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# Coordination of $Co^{2+}$ Ions in the Interior of Poly(propylene amine) Dendrimers Containing Fluorescent Dansyl Units in the Periphery

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**Abstract:** We have investigated the interaction of $Co^{2+}$ ions (as nitrate salt) with dendrimers of the poly(propylene amine) family functionalized in the periphery with fluorescent dansyl units. Each dendrimer ***n*D**, where the generation number $n$ goes from 1 to 5, comprises $2^{(n+1)}$ dansyl functions in the periphery and $2^{(n+1)} - 2$ tertiary amine units in the interior. For comparison purposes, the behavior of a monodansyl reference compound (**I**) has also been investigated. The results obtained have shown that: (i) the absorption and fluorescence spectra of the reference compound **I** are not affected by addition of $Co^{2+}$ ions; (ii) in the case of the dendrimers, the absorption spectra are unaffected, but a strong quenching of the fluorescence of the peripheral dansyl units is observed; (iii) the fluorescence quenching takes place by a static mechanism involving coordination of metal ions in the interior of the dendrimers; (iv) metal ion coordination by the dendrimers is a fully reversible process; (v) a strong amplification of the fluorescence quenching signal is observed with increasing dendrimer generation. For the larger dendrimers ($n = 3$, 4, and 5), at very low metal ion concentration 1:1 metal/dendrimer species are formed, in which the $Co^{2+}$ ion guest quenches each one of the dansyl units that becomes excited after light absorption.

## Introduction

Dendrimer chemistry is rapidly expanding both for fundamental reasons and for technological applications.[1] A recent, interesting development of dendrimer chemistry concerns the coordination of metal ions by the interior branches or the exterior units.[2−6]

Dendrimers containing photoactive units[7−17] are particularly interesting for two reasons: (i) cooperation among the photo-

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active components can allow the dendrimer to perform specific functions, and (ii) changes in the properties of the photoactive components can be exploited to monitor the participation of dendrimers in chemical processes. Continuing our investigations in this field,[11] we have decorated the periphery of poly(propylene amine) dendrimers with fluorescent dansyl units, and we have studied their interaction with metal ions. The formulas of the monodansyl reference compound **I** and of the investigated dendrimers are shown in Figure 1. Each dendrimer ***n*D**, where the generation number $n$ 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.

An investigation of the interaction between the ***n*D** dendrimers and metal ions is interesting for the following reasons: (i) the ***n*D** dendrimers, because of the presence of a great number of amine groups in the interior, should easily coordinate metal ions; (ii) by using a metal ion capable of quenching the dansyl fluorescence, the presence of $2^{(n+1)}$ dansyl groups appended in the periphery of the dendrimers can offer a unique opportunity to observe amplification effects in the fluorescence quenching signal; (iii) the results of the fluorescence quenching experiments can provide information on the coordination properties of the polytopic dendritic ligands.

Preliminary experiments were carried out by using $Co^{2+}$, $Cu^{2+}$, and $Zn^{2+}$ ions. In the case of $Co^{2+}$, reversible formation of complexes with the various dendrimers and quenching of the fluorescence of the appended dansyl units were observed. $Cu^{2+}$ was found to undergo an irreversible chemical reaction with the dansyl groups. $Zn^{2+}$ did not cause any change in the fluorescent properties of the dendrimers. Therefore, we decided to perform systematic experiments only with $Co^{2+}$ ions.

Some results on the interaction of $Co^{2+}$ ions with dendrimer **4D** have been reported in a preliminary communication.[11g]

## Experimental Section

The dansylated ***n*D** compounds (Figure 1) were obtained from the reaction of commercial poly(propylene amine) dendrimers (BASF-AG for generation 1−3, DMS for generation 4 and 5) with dansyl chloride (Merck).[11f,18] Notice that the dendrimer core is a 1,2-diaminoethane group for generations 1−3 and a 1,4-diaminobutane group for generation 4 and 5. $Co(NO_3)_2 \cdot 6H_2O$ was a commercial, high purity reagent.

The absorption spectra and photophysical properties (fluorescence spectra, quantum yields, and excited-state lifetimes) were studied in acetonitrile/dichloromethane (5:1 v/v) solution where even the largest dendrimer is soluble enough to be studied. Titration experiments with $Co(NO_3)_2 \cdot 6H_2O$ were followed by absorption, emission, and lifetime measurements.

