

Poly(Propylene Amine) Dendrimers with Peripheral Dansyl Units: Protonation, Absorption Spectra, Photophysical Properties, Intradendrimer Quenching, and Sensitization Processes

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Abstract: We report the preparation, absorption spectra, and photophysical properties (fluorescence spectrum, quantum yield, and lifetime) of five dendrimers of the poly(propylene amine) family (POPAMs) functionalized with dansyl units at the periphery. Each dendrimer **nD**, where **n** = 1 to 5 is the generation number, 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 branches. In acetonitrile/dichloromethane solution each dansyl unit of the dendrimers exhibits the characteristic properties of a monodansyl model compound. Upon addition of trifluoroacetic or triflic acid, the absorption and emission bands of the dansyl units are gradually replaced by the absorption and emission bands of the protonated dansyl unit. In the case of the dendrimers the titration curves obtained from the changes in emission intensity do not match those obtained from the changes in absorbance. Furthermore, each dendrimer exhibits a different titration curve. The results obtained show that protonation first involves tertiary amine groups of the interior and then the dansyl units of the periphery. In the dendrimers containing both protonated and unprotonated dansyl units, the fluorescence of the protonated units is partly quenched. Corrected excitation spectra have shown that the quenching is due to energy transfer from the excited protonated to the ground-state unprotonated dansyl units, with a consequent amplification of the changes in the fluorescent signals that accompany the protonation/deprotonation of the dansyl units.

Introduction

Dendrimers² are well-defined macromolecules exhibiting a tree-like structure, first derived by the "cascade molecule" approach.³ Dendrimer chemistry is now a rapidly expanding field for both basic and applicative reasons.^{2,4} Such compounds are particularly interesting when they carry photo- and/or electro-active units that manifest specific functions.^{5–10} A recent devel-

opment of dendrimer chemistry concerns the coordination of metal ions in the interior branches^{11,12} or in the exterior units.¹³

Continuing our investigations in the field of photoactive dendrimers,¹⁴ we report here the preparation and properties of poly(propylene amine) dendrimers functionalized with dansyl units at the periphery. Poly(propylene amine) dendrimers are very interesting because of their acid–base properties, which have been investigated in great detail by Koper, et al.¹⁵ The dansyl chromophoric group (5-(dimethylamino)-1-naphthalene-sulfonamido), which shows intense absorption bands in the near UV and a strong fluorescence in the visible region, is extensively used for sensing or labeling purposes.¹⁶

