{Ru(bpy)_3}]^{2+}$-type core carry branches containing the 1,3-dimethoxybenzene- and 2-naphthyl-type units (26).

In the $[\mathrm{Ru(bpy)_3}]^{2+}$ metal complex, the lowest excited state is a metal-to-ligand charge-transfer triplet, ^{3}MLCT, which, because of the presence of the heavy metal atom, is populated with unitary efficiency from the upper lying excited state. The ^{3}MLCT excited state emits a relatively strong phosphorescence ($\lambda_{\mathrm{max}} = 610$ nm). In fact, all the three types of chromophoric groups present in the dendrimer, namely, $[\mathrm{Ru(bpy)_3}]^{2+}$, dimethoxybenzene, and naphthalene, are potentially luminescent species. In the dendrimer, however, the fluorescence of the dimethoxybenzene- and naphthyl-type units is almost completely quenched in acetonitrile solution, with concomitant sensitization of the $[\mathrm{Ru(bpy)_3}]^{2+}$ phosphorescence. Quantitative measurements have shown that upon excitation of the strongly absorbing naphthyl units, the quantum yield of the sensitized $[\mathrm{Ru(bpy)_3}]^{2+}$ phosphorescence is practically equal to the phosphorescence quantum yield obtained upon direct excitation of the metal complex core. These results show that the efficiency of energy transfer (eq. 12) from the excited naphthyl units to the luminescent $[Ru(bpy)_3]^{2+}$ core is close to its maximum value (100%). In other words, the peripheral chromophoric groups can harvest light that ultimately is used to cause the luminescence of the core as efficiently as the light directly absorbed by the core. Since the naphthyl chromophoric units have high molar absorption coefficients in the uv region, the dendrimer has a much larger opportunity to absorb light and, as a consequence, to exhibit luminescence compared with what would happen if the luminescence could only be obtained by direct excitation of the core. This effect, which plays an important role in the natural photosynthetic process (27), is usually called "antenna effect". It should be stressed that the antenna effect is based on the increase in light absorption capacity (coupled with the occurrence of energy transfer), not with an increase in the luminescence quantum yield, a point that is not always clearly stated in the literature (28–30). For example, the use of terms like "amplified emission" could be misleading since the emission is amplified for the only reason that there is an amplified absorption (followed by energy transfer). Needless to say that any comparison between direct and sensitized emission intensities is meaningless if the number of adsorbed photons is different.

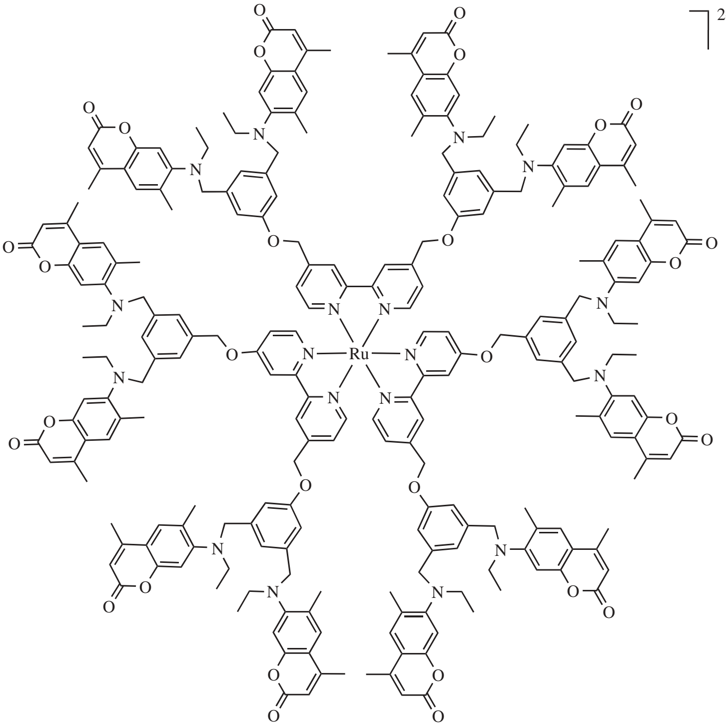
Note also that in aerated solution the phosphorescence intensity of the dendritic core of $\mathbf{5}^{2+}$ is more than twice intense as that of the $[Ru(bpy)_3]^{2+}$ parent compound because the dendrimer branches protect the Ru–bpy based core from dioxygen quenching (31).