UV−vis absorption spectra were recorded with a Perkin-Elmer λ6 spectrophotometer, using quartz cells with path length 1.0 cm. Fluorescence spectra were obtained with a Perkin-Elmer LS-50 spectrofluorimeter, equipped with a Hamamatsu R928 phototube, on air-equilibrated solutions. The fluorescent intensity was measured by exciting at 345 nm and was corrected for inner filter effects when necessary.[19] Fluorescence quantum yields were measured following the methods of Demas and Crosby[20] (standard used: quinine sulfate in 0.5 M $H_2SO_4$, $\Phi = 0.55$).[21] Fluorescence lifetimes were measured by time-correlated single-photon counting (0.5 ns time resolution) with an Edinburgh Instruments DS199 equipment ($D_2$ lamp, $\lambda_{exc} = 340$ nm), and a spectrofluorometer FLUOROLOG Spex FL3−11 equipped with a phase-shift Tau 3 unit capable of measuring luminescence lifetimes with 10 ps time resolution.

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.

## Results and Discussion

**Reference Compound and Uncomplexed Dendrimers.** In acetonitrile/dichloromethane 5:1 v/v solution, the reference compound **I** and the ***n*D** dendrimers exhibit intense absorption bands in the near UV spectral region ($\lambda_{max} = 253$ and 339 nm, $\epsilon_{max} = 12\,200$ and 3940 $M^{-1}\ cm^{-1}$, respectively, for **I**) and a strong fluorescence band in the visible region ($\lambda_{max} = 514$ nm, $\Phi = 0.30$, $\tau = 12$ ns, for **I**).[11f] The absorption and fluorescence band maxima for the dendrimers (see, e.g., the spectra of dendrimer **4D** in Figure 2) occur at the same wavelength as for the reference compound. Along the dendrimer family, the molar absorption coefficient increases linearly with increasing number of dansyl units (Figure 3a), but the $\epsilon$ values for the two larger dendrimers are a little smaller than expected. For example, for dendrimer **5D** the $\epsilon$ values (690 000 $M^{-1}\ cm^{-1}$ at 253 nm, 222 000 $M^{-1}\ cm^{-1}$ at 339 nm) are about 11% lower than expected for 64 dansyl units, taking compound **I** as a reference. If one takes as a reference one-fourth of the $\epsilon$ value found for **1D**, the $\epsilon$ value of **5D** is only 2% lower than expected. The slight decrease in the $\epsilon$ value on increasing generation may be due to (i) a few defects in the structure of the commercial poly(propylene amine) dendrimers before dansyl functionalization, (ii) the failure to achieve 100% yield in the functionalization reaction, and/or (iii) a slightly different “solvation” environment of the dansyl units on increasing generation. The last hypothesis is not unlikely since (a) the flexibility of the dendrimer branches can allow folding for the dendrimers of higher generations,[1a,d,m] and (b) the electronic transitions responsible for the absorption and emission bands, because of their charge-transfer nature, may be influenced by the environment.[22] The small changes in the fluorescence quantum yield and the modest increase of the excited state lifetime on increasing dendrimer generation (Figure 3b, 3c) are consistent with the presence of very slight environmental effects. In all cases the fluorescence decay strictly obeyed a first-order kinetics. This, of course, does not exclude the presence of short components that cannot be revealed by our equipment. Taken together, these results suggest that, even in the largest dendrimer, the interaction among the dansyl groups is, at most, very small and that the tertiary amine units do not cause any quenching effect on the fluorescent excited state of the peripheral dansyl units.

For the dansyl unit (hereafter called DANS) the energy of the fluorescent excited state, as estimated from the onset of the emission band, is about 2.76 eV. Electrochemical experiments in acetonitrile solution have shown that compound **I** undergoes a chemically irreversible one-electron oxidation process ($E_{1/2}$ about 0.9 V vs SCE, as estimated by digital simulation), and a one-electron reduction process, reversible only at low temperature (−40 °C) with $E_{1/2} = -2.02$ V (vs SCE). It follows[23] that