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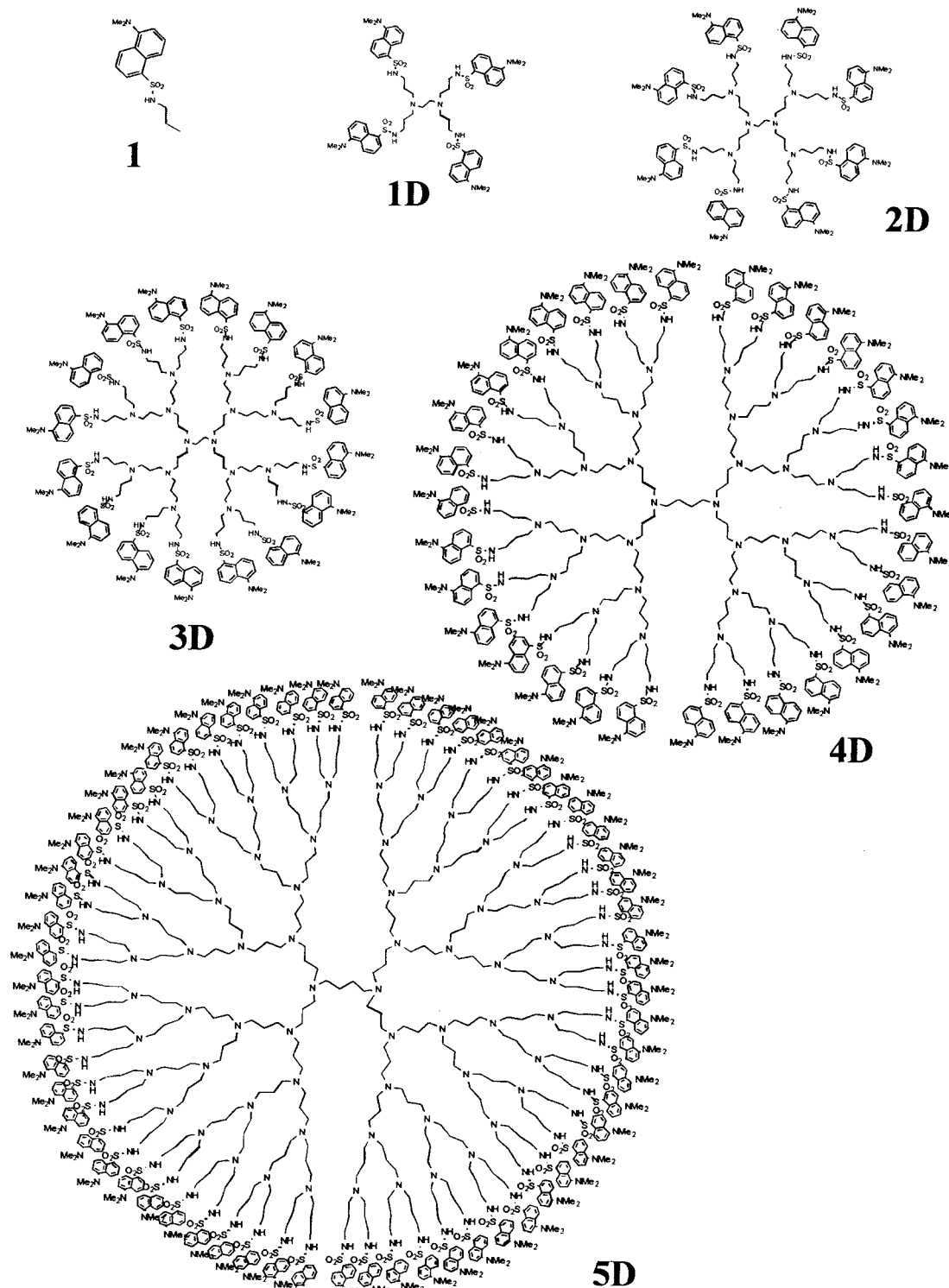


Figure 1. Formulas of the dendrimers and of the reference monodansyl compound **1**.

The formulas of the investigated dendrimers are shown in Figure 1. 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 branches. The spectroscopic and photo-

physical properties of the dendrimers have been studied and compared with those of the monodansyl model compound **1** (Figure 1). The results obtained in acetonitrile/dichloromethane solution upon addition of acid reveal an interesting interplay between the protonation processes of the tertiary amine groups contained in the interior of the dendrimers and the dansyl units appended in the periphery. The occurrence of energy transfer from the fluorescent excited state of the protonated dansyl units to the ground state of the unprotonated ones has also been evidenced.

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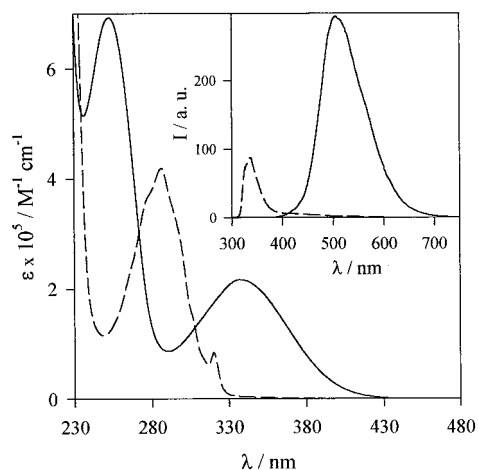


Figure 2. Absorption and (inset) fluorescence spectra of dendrimer **5D** in acetonitrile/dichloromethane solution before (full line) and after (dashed line) addition of an excess of triflic acid. The emission spectra have been obtained by excitation at the isosbestic point at 272 nm.