($\mathbf{5}^{2+}$)

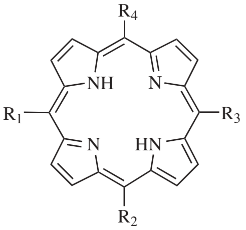
The $[Ru(bpy)_3]^{2+}$ core has more recently been used to construct first generation dendrimers $\mathbf{6}^{2+}$ containing coumarin-450 chromophoric groups.

In acetonitrile solution, energy transfer from the excited coumarin units to the $[Ru(bpy)_3]^{2+}$ core, whose excited state is again protected from dioxygen quenching, takes place with almost unitary efficiency, so that the absorbance of near-uv light leads again to the characteristic orange emission of the core (32).



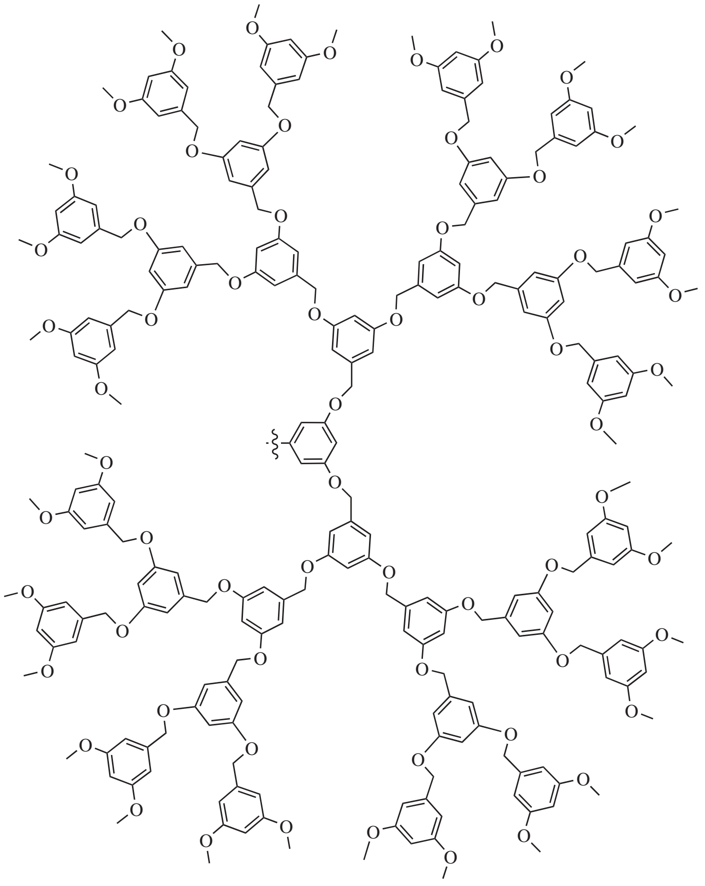
($\mathbf{6}^{2+}$)

Much attention has been focused on light harvesting antenna dendrimers constituted by a porphyrin core and properly chosen dendrons. Morphology-dependent antenna properties have been reported (33) for a series of dendrimers consisting of a free-base porphyrin core bearing different numbers (from 1 to 4) of poly(benzylether) dendrons at the meso position of the central porphyrin (**7–11**). In dichloromethane solutions, excitation of the chromophoric groups of the dendrons causes singlet–singlet energy-transfer processes that lead to the excitation of the porphyrin core. It was found that the dendrimer **11**, which has a spherical morphology, exhibits a much higher energy-transfer efficiency ($\eta_{et} = 0.8$) than the partially substituted species **7–10** ($\eta_{et} < 0.32$). Fluorescence polarization studies on **11** showed that the excitation energy migrates very efficiently over the dendrons within the excited-state lifetime, so that the four dendrons can be viewed as a single, large chromophore surrounding the energy trap. Temperature-dependent effects suggested that increased flexibility and conformational freedom were responsible for the decreased energy-transfer efficiency on decreasing number of dendrons. Only the highly crowded dendrimer 11 retained a constant level of energy transfer, even at high temperatures. It was also postulated that cooperativity between dendrons, which decreases with increasing conformational mobility, is necessary for efficient energy transfer (33). Such a behavior would mimic that of natural photosynthetic systems, where energy migration within “wheels” of chromophoric groups results in an efficient energy transfer to the reaction center (27). More recently, the morphology effect was investigated by using much larger porphyrin dendrimers consisting of a free-base porphyrin core with appended up to four dendrons, each containing seven zinc porphyrin units (compound **12**) (34).

