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Fluorescent guests hosted in fluorescent dendrimers

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Abstract—We have investigated the formation of host–guest complexes between dendrimers of the poly(propylene amine) family functionalized with dansyl units at the periphery (hosts) with dye molecules (guests). Each dendrimer **nD**, where the generation number *n* goes from 1 to 5, comprises 2^{n+1} (i.e. 64 for **5D**) dansyl functions in the periphery and $2^{n+1}-2$ (i.e. 62 for **5D**) tertiary amine units in the interior. The most thoroughly investigated systems were those with eosin as a guest. The results obtained show that: (i) the **nD** dendrimers dissolved in dichloromethane solution extract eosin from aqueous solutions; (ii) the maximum number of eosin molecules hosted in the dendrimers increases with increasing dendrimer generation, up to a maximum of 12 for the **5D** dendrimer; (iii) the fluorescence of the peripheral dansyl units of the dendrimers is completely quenched via energy transfer by the hosted eosin molecules; (iv) the fluorescence of the hosted eosin molecules is partially quenched; (v) the eosin molecules can occupy two different sites (or two families of substantially different sites) in the interior of the dendritic structure; (vi) excitation of eosin hosted in the dendrimers causes sensitization of the dioxygen emission via eosin triplet excited state. The behavior of fluorescein and rose bengal is qualitatively similar to that of eosin, whereas naphthofluorescein is not extracted. The maximum number of dye molecules extracted by the **4D** dendrimer is 25 for rose bengal and ca. 1 for fluorescein, showing that the formation of host–guest species is related to the electronic properties rather than to the size of the dye molecules.

1. Introduction

Highly branched molecules having tree-like structures are called dendrimers (from the Greek word δενδρον). Dendrimers are currently attracting the interest of a great number of scientists because of their unusual chemical and physical properties and the wide range of potential applications in such different fields as medicine, biology, chemistry, physics, and engineering. Research in this field began in 1978 with a report on the synthesis of cascade molecules,[1] but exploded only in the early 90s.[2] Like trees, dendrimers usually exhibit aesthetically pleasant structures, but the interest in a specific dendrimer does not depend, of course, on its beauty; rather, it depends on the 'fruit' (i.e. the specific function) that the dendrimer is able to produce.[3]

Dendrimers are complex, but well defined chemical compounds, with a high degree of order and the possibility to contain selected chemical units in predetermined sites of their structure. In the last few years it has been shown that dendrimers containing photoactive components[2o,4–12] are particularly interesting since: (i) luminescence signals offer a handle to better understand the dendritic structures and superstructures, (ii) cooperation among the photoactive components can allow the dendrimer to perform useful functions such as light harvesting, and (iii) changes in the photophysical properties can be exploited for sensing purposes with signal amplification.

Another important property of dendrimers is the presence of dynamic internal cavities where ions or neutral molecules can be hosted.[13–20] In a previous paper[8f] we have investigated the photophysical properties of poly(propylene amine) dendrimers (usually called POPAM or PPI) decorated at the periphery with dansyl units. Each dendrimer **nD** of this family (Fig. 1), where *n* indicates the generation number which goes from 1 to 5, comprises 2^{n+1} dansyl functions in the periphery and $2^{n+1}-2$ tertiary amine units in the branches. We have studied the effects caused on the fluorescence properties by protonation of the interior amine units and of the peripheral dansyl moieties,[8f] and we have shown that the unprotonated dendrimers can host metal ions (e.g. Co^{2+}) capable of quenching the dansyl fluorescence.[8g,h] In a preliminary communication[20] we have recently reported that eosin molecules can be hosted in the interior of the **4D** dendrimer, and that light excitation of such host–guest species results in fluorescence quenching and sensitization processes. In this paper we present a full account of the results obtained in a systematic investigation of the host–guest complexes

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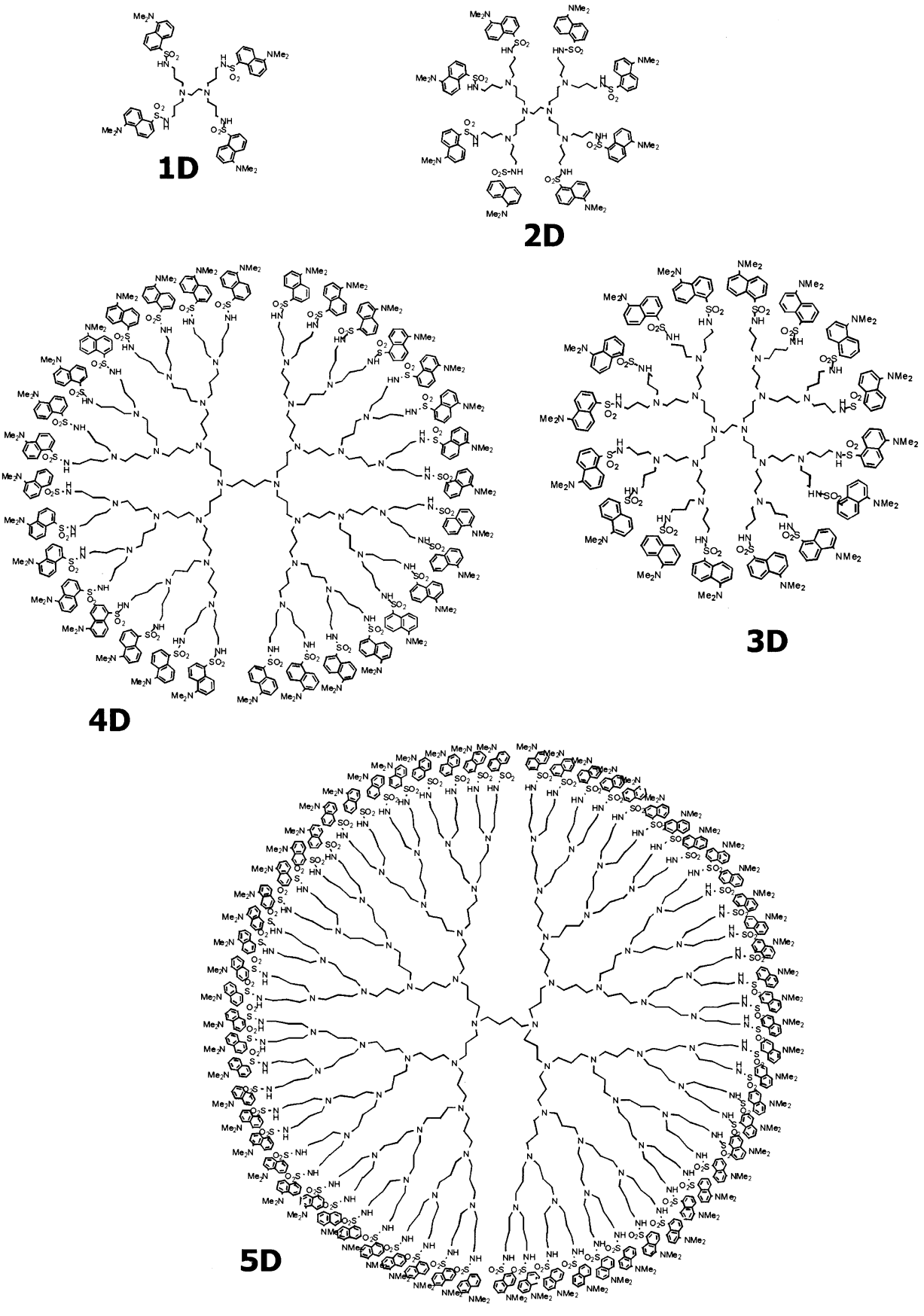