Experimental Section

The dansylated **nD** dendrimers were obtained from the reaction of poly(propylene amine) dendrimers (BASF-AG for generations 1–3, DSM for generations 4 and 5) with dansyl chloride (Merck). Notice that the dendrimer core is a 1,2-diaminoethane group for generations 1–3 and a 1,4-diaminobutane group for generations 4 and 5. The reactions were carried out in boiling dichloromethane under argon atmosphere with triethylamine as a base.¹⁷ With increasing dendrimer generation, a longer reaction time (up to 5 days) and a higher excess of dansyl chloride (from 1.5 to 3.0) were used. After washing the reaction mixture with water and aqueous NaHCO₃, the crude products were purified by chromatography and characterized by ¹H NMR, ¹³C NMR and by mass spectrometry. Details on the preparation, purification, and characterization of the dendrimers are given in the Supporting Information.

The absorption spectra and photophysical properties (fluorescence spectra, quantum yields, and excited-state lifetimes) have been studied in acetonitrile/dichloromethane (5:1 v/v) solution where even the largest dendrimer is soluble enough to be studied. The equipment used has been described elsewhere.¹⁴ Luminescence quantum yields were measured following the method described by Demas and Crosby^{18a} (standard used: quinine sulfate in 0.05 M H₂SO₄, $\Phi = 0.52^{18b}$ for unprotonated species and naphthalene in cyclohexane, $\Phi = 0.23^{18c}$ for protonated species). When necessary, the emission intensity was corrected for inner filter effects.¹⁹ The estimated experimental error is 2 nm on the band maximum, 5% on the molar extinction coefficient, 10% on the fluorescence quantum yield, and 5% on the fluorescence lifetime.

Results

Dendrimers in Acetonitrile/Dichloromethane Solution. The reference compound **1** exhibits intense absorption bands in the near UV spectral region ($\lambda_{\text{max}} = 252$ and 339 nm, $\epsilon_{\text{max}} = 12\,200$ and $3940\text{ M}^{-1}\text{ cm}^{-1}$, respectively) and a strong fluorescence band in the visible region ($\lambda_{\text{max}} = 514$ nm; $\Phi = 0.25$, $\tau = 12$ ns). Each dendrimer shows absorption and emission bands practically at the same wavelengths as **1**. The absorption and fluorescence spectra of **5D** are displayed in Figure 2. Along the dendrimer family, the molar absorption coefficient (e.g., at

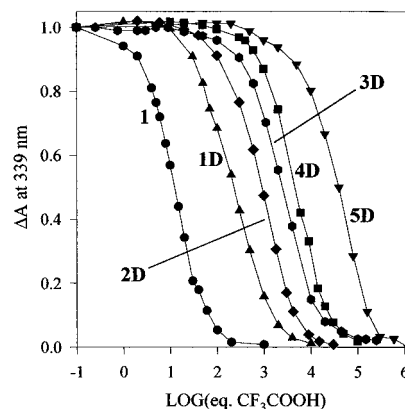


Figure 3. Normalized changes in absorbance at 339 nm observed for **1** and the **nD** dendrimers upon titration with trifluoroacetic acid.

339 nm) increases linearly with increasing number of dansyl units. For **5D**, the huge ϵ values (6.9×10^5 and $2.2 \times 10^5\text{ M}^{-1}\text{ cm}^{-1}$ at 253 and 339 nm, respectively) are slightly smaller (about 10–15%) than expected for 64 dansyl units, presumably because of a few defects in the structure of the original poly(propylene amine) dendrimer. The fluorescence quantum yield and the excited state lifetime (single exponential decay) of the dansyl chromophoric groups in the dendrimers are practically the same as for **1**. 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.