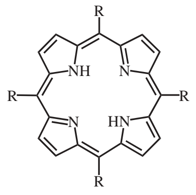


	R_1	R_2	R_3	R_4
(**7**)	L	tolyl	tolyl	tolyl
(**8**)	L	tolyl	L	tolyl
(**9**)	L	L	tolyl	tolyl
(**10**)	L	L	L	tolyl
(**11**)	L	L	L	L

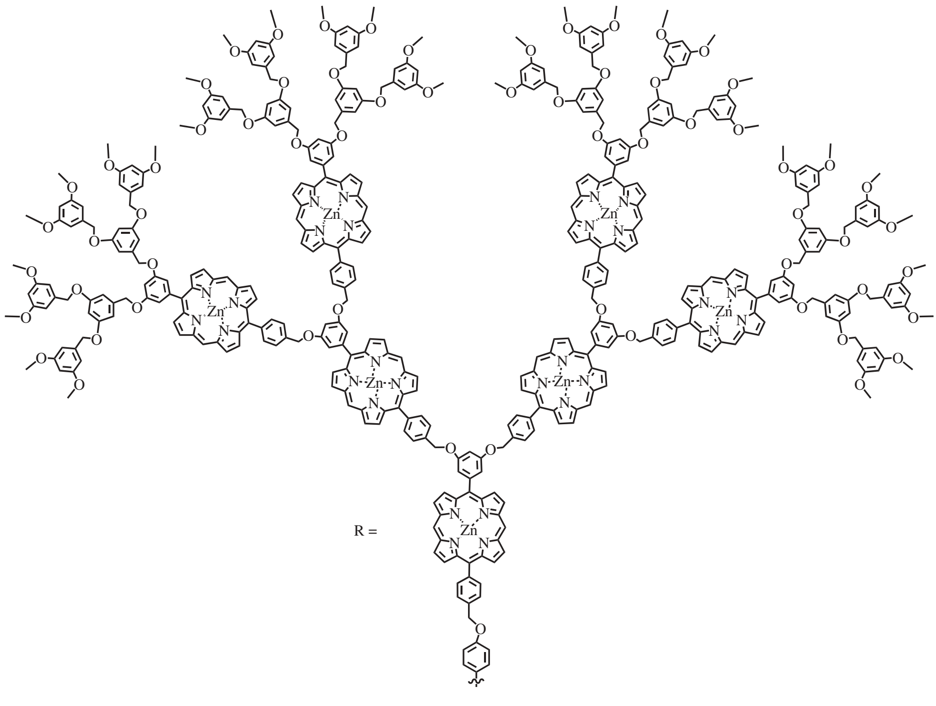
L =



The presence of poly(benzylether) dendritic wedges at the periphery makes such dendrimers soluble in common organic solvents. The experiments performed in THF showed that in the star-shaped dendrimer **12**, energy transfer from the excited singlet states of dendrons to the focal core takes place with rate constant 1.0×10^9 s^{-1} and 71% efficiency, whereas in the conically shaped dendrimer containing a single dendron substituent the energy-transfer rate constant was 10 times smaller and the efficiency was 19%. This result shows that morphology has indeed a noticeable effect on the energy-transfer rate. Excitation of **12** at 544 nm with polarized light resulted in a highly depolarized fluorescence from the Zn–porphyrin units (fluorescence anisotropy factor 0.03, to be compared with 0.19 of a monomeric reference compound), indicating an efficient energy migration among the Zn porphyrin units before energy transfer to the free base core. In the case of the conically shaped compound containing a single dendron substituent, the fluorescence anisotropy factor was much higher (0.10). These results suggest a cooperation of the four dendrons of **12** in facilitating the energy migration among the Zn porphyrin units. Clearly, **12**, which incorporates 28 light absorbing Zn porphyrin units into a dendritic scaffold having an energy accepting core, mimics several aspects of the natural light harvesting. A fast