Figure 1. Structure formulas of the dendrimers (hosts).

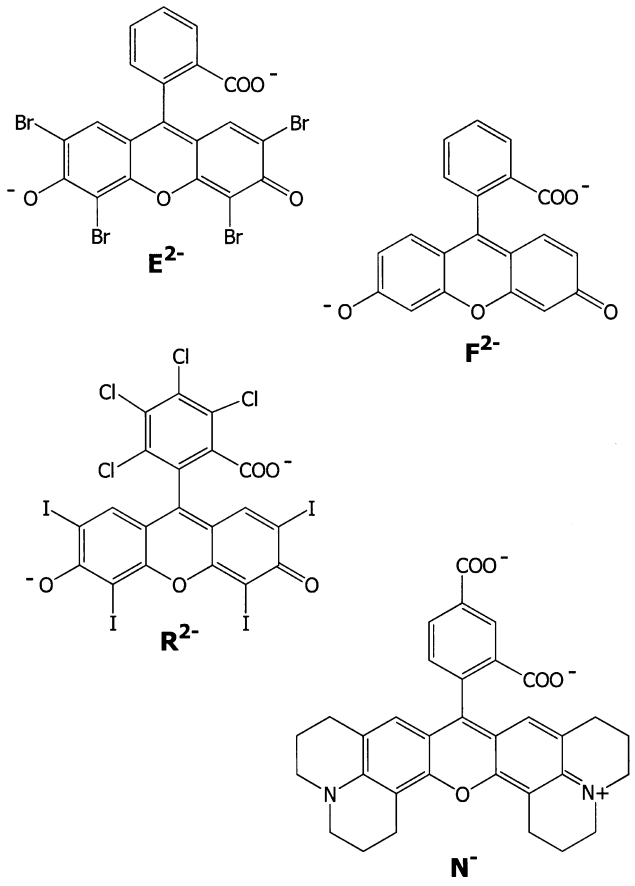

Figure 2. Structure formulas of the dyes (guests).

formed by the whole family of the **nD** dendrimers with eosin Y ($\mathbf{E}^{2-}$) and by the **4D** dendrimer with other dyes like fluorescein ($\mathbf{F}^{2-}$), 5-(and-6)-carboxynaphthofluorescein (hereafter called naphthofluorescein, $\mathbf{N}^{-}$) and rose bengal ($\mathbf{R}^{2-}$), Fig. 2. The use of dendrimers as extracting agents is a topic of current interest.[13–20] Particularly worth mentioning in this field are the investigations on the extraction of dyes performed by Meijer et al.[14]

2. Results and discussion

2.1. Properties of the nD dendrimers

The **nD** dendrimers (Fig. 1) are soluble in dichloromethane, but not in water. In dichloromethane solution all the **nD** dendrimers exhibit, within the experimental error, substantially the same spectroscopic properties,[8f,g] namely intense absorption bands in the near UV spectral region (λ_{max}=252 and 339 nm; $\epsilon_{max}\sim$12000 and 3900 $M^{-1}\,cm^{-1}$, respectively, for each dansyl unit) and a strong fluorescence band in the visible region (for **4D**: λ_{max}=500 nm; Φ_{em}=0.46, τ=16 ns). These results show that there is no appreciable interaction among the dansyl groups and that the tertiary amine units of the dendrimer branches do not cause any quenching effect on the dansyl fluorescent excited state. The absorption and emission spectra of a 2.7×10^{-6} M dichloromethane solution of **5D** are shown in Fig. 3.

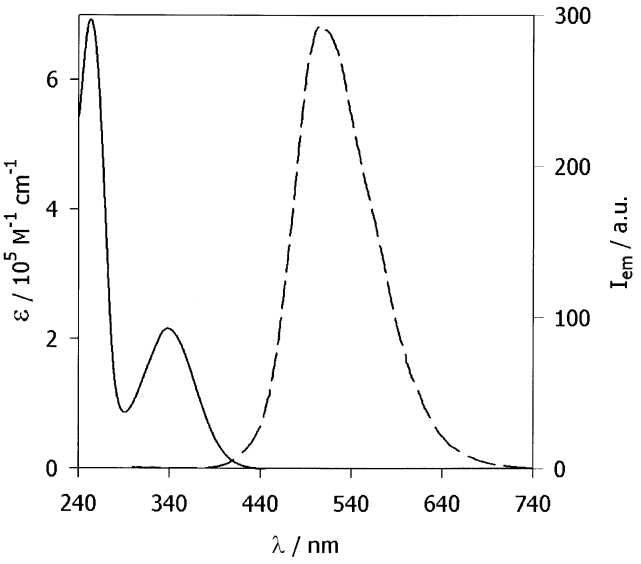

Figure 3. Absorption and emission spectra of dendrimer **5D** in dichloromethane solution.

2.2. Properties of the dyes

The dyes used as potential guests (Fig. 2) are fluorescent indicators. Eosin Y (as a disodium salt) is soluble in water, but not in dichloromethane. The absorption and emission spectra of a 1.0×10^{-5} M solution of eosin Y in water at pH 7.0 are shown in Fig. 4. The intense absorption band in the visible region, responsible for the red color, has λ_{max}=515 nm and ε_{max}=69800 $M^{-1}\,cm^{-1}$. Fluorescence occurs with λ_{max}=546 nm, Φ_{em}=0.20, τ=1.3 ns. These spectroscopic and photophysical properties concern the dianion species $\mathbf{E}^{2-}$ shown in Fig. 2. The absorption and fluorescence properties do not change in going to basic solution. In acid solution, however, both the absorption band responsible for the red color (Fig. 5, curve a) and the fluorescence band with λ_{max}=546 nm disappear because of the formation of a leuco form and successive precipitation around pH 2.