Protonation of the Dendrimers. It is well known that the absorption and emission properties of the dansyl group are very sensitive to the addition of acid because of the protonation of the dansylamine subunit.^{16b} In the acid titration experiments, the concentration of **1** was $1.5 \times 10^{-4}\text{ M}$ and that of the **nD** dendrimers was $(1.5/2^{n+1}) \times 10^{-4}\text{ M}$, to have the same number of dansyl units in each case. The emission intensity values have been obtained by excitation in an isosbestic point ($\lambda = 272$ nm), as better explained below. At the end of the acid titration, the absorption bands of the dansyl unit are no longer present, and a new absorption band is formed ($\lambda_{\text{max}} = 286$ nm; $\epsilon_{\text{max}} = 6800\text{ M}^{-1}\text{ cm}^{-1}$ per dansyl unit), accompanied by a smaller feature with $\lambda_{\text{max}} = 330$ nm. Three isosbestic points are present in all cases. Besides the changes in absorbance, protonation causes the disappearance of the strong dansyl fluorescence band and the appearance of a weaker ($\Phi = 0.002$), shorter-lived ($\tau < 1$ ns) fluorescence band with $\lambda_{\text{max}} = 336$ nm. The final spectra obtained in the case of dendrimer **5D** are shown in Figure 2. The absorption and fluorescence band maxima in the presence of an excess of acid are the same for all of the examined compounds, including **1**, and can therefore be attributed to the protonation of the dansyl units. The dendrimers, however, exhibit some peculiar features, that are summarized below.

(a) The amount of acid needed to cause the above-mentioned overall spectral changes is much larger for the dendrimers than for compound **1** and increases with increasing the dendrimer generation number (Figure 3).

(b) For the dendrimers, but not for compound **1**, addition of acid causes first a very small red shift of the absorption and emission bands of unprotonated dansyl.

(c) In the case of **1**, the decrease of the absorption band of unprotonated dansyl at 339 nm is accompanied by (i) a parallel increase of the absorption band of protonated dansyl at 286 nm, (ii) a parallel decrease of the unprotonated dansyl emission intensity at 514 nm, and (iii) a parallel increase of the protonated dansyl emission intensity at 336 nm (Figure 4, inset). For the

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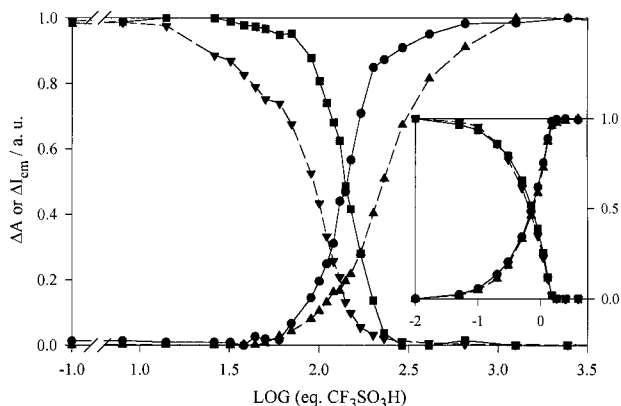


Figure 4. Normalized changes in absorbance and fluorescence intensity observed upon titration with triflic acid of reference compound **1** (inset) and dendrimer **5D**. The emission intensities have been obtained by excitation at the 272 nm isosbestic point. The other dendrimers behave qualitatively as **5D**. (■) ΔA at 339 nm; (●) ΔA at 286 nm; (▼) ΔI_{em} at 514 nm; (▲) ΔI_{em} at 336 nm.

dendrimers (see, e.g., Figure 4, which shows the behavior of **5D**), the decrease of the absorption band of unprotonated dansyl at 339 nm is accompanied by a parallel increase of the absorption band of protonated dansyl at 286 nm, but the changes in the emission intensities do not parallel the changes in absorption, as described below.