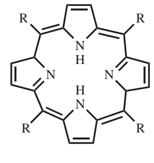


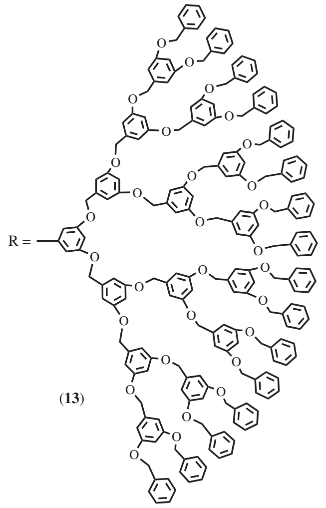
(**12**)



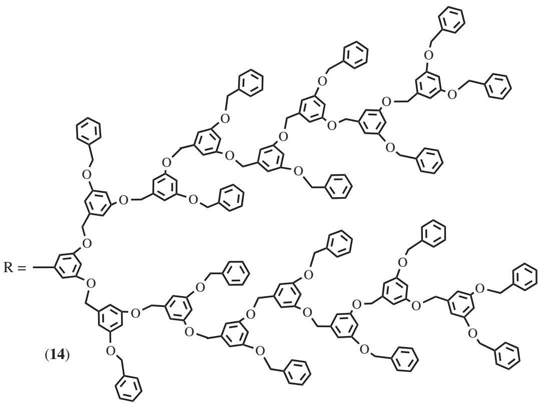
dynamics of energy migration has also been observed for multiporphyrin functionalized poly(propylene amine) dendrimers (35).

The influence of the macromolecular architecture on the energy-transfer efficiency is well exemplified by the comparison between a dendrimer containing a free-base porphyrin core and Fréchet-type poly(benzyl ethers) dendrons (structure **13** represents the fourth generation) and isomeric monodisperse macromolecules containing the same porphyrins core and benzyl ethers units arranged in a linear fashion, as represented by structures **14** and **15** (36).





(13)



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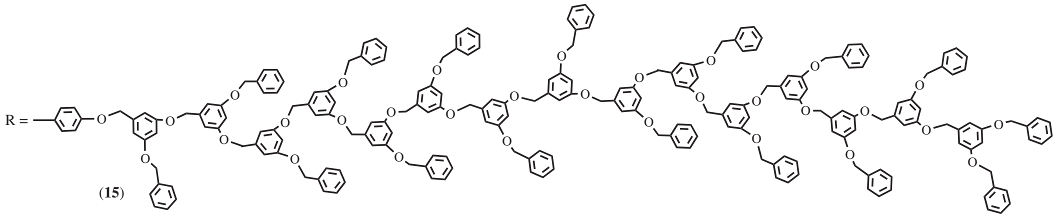
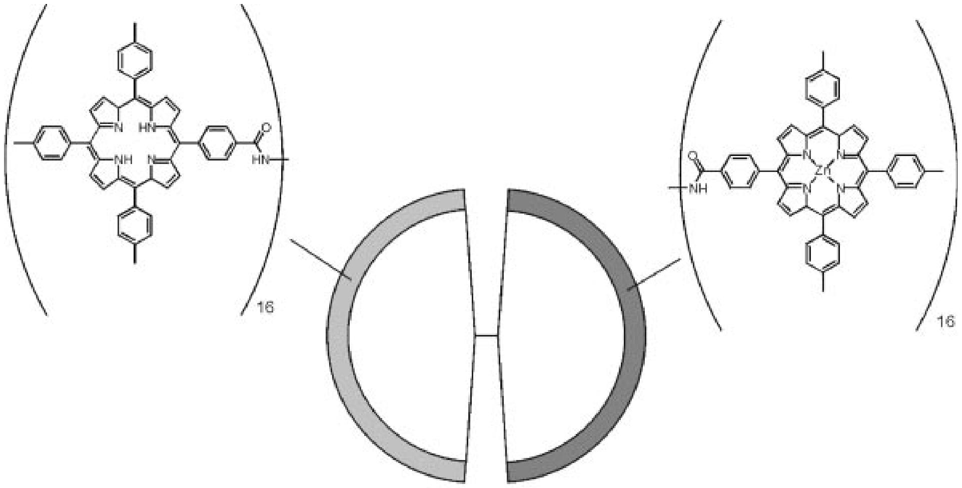


(15)

The absorption spectra in THF solutions show no electronic interactions between the dimethoxybenzene units in the ground state and only minor bathochromic shifts of the porphyrins Soret bands, more pronounced in the dendrimer series and attributed to increasing core encapsulation. On the other hand, the emission spectra evidenced an energy-transfer migration from the dimethoxybenzene units of the backbone to the porphyrins core. However, in the case of the dendrimers the efficiency of this process is much higher, even for the fifth generation, than for their macromolecular analogues. This effect is likely due to the relatively short distances between the donor units and the acceptor core in the dendrimer architecture.