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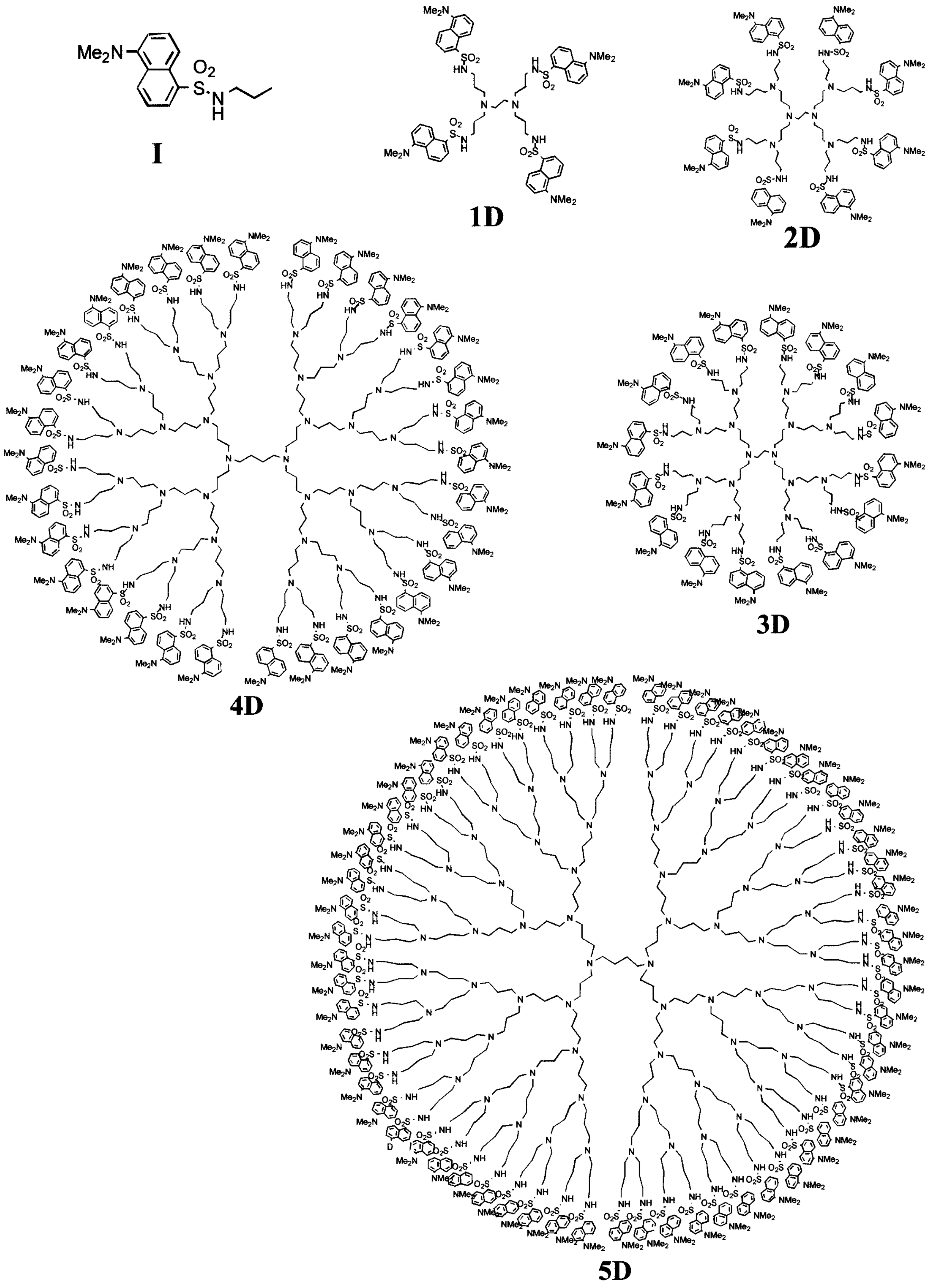

**Figure 1.** Structure formulas of the monodansyl reference compound **I** and the ***n*D** dendrimers.

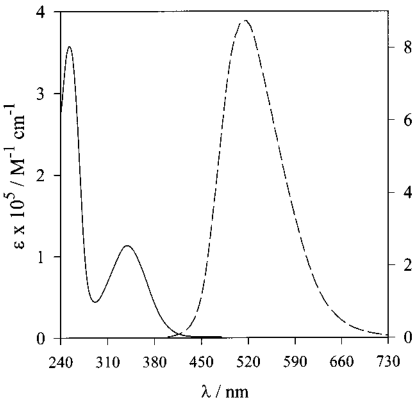

**Figure 2.** Absorption (full line) and fluorescence (dashed line) spectra of dendrimer **4D** in acetonitrile/dichloromethane (5:1 v/v) solution at room temperature. The fluorescence spectrum has been obtained by excitation at 345 nm.