(d) As one can see from Figure 4, the emission intensity of the unprotonated dansyl units begins to decrease when, according to the absorption spectra, no dansyl unit has yet been protonated. Notice also that on continuing acid addition the slope of the curve corresponding to the decrease of the unprotonated dansyl emission becomes smaller than the slope of the curve reporting the change in absorbance at 339 nm, which measures the decrease in the number of unprotonated species.

(e) Figure 4 also shows that the appearance and the increase in intensity of the emission at 336 nm, characteristic of the protonated dansyl units, occur later than expected from the appearance and increase in concentration of such protonated units, as measured from the changes in absorbance at 286 nm.

(f) For compound **1** the excitation spectrum of the emission at 514 nm (which is due to the unprotonated dansyl units) always matches the absorption spectrum of the unprotonated dansyl units (Figure 5, inset). In the case of the dendrimers, however, the excitation spectrum of such an emission, in the acidity region between 100 and 200 equiv of $\text{CF}_3\text{SO}_3\text{H}$, shows the absorption features of both unprotonated and protonated dansyl units (Figure 5).

(g) In the case of the largest dendrimer **5D**, when in the titration experiment triflic acid is replaced by trifluoroacetic acid, the titration curve differs not only, as expected, for the higher acid concentration needed but also for a more pronounced initial decrease in the 514 nm emission intensity.

(h) Solutions containing partially protonated dendrimers exhibit multiexponential fluorescence decay.

(i) The fluorescence quantum yield of the fully protonated dendrimers is 0.15, i.e., about 15 times higher than that of the fully protonated compound **1**.

Discussion

The very simple titration behavior of compound **1** (Figure 4, inset) is due, of course, to the presence of only one basic site, namely the amine subunit of the dansyl chromophoric group. Addition of acid causes the protonation of this site, with the consequent disappearance of the unprotonated dansyl absorption

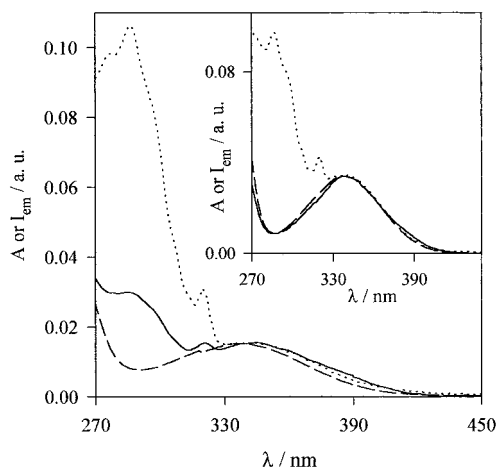


Figure 5. Excitation spectra (full lines) of the emission of unprotonated dansyl units at 514 nm for solutions corresponding to the crossing point of the absorbance changes (Figure 4) for reference compound **1** (inset) and dendrimer **5D**. The dotted lines are the absorption spectra of the same solutions, and the dashed lines show the contribution to the absorbance by the unprotonated dansyl units.

($\lambda_{\text{max}} = 252$ and 339 nm) and fluorescence ($\lambda_{\text{max}} = 514$ nm) bands, and the concomitant appearance of the absorption and emission bands ($\lambda_{\text{max}} = 286$ and 336 nm, respectively) of protonated dansyl. In the **nd** dendrimers, however, there are $2^{n+2} - 2$ protonation sites distributed in concentric shells (i.e., 126 protonation sites distributed in six shells in the case of **5D**). The complex titration curves exhibited by the dendrimers (see, e.g., Figure 4) clearly result from competitions and interactions among the various protonation sites.