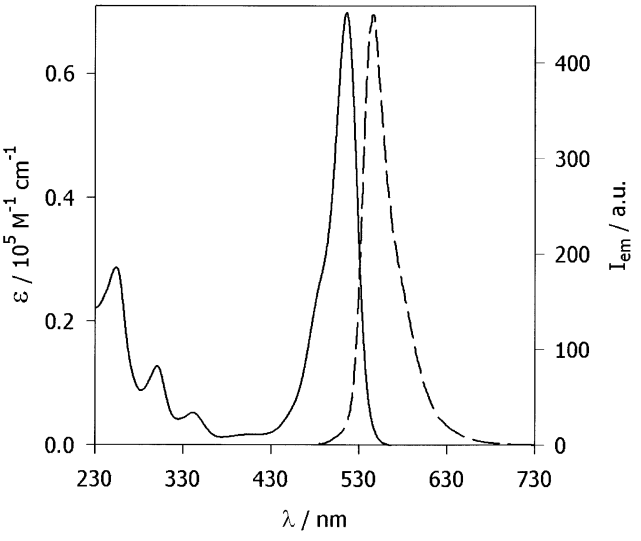

Figure 4. Absorption and emission spectra of eosin Y in H_2O at pH 7.0 ($\mathbf{E}^{2-}$ form, Fig. 2).

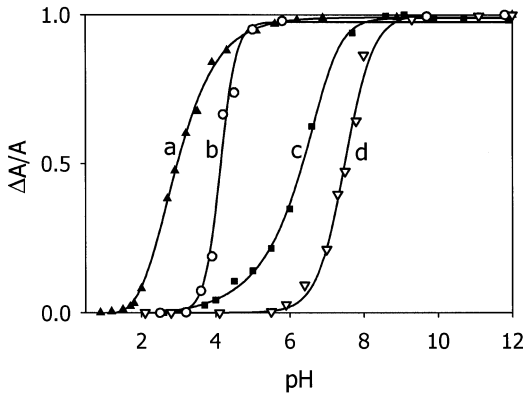

Figure 5. Normalized absorbance changes for eosin (curve a, 515 nm), rose bengal (curve b, 540 nm), fluorescein (curve c, 490 nm), naphtofluorescein (curve d, 600 nm) as a function of pH.

The other dyes substantially behave as eosin (Fig. 5). Their conjugated forms (Fig. 2), which have been used in this work, exhibit a strong absorption band in the 450–650 nm region. Naphthofluorescein shows also moderately intense absorption bands in the 350–450 nm region. All the dyes exhibit a strong fluorescence band in the visible spectral region. As in the case of eosin, the disodium salts of fluorescein and rose bengal and the triethylammonium salt of naphthofluorescein are soluble in water, but not in dichloromethane. For rose bengal in aqueous solution, the fluorescence lifetime is 0.2 ns and the fluorescence quantum yield ca. 0.01. When the disodium salt of rose bengal is dissolved in dichloromethane solution by using [18]crown6, a noticeable increase of both lifetime and quantum yield are observed (2.5 ns and 0.24, respectively).

2.3. Extraction experiments with eosin

As shown in Fig. 5, in aqueous solution above pH 5 eosin is present as the dianionic species $\mathbf{E}^{2-}$ (Fig. 2). When a strongly colored aqueous solutions of the disodium salt of eosin at pH>5 is shaken with dichloromethane, no change in color of the two phases is observed and spectrophotometric measurements show that no extraction of eosin takes place. Eosin, however, can be solubilized at low concentrations in dichloromethane containing 0.01 M [18]crown6, which is capable of hosting Na^+ ions.[21] The absorption (λ_{max}=529 nm, ε_{max}=61000 M^{-1} cm^{-1}) and emission (λ_{max}=555 nm, Φ_{em}=0.65, τ=3.8 ns) properties of eosin in dichloromethane are somewhat different from those exhibited in water by the $\mathbf{E}^{2-}$ species.

When an aqueous solution of $\mathbf{E}^{2-}$ is shaken with a dichloromethane solution containing one of the **nD** dendrimers, except in the case of **1D**, the color of the aqueous solution fades and the dichloromethane solution becomes colored, showing that eosin molecules leave the aqueous phase and are hosted by the dendrimers. The amount of eosin transferred from the aqueous to the dichloromethane solution was measured from the absorbance changes at the wavelength of the maximum of the eosin absorption spectrum in water (λ_{max}=515 nm). The absorption spectrum of the eosin molecules hosted in the dendrimers (λ_{max}=530 nm, ε_{max}=60000 M^{-1} cm^{-1}) is similar to that of the $\mathbf{E}^{2-}$ solubilized in dichloromethane with the aid of [18]crown6 (vide supra), but the intensity of the shoulder around 500 nm increases with increasing dendrimer generation (Fig. 6).

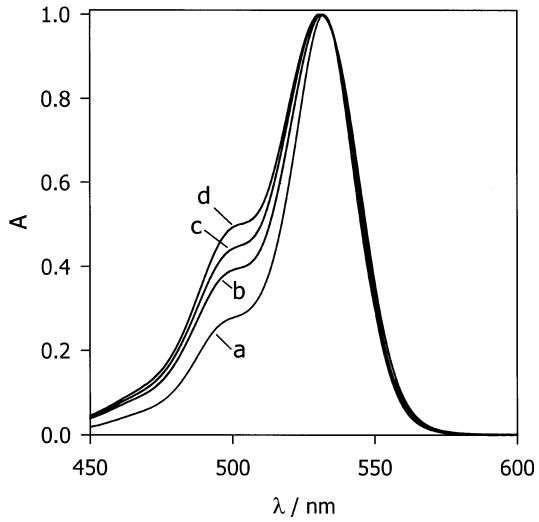

Figure 6. Absorption spectra of eosin solubilized in dichlorometane solution by the presence of [18]crown6 (a), and hosted in the dendrimers **3D** (b), **4D** (c), and **5D** (d).