A peculiar structure is represented by a poly(L-lysine) dendrimer **16**, which carries 16 free base porphyrins in one hemisphere and 16 Zn–porphyrins in the other one (37).

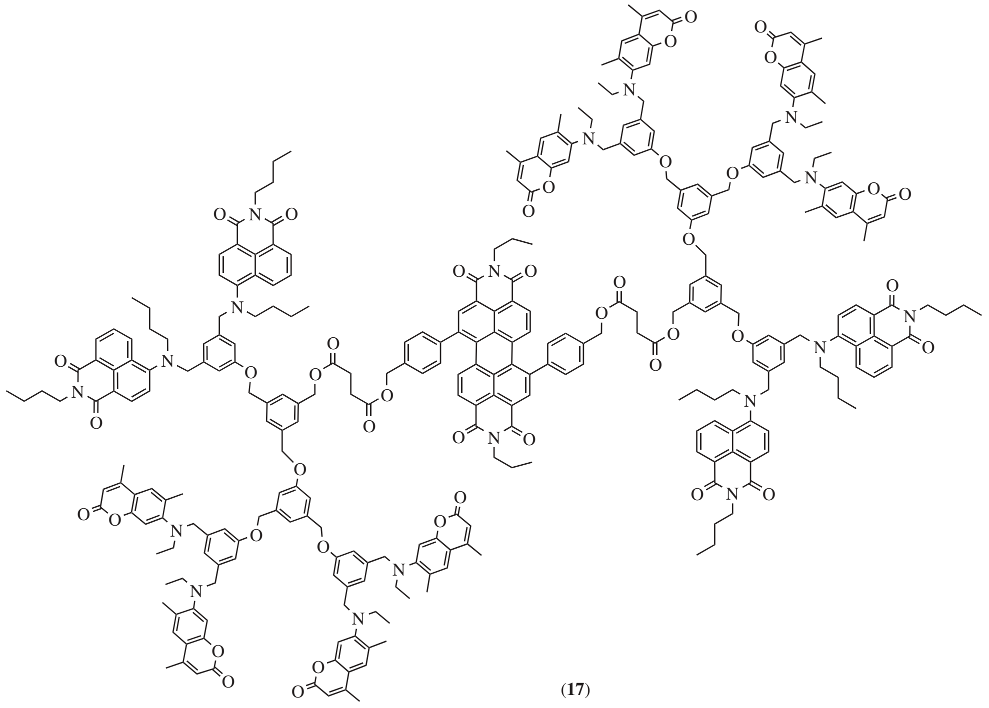


(16)

In such a dendrimer, intradendrimer energy transfer from the Zn–porphyrin units of one hemisphere to the free base ones of the other hemisphere has been observed to occur with 43% efficiency in DMF solution. When the 32 free base and zinc porphyrins were placed in a scramble fashion, the efficiency of energy transfer was estimated to be 83% (38). Very efficient (98%) energy transfer from Zn to free base porphyrins was also observed in a rigid, snowflake-shaped structure where three Zn–porphyrin units alternate with three free-base porphyrin units (39).

Development in synthetic procedure has recently brought to the construction of dendrimers containing, in selected region of their architecture, three different types of properly chosen chromophoric units, among which energy-transfer processes can take place.

For example, dendrimer **17** presents eight coumarin-2 dyes, four fluorol 7GA units and a perylene core (29). In this architecture there is a cascade of energy from coumarin groups to fluorol units to the perylene core following the electronic excited-states energy order. Upon excitation of the high energy coumarin moieties, an efficient energy transfer to the perylene core is observed with an overall efficiency >95%. In particular, a cascade energy transfer from coumarin to fluorol and subsequently to the perylene core is favoured compared to the direct energy transfer from coumarin to perylene because of poor spectral overlap between coumarin emission and perylene absorption.