The protonation of poly(propylene amine) dendrimers in water has been carefully investigated by Koper, et al.¹⁵ Their results are quite useful for our discussion even if the two families of compounds and the experimental conditions used are somewhat different (peripheral primary amine groups instead of dansyl groups; maximum generation 3 instead of 5; the two central N atoms separated by 4 C; water instead of acetonitrile/dichloromethane solution). According to Koper, et al.¹⁵ the protonation pattern of the poly(propylene amine) dendrimers is governed not only by the intrinsic protonation constants of the different sites but also by electrostatic repulsions between nearby protonated sites and entropic effects deriving from the degeneracy of the protonation states. Because of the interplay of these factors, they found that the protonation behavior of a third generation dendrimer, which consists of three shells of tertiary amines (α , β , γ) and an outer shell of primary amines (δ), is very intricate and can be summarized as follows. At low proton concentration, all shells are slightly protonated. With continuing addition of acid, the outer δ shell is the first to undergo full protonation because of the highest proton affinity of the primary amines. At lower pH the predominant microstate has the outer δ shell and the middle β shell fully protonated. On further addition of acid the γ shell begins to be protonated and this causes initially a deprotonation of the β shell to avoid too many neighboring protonated sites. This also favors a more complete protonation of the innermost α shell. At very low pH, all shells are fully protonated. Best fitting of the results obtained lead Koper, et al.¹⁵ to conclude that in water the pK_a values of the α , β , γ tertiary amine sites are 9.80, 10.35, and 10.35, respectively, and that of the peripheral primary amine sites is 10.70.

In our **nd** dendrimers the peripheral dansylamine sites are weaker bases than the tertiary amines of the interior. Therefore,

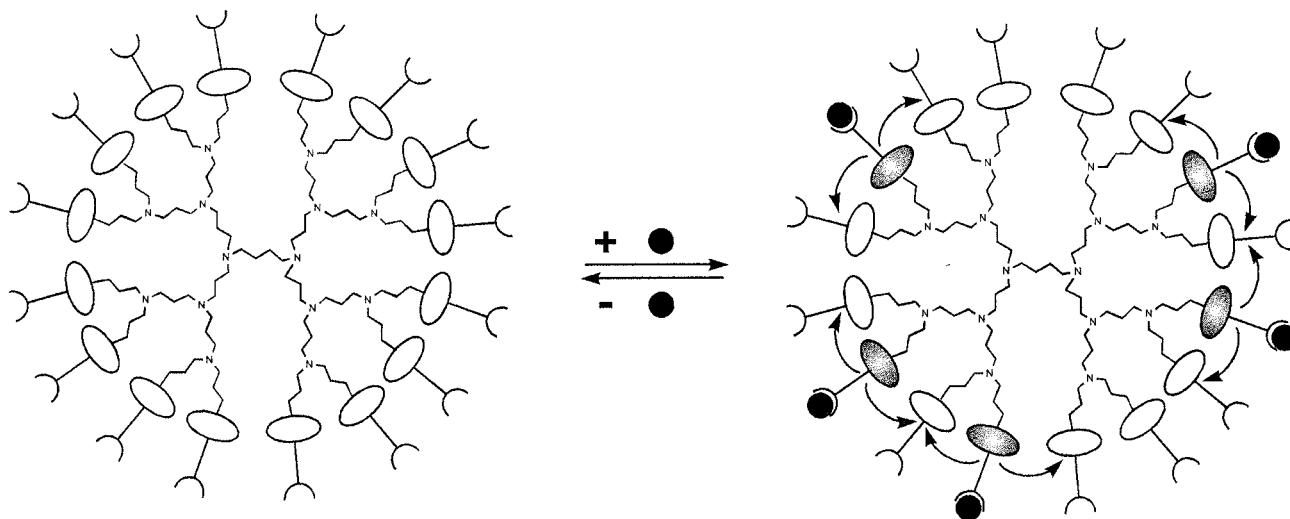


Figure 6. Sensory signal amplification within a dendritic structure. For the dendrimers studied in this paper the solid circles represent protons. The lowest-energy level of the protonated dansyl units is higher than the lowest-energy level of the unprotonated ones, so that energy transfer from the former units to the latter ones takes place, as schematically shown by the arrows, with a corresponding quenching/sensitization effect.