We have quantitatively investigated the extraction process changing the pH of the solution from 5 to 12, the dendrimer generation from 1 to 5, and the concentrations of dendrimer and eosin. First of all, we have found that the extraction is influenced by the pH of the aqueous phase. Fig. 7 shows the case of a system containing equal volumes of 3.5×10^{-5} M eosin as a disodium salt in the aqueous solution at pH 7.0 and 5.4×10^{-6} M **4D** in the dichloromethane solution. The amount of eosin extracted, as measured by the eosin absorbance of the two phases, decreases in going from pH 5 to higher pH values and becomes negligible at pH 12. This result suggests that eosin is not extracted as a disodium salt. In order to verify such a hypothesis, we have measured the concentration of Na^+ ions in an aqueous phase containing 1.0×10^{-5} M eosin disodium salt before and after complete eosin extraction by a 2.8×10^{-6} M dichloromethane solution of the **4D** dendrimer. We have found that the concentration of Na^+ ions in the aqueous phase

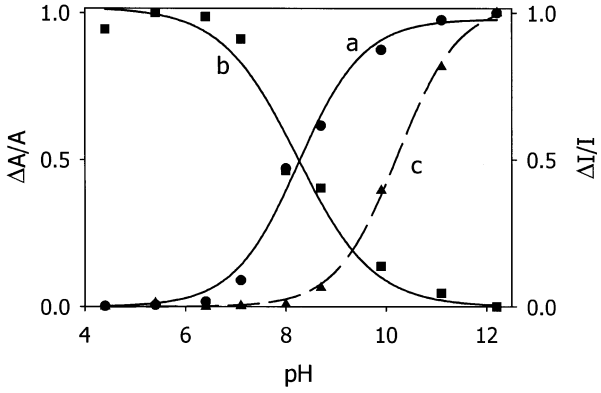

Figure 7. Extraction of the $\mathbf{E}^{2-}$ form of eosin for an aqueous solution 3.5×10^{-5} M by a 5.4×10^{-6} M dichloromethane solution of dendrimer **4D** as a function of pH: (a) absorbance of the aqueous solution at 515 nm; (b) absorbance of the dichloromethane solution at 530 nm; (c) intensity of the fluorescence emission (λ_{exc} 370 nm) of the dansyl dendrimer moieties at 450 nm.

before and after the extraction was the same, confirming that eosin extraction is not accompanied by sodium ions extraction. We have also established that the peripheral dansyl groups are not involved in the extraction process since no extraction can be observed when a previously studied[8i] polylysin dendrimer decorated at the periphery with 24 dansyl groups was used. Finally, we have found that extraction of eosin from a non-buffered aqueous solution at pH ca. 6 causes an increase of pH up to ca. 8. All these results lead us to believe that eosin is extracted from water as its diacid form, $\mathbf{E}H_2$, and is hosted in the interior of the dendrimers presumably because of formation of O–H···N or $O^-\cdots HN^+$ interactions with the tertiary amine units. In any case, the absorption and emission spectra exhibited by the hosted eosin molecules are those of the conjugated $\mathbf{E}^{2-}$ form.

The study was then continued working with aqueous solutions of the disodium eosin salt at pH 7.0 (phosphate buffer), where eosin is present only as its $\mathbf{E}^{2-}$ form (Fig. 5) and extraction is efficient (Fig. 7). We have found that the amount of eosin that can be extracted increases with increasing dendrimer concentration and dendrimer generation. The maximum number of eosin molecules that can be extracted per dendrimer (Fig. 8) increases with increasing dendrimer size. More specifically, the increase is roughly exponential as a function of the generation number n, and roughly linear as a function of the number of tertiary amine units $(2^{n+1}-2)$ contained in the dendrimer.

Some more detailed experiments showed that with dendrimer **2D**, **3D**, and **4D** extraction of eosin does not affect the absorption spectrum of the dansyl units (Fig. 3), whereas the dansyl fluorescence is quenched (vide infra). Practically no quenching was observed in the case of **1D**, confirming that it does not extract eosin. With dendrimer **5D**, extraction of eosin from a pH 7.0 buffered solution is accompanied by a concomitant decrease of the dansyl absorption bands in the entire spectral range; since practically no dansyl absorption appears in the aqueous phase, we believe that a partial precipitation of the dendrimer takes place. Because of this complication, most of the quantitative experiments concerning the fluorescence properties were performed by using the **4D** dendrimer.

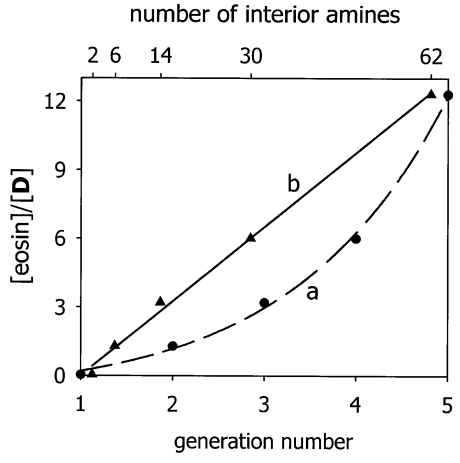

Figure 8. Maximum number of eosin molecules that can be extracted per dendrimer as a function of the dendrimer generation number (a) and the number of aliphatic amines contained in the dendrimer (b).

In order to establish the reversibility of eosin complexation with the **4D** dendrimer, we have first prepared, by the above mentioned extraction technique at pH 7.0, a dichloromethane solution containing 5.4×10^{-6} M **4D** and 6 eosin molecules per dendrimer. When such a dichloromethane solution was shaken with an equal volume of water buffered at pH 7.0, no significant change was observed in the absorption spectra of the two phases; however, when an aqueous solution at pH 12 was used, eosin molecules were back extracted from the dichloromethane to the aqueous phase.

2.4. Fluorescence properties of the dendrimers–eosin systems

Fluorescent investigations have been performed on several host–guest systems, but a systematic study was carried out only on the fully characterized (vide supra) **4D**/eosin system.

As shown in Figs. 3 and 4, the absorption spectra of the dendrimer host and of the eosin guest are quite different. Therefore, fully selective excitation of the eosin guest can be performed by 530 nm light, whereas 370 nm light can be used for selective excitation (when necessary, with minor corrections) of the dansyl units of the dendrimer. This favorable circumstance allowed us to investigate the effect of the