(17)

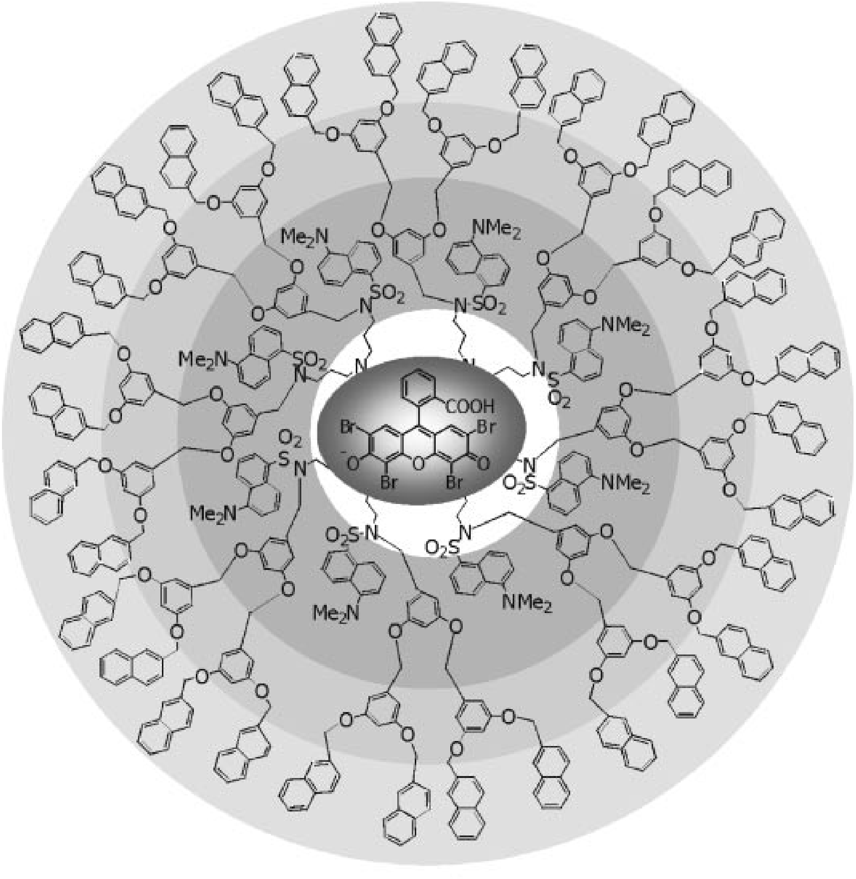
Other interesting examples of dendrimer with a cascade energy transfer among three different types of chromophoric units are (1) a shape-persistent dendrimer with a polyphenylene backbone, a terrylene tetracarboxdiimide core, perylene and naphthalene dicarboxmonoimide chromophores in the scaffold and at the periphery, respectively (30); and (2) the dendrimer containing dansyl, dimethoxybenzene, and naphthalene units discussed below (40); and (3) a dendrimer made of Os(II)- and Ru(II)-based chromophores and pyrene units (41).

6. Luminescent Dendrimers Hosting Luminescent Guests

An important property of dendrimers is the presence of internal cavities where ions or neutral molecules can be hosted (42).