addition of acid first causes the protonation of inner tertiary amines. This is the reason (Results, point a) the amount of acid needed to cause the conversion of the unprotonated to protonated dansyl units (and the consequent spectral changes) is larger for the dendrimers compared with that for the reference compound **1**. The increase in the amount of acid needed to protonate the dansyl units with increasing dendrimer generation is due to both the increase in the number of tertiary amine sites²⁰ and to the increasing electrostatic repulsions. Protonation of the inner tertiary amine sites causes small perturbations on the energy of the absorption and emission bands of unprotonated dansyl (point b) and a more sizable perturbation on the emission intensity both of the unprotonated (point d) and protonated dansyl units (point i).

The delay in the appearance and the increase in intensity of the protonated dansyl emission at 336 nm (point e) indicate that the fluorescent excited state of the protonated dansyl units can be quenched in the partially protonated species. The concomitant slower than expected decrease in the intensity of the unprotonated dansyl emission (second part of point d) and the presence of the protonated dansyl absorption bands in the excitation spectrum of the unprotonated dansyl emission (point f, Figure 5) show that the above-mentioned quenching takes place by electronic energy transfer to the unprotonated units, whose fluorescence excited-state lies below that of the protonated species.²¹ Energy transfer in dendrimers is an important process for several reasons,^{6,14,22–24} including sensory signal amplification, a process discussed by Swager²⁵ for polymeric chains of sensors and illustrated in Figure 6 in the case of dendrimers such as those studied in this paper.

Besides the above-discussed features, other intriguing aspects emerge from our investigation. For example, the different initial

behavior of the titration curves, depending on whether trifluoroacetic or triflic acid is used, shows that the nature of the counterion can play a role in the protonation of the interior dendrimer sites. This is likely related to the size of the dendrimer cavities, as already discussed for encapsulation of radicals²⁶ in poly(propylene amine) and of Cu(II) complexes in poly(amidoamine)²⁷ dendrimers.

Conclusions

We have prepared poly(propylene amine) dendrimers of generation number 1 to 5, functionalized with dansyl units at the periphery. The largest dendrimer, **5D**, contains 64 dansyl functions in the periphery and 62 tertiary amine units in the branches. Altogether, **5D** contains 126 protonation sites. In acetonitrile/dichloromethane solution, each dansyl unit maintains the characteristic properties of the monodansyl model compound **1**. The changes in the absorption spectra and fluorescence properties upon addition of acid show that there is an interesting interplay between the protonation processes of the tertiary amine groups contained in the interior of the dendrimers and the dansyl units appended in the periphery. In the species where only part of the peripheral dansyl units are protonated, electronic energy transfer is observed from the fluorescent excited state of the protonated units to the ground state of the unprotonated ones. This causes an amplification of the changes in the spectroscopic signals that accompany the protonation/deprotonation of separated dansyl units. Other subtle effects, such as that observed on changing the acid, may prove interesting for the use of these species as anion sensors.²⁸ Dendrimers containing protonation sites and fluorescent units such as those investigated in this paper are promising for the development of controlled-release systems.²⁹ It should be noted that the presence of charged guests inside the dendrimer may affect the reactivity of the peripheral units: this may be relevant for functionalization of the dendrimer periphery. Finally, it is interesting to recall that protonated

(20) The ratio between the numbers of tertiary amines and dansyl units, given by the expression $(2^{n+1} - 2)/2^{n+1}$, increases from 0.5 for $n = 1$ to 0.97 for $n = 5$.

(21) Examination of the corrected excitation spectra show that, within the experimental error, the quenching of the protonated units is quantitatively accompanied by energy transfer to the unprotonated ones.

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dendrimers may be biologically relevant since they can efficiently interact with DNA and transport it in the nucleus of eukaryotic cells.³⁰

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Supporting Information Available: Synthesis details and characterization (by NMR and FAB and MALDI-TOF techniques) of the dansylated poly(propylene amine) dendrimers from generation 1 to 5 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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