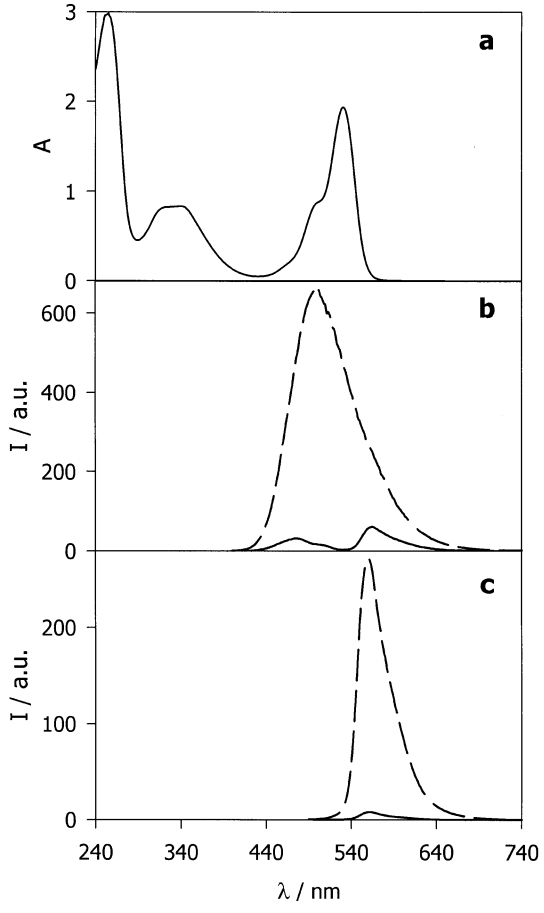

Figure 9. Absorption (a) and emission spectra upon excitation at 370 nm (b) and 530 nm (c) of a 5.4×10^{-6} M **4D** solution in dichloromethane containing six eosin molecules per dendrimer. For comparison purposes, the emission spectra of the free dendrimer (b, dashed line) and 'free' eosin (c, dashed line) are also reported.

eosin guest on the fluorescence properties of the dendrimer hosts and viceversa in great detail.

Fig. 9(a) shows the absorption spectrum of a 5.4×10^{-6} M **4D** solution in dichloromethane containing six eosin molecules per dendrimer. Upon excitation at 370 nm the emission spectrum is much different from those exhibited by the dendrimer in the absence of eosin (Fig. 9(b)). One can notice a strong decrease of the dansyl emission and the appearance of a weak emission due to eosin. Excitation at 530 nm shows that the intensity of the eosin band is much weaker than that shown by eosin solubilized in dichloromethane with the aid of [18]crown6 (Fig. 9(c)).

A more detailed investigation has shown that the dansyl fluorescence intensity decreases with increasing eosin concentration (Fig. 10), but the fluorescence decay remains monoexponential with lifetime 16 ns. The initial slope of the quenching plot of Fig. 10 shows that a single eosin guest is sufficient to quench completely the fluorescence of any excited dansyl unit of the host dendrimer. The curvature of the plot at higher eosin concentrations can be related to the fact that each dendrimer has several sites for hosting eosin molecules, so that even at relatively high [eosin]/[**4D**] ratios there are still some 'empty' dendrimers (Poisson distribution), in agreement with the unquenched fluorescence lifetime. The small amount of residual dansyl fluorescence (<8%) at the maximum eosin loading could be due to experimental errors due to overlapping between dansyl and eosin emission and/or to the presence of a small number of free dansyl-type 'impurities'. An efficient quenching of the dansyl fluorescence by eosin via energy transfer was expected in view of the strong overlap between the emission spectrum of the dansyl units (Fig. 3) and the absorption spectrum of the eosin molecules (Fig. 4). Comparison between fluorescence intensities obtained upon excitation at 370 nm (dansyl absorption) and 530 nm (eosin absorption) showed that the quenching of the dansyl fluorescence by eosin occurs via a singlet–singlet energy transfer process with unitary efficiency. Assuming that the unquenched fluorescence intensity of the dansyl unit is <2% of the original intensity and considering that the lifetime of the dansyl fluorescence is 16 ns, the rate constant for the quenching process must be higher than 3×10^{9} s^{-1}. This value is consistent with the value 4.4×10^{9} s^{-1} estimated from the equation for the dipole–dipole (Förster) mechanism[22]

$$k_{en} = \frac{8.8\times10^{-25}K^2\Phi}{r^6n^4\tau}J$$

where Φ and τ are the fluorescence quantum yield and lifetime, respectively, of the donor (dansyl), J (6.8×10^{-14} cm^3 M^{-1}) is the integral overlap between the fluorescence spectrum of the donor and the absorption spectrum of the acceptor (eosin), K^2 is a geometric factor (taken as 2/3), and n is the refractive index of the solvent (1.424), assuming a dansyl–eosin distance r of 2 nm, which is the estimated dendrimer radius. In a complex system like the present one, in which an acceptor is surrounded by donors placed at variable distances, a distribution of rate constants would of course be observed by femto- and pico-second studies.[10e]

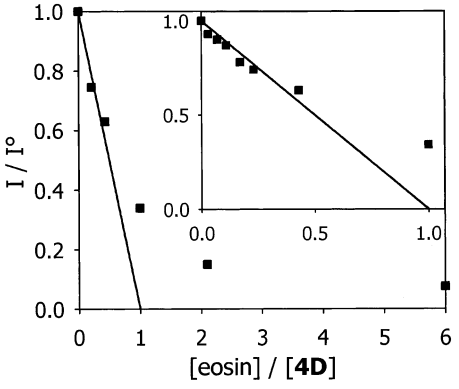

Figure 10. Quenching of the dansyl fluorescence for dendrimer **4D** on increasing of extracted eosin concentration. The dendrimer concentration was 5.4×10^{-6} M. The initial slope is 1 (inset), indicating that a single eosin guest is sufficient to completely quench the fluorescence of any excited dansyl unit of the dendritic host.

Examination of the fluorescence properties of the eosin molecules encapsulated into the dendrimers has revealed other interesting features of this fluorescent host/fluorescent guest system. In order to have a better reference for the eosin molecules hosted by the dendrimer in dichloromethane solution, we solubilized eosin in this solvent by using the [18]crown6. As we have seen earlier, under such conditions eosin shows a fluorescence band with λ_{max}=555 nm, τ=3.8 ns, and Φ_{em}=0.65 (note that the previously reported[20] value, 0.45, was wrong). When eosin is hosted in the dendrimer dissolved in dichloromethane, the fluorescence quantum yield is more than 10 times lower and the fluorescence decay is no longer monoexponential. A two-exponential decay is observed even at very low eosin concentration ([eosin]/[**4D**]=0.21), i.e. under conditions in which there is at most one eosin molecule per dendrimer. This means that eosin molecules can occupy two different sites (or two families of substantially different sites) in the interior of the dendrimer, which give rise to different radiative and/or nonradiative rate constants for the decay of the fluorescent excited state of the eosin guest. At least two different sites for inclusion of a spin probe in a differently functionalized POPAM dendrimer has previously been noted by Meijer et al.[14b] The data obtained with higher eosin concentrations confirm that there are two substantially different sites where eosin can be hosted even when six eosin molecules are contained in the same dendrimer (Table 1). The changes in the fluorescence quantum yield and lifetimes with changing the [eosin]/[**4D**] ratio show that the properties of the hosting sites (and, therefore, their influence on the decay processes of the eosin excited state) are somewhat affected by the number of hosted molecules, as expected for a flexible structure like that of the poly(propylene amine) dendrimers.