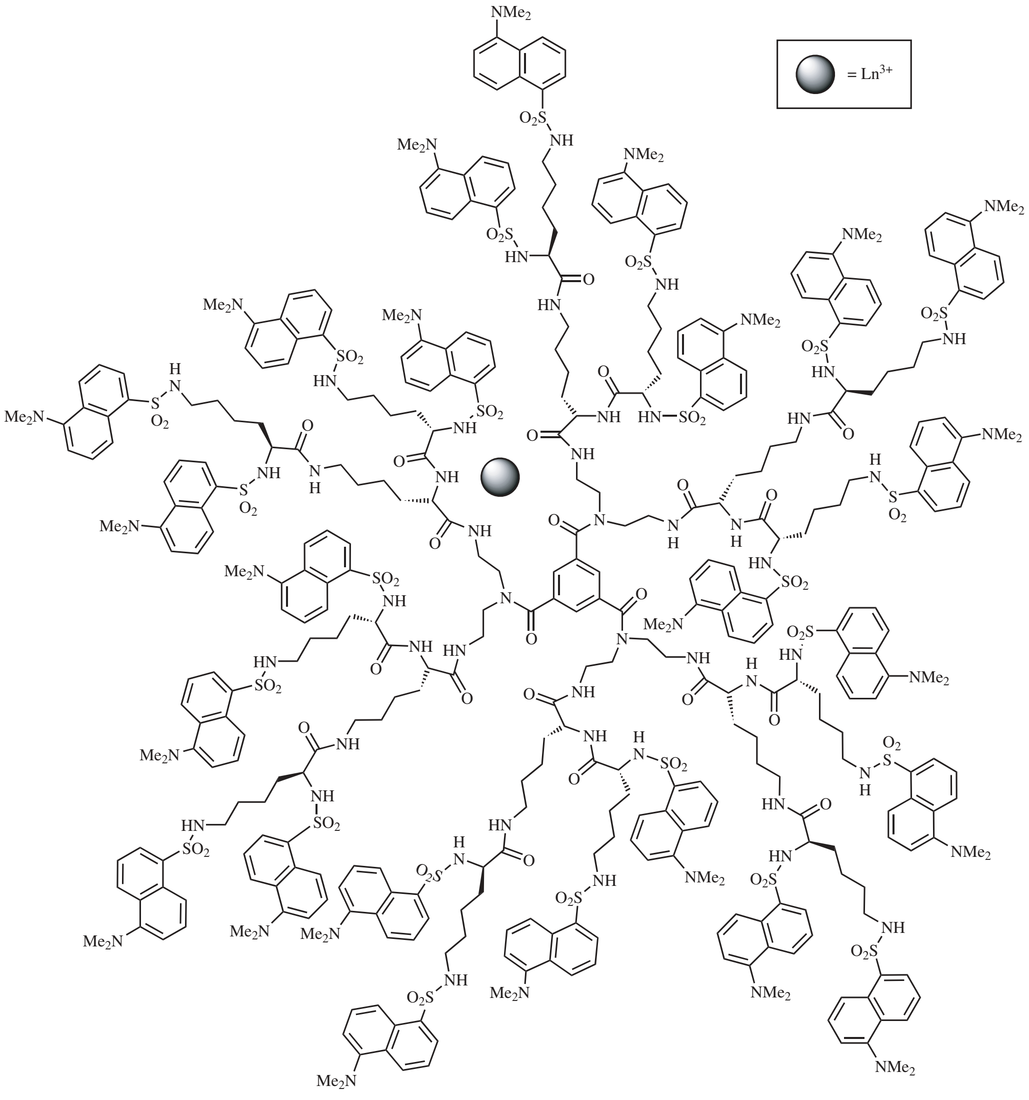
Energy transfer from the numerous chromophoric units of a suitable dendrimer to a luminescent guest may be exploited to construct systems for changing the color of the incident light and for light harvesting. An advantage shown by such host–guest systems compared with dendrimers with a luminescent core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

Dendrimer **18**, consists of a hexaamine core surrounded by 8 dansyl-, 24 dimethoxybenzene-, and 32 naphthalene-type units (40). In dichloromethane solution, **18** 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% efficiency. When the dendrimer hosts a molecule of the fluorescent eosin dye (**18** ⊃ eosin), the dansyl fluorescence, in its turn, is quenched 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 (ie, within dendrimer) and intermolecular (ie, dendrimer host → eosin guest) energy-transfer processes occur very efficiently by a Förster-type mechanism because of the strong overlap between the emission and absorption spectra of the relevant donor–acceptor units.



(18) ⊃ eosin

Dendrimer **19** is quite interesting since it contains in the interior 18 amide groups, which are known to strongly coordinate lanthanide ions, and in the periphery 24 chromophoric dansyl units, which, as mentioned above, show intense absorption bands in the near-uv spectral region and an intense fluorescence band in the visible region (43). Addition of lanthanide ions to acetonitrile/dichloromethane (5:1 v/v) solutions of dendrimer **19** causes a quenching of the fluorescence of the dansyl units. At low metal ion concentration, each dendrimer can host no more than one metal ion and, when the encapsulated metal ion is Nd^{3+} or Eu^{3+}, the fluorescence of all the 24 dansyl units is quenched with unitary efficiency. Quenching by Nd^{3+} occurs by Förster-type energy transfer from the fluorescent excited state of the dansyl units to a manifold of Nd^{3+} energy levels and is accompanied by the sensitized emission in the near-ir region ($\lambda_{max} = 1064$ nm) of the lanthanide ion. Quenching by Eu^{3+} is not accompanied by any sensitized emission since it occurs by electron transfer owing to the low reduction potential of Eu^{3+}. In rigid matrix at 77 K, however, where electron transfer is disfavoured, the quenching of the dansyl unit by Eu^{3+} takes place by energy transfer, as demonstrated by the presence of the sensitized Eu^{3+} emission (43b).



(19)

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