Table 1. Emission properties of eosin in dichloromethane solution upon excitation at 530 nm

	[Eosin]/[**D**]	Φ_{em}	τ_1 (ns)	τ_2 (ns)
Crown	–	0.65	3.8	–
2D	1.3	0.078	2.5	0.9
3D	3.2	0.046	2.8	0.8
4D	6.0	0.020	2.2	0.6
5D	12.3	0.013	3.0	0.8

Quenching of the eosin fluorescence occurs also in dendrimers **2D**, **3D**, and **5D**. The residual eosin fluorescence intensity decreases in going from the second to the fifth generation as shown in Table 1.

The reason why the eosin fluorescence is quenched when eosin is encapsulated into the dendrimer is difficult to establish. An energy transfer processes can certainly be ruled out because none of the dendrimer components has excited states at lower energy than the fluorescent excited state of eosin. Quenching by electron transfer involving the dendrimer amine functions cannot be excluded, considering that quenching of eosin triplet by amines has been observed.[23] In a low polarity environment, however, electron-transfer processes are disfavored. A more plausible quenching mechanism can perhaps be related to radiationless transitions involving the hydrogen bonds which are likely responsible for the formation of the host–guest species.

We have found that excitation of eosin (both free and hosted into the dendrimer) causes the characteristic dioxygen emission with maximum at 1260 nm. Since the intensity and lifetime of eosin fluorescence are not affected by dioxygen, the sensitization of the dioxygen emission has to occur via eosin triplet excited state. Interestingly, the intensity of the sensitized dioxygen emission is four times stronger upon excitation of free eosin compared with eosin hosted inside the dendrimer. This result can be due to a shorter lifetime of triplet eosin in the dendrimer and/or protection[8a,d,e] of the guest by the dendrimer branches towards dioxygen.

2.5. Experiments on other dyes

Extraction experiments have been performed, using the **4D** dendrimer as a potential host, on aqueous solutions at pH 7.0 containing fluorescein, rose bengal and naphthofluorescein. We have found that fluorescein and rose bengal can be extracted, but naphthofluorescein cannot. Since at pH 7.0 naphthofluorescein is not fully deprotonated (Fig. 5, curved), we have also tried to extract this dye at pH 9.0, without success. The average maximum number of dye molecules extracted at pH 7.0 was 1.4 for fluorescein and 25 for rose bengal. These results, together with those reported above concerning eosin (Table 1), show that extraction is somewhat unrelated to the dimension of the dye molecule, but strongly dependent on pH (Fig. 7) and specific chemical properties.

As in the case of eosin, the other extracted dyes quench the dansyl fluorescence and, in their turn, both the fluorescence intensity and lifetime of the dye decrease. In particular, when 25 rose bengal molecules are hosted in the **4D** dendrimer, the dansyl fluorescence intensity is reduced to less than 3% and the quantum yield of rose bengal fluorescence is <0.01. Furthermore, the rose bengal fluorescence show a biexponential decay with lifetimes 1.6 and 0.5 ns, confirming that the dye molecules can occupy two different sites (or two families of substantially different sites) in the interior of the dendrimer.

We have also performed a competition experiment shaking a 2.2×10^{-6} M dichloromethane solution of the **4D** dendrimer with an equal volume of a water solution at pH 7.0 containing 6.0×10^{-5} M eosin and 6.0×10^{-5} M rose bengal. We have found that no eosin and 25 rose bengal molecules were extracted per dendrimer molecule, to be compared with 6 and 25 extracted dye molecules, respectively, for aqueous solution containing either eosin or rose bengal. When eosin and rose bengal were diluted six times, all the rose bengal molecules were extracted (five for each dendrimer, as an average), whereas the number of extracted eosin molecules (2.5) was half that found in the same experimental condition in the absence of rose bengal. These results emphasize that the **4D** dendrimer is a very selective host, a property reminiscent of the behavior of enzymes.[24]

3. Conclusions

An important property of dendrimers is the presence or possibility of dynamic formation of internal cavities where ions or neutral molecules can be hosted. Such a property can potentially be exploited for a variety of purposes, which include catalysis and drug delivery. In order to explore the hosting properties of the dendrimers of the poly(propylene amine) family, we have functionalized such dendrimers (generations 1–5) with fluorescent dansyl units at the periphery and we have then used the resulting fluorescent dendrimers as hosts for fluorescent dye molecules. We have found that the formation of host–guest species is related to the size of the dendrimer and to the electronic properties, rather than to the size of the dye molecules. As many as 12 eosin molecules can be hosted in the **5D** dendrimer and 25 rose bengal molecules in the **4D** dendrimer. The fluorescence properties of the host–guest species are quite different from those of the separated components because of the occurrence of quenching/sensitization processes. The fluorescence of the peripheral dansyl units of the dendrimers is quenched via energy transfer by the hosted eosin molecules, whose fluorescence, in its turn, is partially quenched. Quantitative analysis of the results obtained has shown that a single eosin guest is sufficient to quench completely the fluorescence of any excited dansyl unit in the **4D** host dendrimer, and fluorescence lifetime measurements has allowed us to establish that the dye molecules can occupy two different sites (or two family of substantially different sites) in the interior of the dendritic structure. Competition experiments showed that **4D** selectively extract rose bengal from a water solution containing an excess of both rose bengal and eosin. The results obtained emphasize the strong selectivity of the host–guest interactions in suitably designed dendrimers,[24] an enzyme-like property that can be useful for catalysis and other applications.

Combination of fluorescent dendritic hosts with fluorescent guests gives rise to quenching/sensitization processes that can be exploited for a variety of purposes which include development of chemosensors, construction of light harvesting antennas, and elucidation of the intimate dendritic structure.

4. Experimental

The synthesis and characterization of the **nD** dendrimers (Fig. 1) was previously reported.[8f] The disodium salts of eosin, fluorescein and rose bengal, and the triethylammonium salt of naphthofluorescein (Fig. 2) were commercial products. In most of the experiments, the aqueous phase was buffered at pH 7.0 by a phosphate buffer. The concentration of Na^+ ions in aqueous solution was measured by atomic absorption spectroscopy. Spectroscopic equipment and techniques have been described elsewhere.[8f] Unless otherwise noted, the experiments were carried out in air equilibrated solutions. Fluorescence lifetimes were measured with a FLUOROLOG Spex FL3/11 spectrofluorometer equipped with a phase-shift Tau 3 unit (10 ps time resolution). Dioxygen emission was measured by a home-modified apparatus based on an Edinburg CD900 spectrofluorimeter, equipped with an Ar ion laser (Spectra Physics model 164-09) for the sample excitation at 514 nm and a liquid nitrogen cooled hyperpure germanium crystal detector. The estimated experimental errors are: ±2 nm on the band maximum, ±5% on the molar absorption coefficient, ±10% on the fluorescence quantum yield, and ±5% on the fluorescence lifetime.

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References

1. Buhleier, E.; Wehner, W.; Vögtle, F. *Synthesis* **1978**, 155.
2. (a) Tomalia, D. A.; Durst, H. D. *Top. Curr. Chem.* **1993**, *165*, 193. (b) Fréchet, J. M. J. *Science* **1994**, *263*, 1710. (c) Ardoin, N.; Astruc, D. *Bull. Soc. Chim. Fr.* **1995**, *132*, 875. (d) Newkome, G. R.; Moorefield, C.; Vögtle, F. *Dendrimers and Dendrons: Concepts, Syntheses, Perspectives*; VCH: Weinheim, 2001. (e) Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681. (f) Venturi, M.; Serroni, S.; Juris, A.; Campagna, S.; Balzani, V. *Top. Curr. Chem.* **1998**, *197*, 193. (g) Majoral, J.-P.; Caminade, A.-M. *Top. Curr. Chem.* **1998**, *197*, 79. (h) Matthews, O. A.; Shipway, A. N.; Stoddart, J. F. *Prog. Polym. Sci.* **1998**, *23*, 10. (i) Smith, D. K.; Diederich, F. *Chem. Eur. J.* **1998**, *4*, 1353. (j) Chow, H.-F.; Mong, T. K.-K.; Nongrum, M. F.; Wan, C.-W. *Tetrahedron* **1998**, *54*, 8543. (k) Fischer, M.; Vögtle, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 884. (l) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665. (m) Newkome, G. R.; He, E.; Moorefield, C. *Chem. Rev.* **1999**, *99*, 1689. (n) Adronov, A.; Fréchet, J. M. J. *Chem. Commun.* **2000**, 1701. (o) Juris, A. *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, 2001; Vol. 3, p 655. (p) Hecht, S.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 75. (q) Gorman, C. B.; Smith, J. C. *Acc. Chem. Res.* **2001**, *34*, 60. (r) Juris, A.; Venturi, M.; Ceroni, P.; Balzani, V.; Campagna, S.; Serroni, S. *Collect. Czech. Chem. Commun.* **2001**, *66*, 1.
3. (a) Schlüter, A. D.; Rabe, J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 864. (b) Tomalia, D. A.; Uppuluri, S.; Swanson, D. R.; Li, J. *Pure Appl. Chem.* **2000**, *72*, 2343.
4. (a) Campagna, S.; Denti, G.; Serroni, S.; Juris, A.; Venturi, M.; Ricevuto, V.; Balzani, V. *Chem. Eur. J.* **1995**, *1*, 211. (b) Serroni, S.; Juris, A.; Venturi, M.; Campagna, S.; Resino, I. R.; Denti, G.; Credi, A.; Balzani, V. *J. Mater. Chem.* **1997**, *7*, 1227. (c) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759. (d) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Accounts Chem. Res.* **1998**, *31*, 26. (e) Balzani, V.; Ceroni, P.; Juris, A.; Venturi, M.; Campagna, S.; Puntoriero, F.; Serroni, S. *Coord. Chem. Rev.* **2001**, 219–221, 545. (Ref. 4e).
5. (a) Shorttreed, M. R.; Swallen, S. F.; Shi, Z. Y.; Tan, W.; Xu, Z.; Devadoss, C.; Moore, J. S.; Kopelman, R. *J. Phys. Chem. B* **1997**, *101*, 6318. (b) Devadoss, C.; Bharathi, P.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1709. (c) Swallen, S. F.; Zhengguo, Z.; Moore, J. S.; Kopelman, R. *J. Phys. Chem. B* **2000**, *104*, 3988.
6. Stewart, G. M.; Fox, M. A. *J. Am. Chem. Soc.* **1996**, *118*, 4354.
7. (a) Junge, D. M.; McGrath, D. V. *Chem. Commun.* **1997**, 857. (b) Junge, D. M.; McGrath, D. V. *J. Am. Chem. Soc.* **1999**, *121*, 4912. (c) Li, S.; McGrath, D. V. *J. Am. Chem. Soc.* **2000**, *122*, 6795.
8. (a) Issberner, J.; Vögtle, F.; De Cola, L.; Balzani, V. *Chem. Eur. J.* **1997**, *3*, 706. (b) Archut, A.; Vögtle, F.; De Cola, L.; Azzellini, G. C.; Balzani, V.; Ramanujam, P. S; Berg, R. H. *Chem. Eur. J.* **1998**, *4*, 699. (c) Archut, A.; Azzellini, G. C.; Balzani, V.; De Cola, L.; Vögtle, F. *J. Am. Chem. Soc.* **1998**, *120*, 12187. (d) Plevoets, M.; Vögtle, F.; De Cola, L.; Balzani, V. *New J. Chem.* **1999**, *23*, 63. (e) Vögtle, F.; Plevoets, M.; Nieger, M.; Azzellini, G. C.; Credi, A.; De Cola, L.; De Marchis, V.; Venturi, M.; Balzani, V. *J. Am. Chem. Soc.* **1999**, *121*, 6290. (f) Vögtle, F.; Gestermann, S.; Kauffmann, C.; Ceroni, P.; Vicinelli, V.; De Cola, L.; Balzani, V. *J. Am. Chem. Soc.* **1999**, *121*, 12161. (g) Vögtle, F.; Gestermann, S.; Kauffmann, C.; Ceroni, P.; Vicinelli, V.; Balzani, V. *J. Am. Chem. Soc.* **2000**, *122*, 10398. (h) Balzani, V.; Ceroni, P.; Gestermann, S.; Kauffmann, C.; Gorka, M.; Vögtle, F. *Chem. Commun.* **2000**, 853. (i) Balzani, V.; Ceroni, P.; Gestermann, C.; Gorka, M.; Kauffmann, C.; Vögtle, F. *J. Chem. Soc., Dalton Trans.* **2000**, 3765. (j) Ceroni, P.; Vicinelli, V.; Maestri, M.; Balzani, V.; Müller, W. M.; Müller, U.; Hahn, U.; Osswald, F.; Vögtle, F. *New J. Chem.* **2001**, *25*, 989.
9. (a) Aida, T.; Jiang, D.-L. *Nature* **1997**, *388*, 454. (b) Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **1998**, *120*, 10895. (c) Sato, T.; Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **1999**, *121*, 10658. (d) Nishioka, T.; Tashiro, K.; Aida, T.; Zheng, J.-Y.; Kinbara, K.; Saigo, K.; Sakamoto, S.; Yamaguchi, K. *Macromolecules* **2000**, *33*, 9182.
10. (a) Pollak, K. W.; Leon, J. W.; Fréchet, J. M. J.; Maskus, M.; Abruna, H. D. *Chem. Mater.* **1998**, *10*, 30. (b) Gilat, S. L.; Andronov, A.; Fréchet, J. M. J. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1422. (c) Andronov, A.; Gilat, S. L.; Fréchet, J. M. J.; Ohta, K.; Neuwahl, F. V. R.; Fleming, G. R. *J. Am. Chem. Soc.* **2000**, *122*, 1175. (d) Chrisstoffels, L. A.; Adronov, A.; Fréchet, J. M. J. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 2163. (e) Neuwahl, F. V. R.; Righini, R.; Adronov, A.; Malenfant, P. R. L.; Fréchet, J. M. J. *J. Phys. Chem. B* **2001**, *105*, 1307.
11. (a) Vinogradov, S. A.; Lo, L.-W.; Wilson, D. F. *Chem. Eur. J.* **1999**, *5*, 1338. (b) Cardona, M.; Alvarez, J.; Kaifer, A. E.; McCarley, T. D.; Pandey, S.; Baker, G. A.; Bonzagni, N. J.;

Bright, F. V. *J. Am. Chem. Soc.* **2000**, *122*, 6139. (c) Lammi, R. K.; Ambrois, A.; Balasubramanian, T.; Wagner, R. W.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 7579. (d) Ng, A. C. H.; Li, X.-Y.; Ng, D. K. P. *Macromolecules* **1999**, *32*, 5292. (e) Gong, L.-Z.; Hu, Q.; Pu, L. *J. Org. Chem.* **2001**, *66*, 2358.

12. (a) Gensh, T.; Hofkens, J.; Heirmann, A.; Tsuda, K.; Verheijen, W.; Vosch, T.; Christ, T.; Basché, T.; Müllen, K.; De Schryver, F. C. *Angew. Chem., Int. Ed.* **1999**, *38*, 3752. (b) Tsuda, K.; Dol, G. C.; Gensch, T.; Hofkens, J.; Latterini, L.; Weener, J. W.; Meijer, E. W.; De Schryver, F. C. *J. Am. Chem. Soc.* **2000**, *122*, 3445. (c) De Belder, G.; Schweitzer, G.; Jordens, S.; Lor, M.; Mitra, S.; Hofkens, J.; De Feyter, S.; Van der Auweraer, M.; Herrmann, A.; Weil, T.; Müllen, K.; De Schryver, F. C. *Chem. Phys. Chem.* **2001**, 49.
13. Newkome, G. R.; Moorfield, C. N.; Baker, G. R.; Saunders, M. J.; Grossman, S. H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1178.
14. (a) Jansen, J. F. G. A.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Science* **1994**, *266*, 1226. (b) Jansen, J. F. G. A.; Meijer, E. W. *J. Am. Chem. Soc.* **1995**, *117*, 4417. (c) Baars, M. W. P. L.; Froehling, P. E.; Meijer, E. W. *Chem. Commun.* **1997**, 1959. (d) Schenning, A. P. H. J.; Peeters, E.; Meijer, E. W. *J. Am. Chem. Soc.* **2000**, *122*, 4489. (e) Baars, M. W. P. L.; Kleppinger, R.; Koch, M. H. J.; Yeu, S.-L. *Angew. Chem., Int. Ed.* **2000**, *39*, 1285. (f) Baars, M. W. P. L.; Meijer, E. W. *Top. Curr. Chem.* **2001**, *210*, 131.
15. (a) Zhao, M.; Sun, L.; Crooks, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 4877. (b) Zhao, M.; Crooks, R. M. *Adv. Mater.* **1999**, *11*, 217. (c) Zhao, M.; Crooks, R. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 364. (d) Chechik, V.; Zhao, M.; Crooks, R. M. *J. Am. Chem. Soc.* **1999**, *121*, 4910. (e) Chechik, V.; Crooks, R. M. *J. Am. Chem. Soc.* **2000**, *122*, 1243. (f) Zhou, L.; Russell, D. H.; Zhao, M.; Crooks, R. M. *Macromolecules* **2001**, *34*, 3567. (g) Crooks, R. M.; Zhao, M.; Sun, L.; Chechik, V.; Yeung, L. K. *Acc. Chem. Res.* **2001**, *34*, 181.
16. (a) Watkins, D. M.; Sayed-Sweet, Y.; Klimash, J. W.; Turro, N. J.; Tomalia, D. A. *Langmuir* **1997**, *13*, 3136. (b) Balogh, L.; Tomalia, D. A. *J. Am. Chem. Soc.* **1998**, *120*, 7355. (c) Kleinman, M. H.; Flory, J. H.; Tomalia, D. A.; Turro, N. J. *J. Phys. Chem. B* **2000**, *104*, 11472. (d) Chen, W.; Tomalia, D. A.; Thomas, J. L. *Macromolecules* **2000**, *33*, 9169.
17. (a) Pistolis, G.; Malliaris, A.; Tsiourvas, D.; Paleos, C. M. *Chem. Eur. J.* **1999**, *5*, 1440. (b) Sideratou, Z.; Tsiourvas, D.; Paleos, C. M. *Langmuir* **2000**, *16*, 1766.
18. Stephan, H.; Spies, H.; Johannsen, B.; Klein, L.; Vögtle, F. *Chem. Commun.* **1999**, 1875.
19. Smith, D. K. *Chem. Commun.* **1999**, 1685.
20. Balzani, V.; Ceroni, P.; Gestermann, S.; Gorka, M.; Kauffmann, C.; Maestri, M.; Vögtle, F. *Chem. Phys. Chem.* **2000**, 224.
21. Gokel, G. W. Monograph in Supramolecular Chemistry. In *Crown Ethers and Cryptands*; Stoddart, J. F., Ed.; Royal Society of Chemistry: Cambridge, 1991.
22. (a) Förster, Th. *Discuss. Faraday Soc.* **1959**, *27*, 7. (b) Barigelletti, F.; Flamigni, L. *Chem. Soc. Rev.* **2000**, *29*, 1.
23. Bartholomew, R. F.; Davidson, R. S. *J. Chem. Soc. (C)* **1971**, 2347.
24. Smith, D. K.; Diederich, F. *Chem. Eur. J.* **1998**, *4*, 1353.