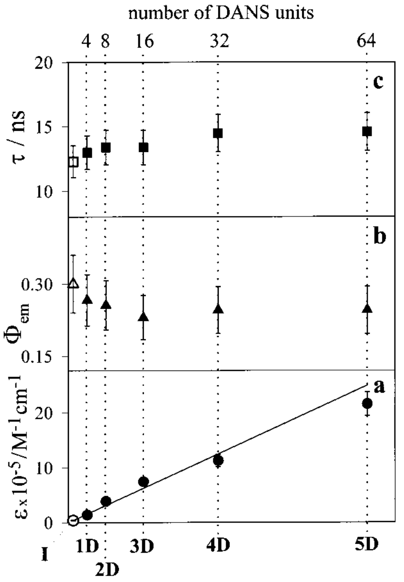

**Figure 3.** Molar absorption coefficients (a), fluorescence quantum yields (b), and fluorescence lifetimes (c) of the reference compound **I** and of the ***n*D** dendrimers.

the fluorescent excited state of DANS is a weak oxidant, $E(^*\mathrm{DANS}/\mathrm{DANS}^-$ ∼+ 0.7 V) and a strong reductant, $E(\mathrm{DANS}^+/^*\mathrm{DANS})$ ∼−1.9 V). These data account for the observed lack of quenching of the dansyl fluorescence by the tertiary amine units contained in the interior of the dendrimer, since tertiary amines (i) have no excited state below 2.76 eV, (ii) are rather difficult to oxidize (oxidation of tertiary amine occurs around +1.1 V vs SCE),[23b] and (iii) cannot be reduced up to −3.0 V vs SCE.[24] It is well-known, however, that the dansyl fluorescence can be quenched by transition metal ions via energy and/or electron-transfer processes.[25]

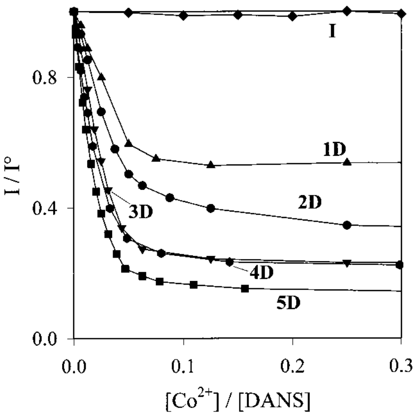

**Figure 4.** Effect of addition of $Co^{2+}$ ions on the fluorescence intensity of the reference compound **I** and of the ***n*D** dendrimers at constant concentration of the dansyl units ([DANS] = $1.5 \times 10^{-4}$ M).

**Table 1.** Some Relevant Fluorescence Quenching Data[a]

| ***n*D** | DANS[b] | $[Co^{2+}]$/ $10^{-6}$ M | $[Co^{2+}]$/ [DANS] | $[Co^{2+}]$/ [***n*D**] | $\eta_q$[c] | $[DANS]_q$/ $[Co^{2+}]$[d] |
|---|---|---|---|---|---|---|
| **1D** | 4 | 0.95 | 0.0063 | 0.025 | 0.05 | 8[e] |
| | | 7.5 | 0.05 | 0.2 | 0.33 | |
| | | 19 | 0.13 | 0.5 | 0.47 | |
| **2D** | 8 | 0.47 | 0.0031 | 0.025 | 0.05 | 16[e] |
| | | 7.5 | 0.05 | 0.4 | 0.53 | |
| | | 38 | 0.25 | 2.0 | 0.68 | |
| **3D** | 16 | 0.47 | 0.0031 | 0.05 | 0.05 | 16[e] |
| | | 7.5 | 0.05 | 0.8 | 0.66 | |
| | | 38 | 0.25 | 4.0 | 0.77 | |
| **4D** | 32 | 0.24 | 0.0016 | 0.05 | 0.05 | 32[e] |
| | | 7.5 | 0.05 | 1.6 | 0.71 | |
| | | 24 | 0.16 | 5.0 | 0.78 | |
| **5D** | 64 | 0.12 | 0.0008 | 0.05 | 0.05 | 64[e] |
| | | 7.5 | 0.05 | 3.2 | 0.73 | |
| | | 23 | 0.16 | 10 | 0.86 | |

[a] $CH_3CN/CH_2Cl_2$ (5:1 v/v) solutions. Under the experimental conditions used, no fluorescence quenching was observed for **I**. In all experiments the concentration of dansyl units was [DANS] = $1.5 \times 10^{-4}$ M. Accordingly, the concentration of the ***n*D** dendrimers was $(1.5/2^{(n+1)}) \times 10^{-4}$ M. [b] Number of dansyl units in each dendrimer. [c] Efficiency of fluorescence quenching, $(I° - I)/I°$, which is also equal to the fraction of quenched DANS units, $[DANS]_q/[DANS]_{tot}$. [d] Number of DANS units quenched per $Co^{2+}$ ion. [e] Stoichiometry of $Co^{2+}$ complexation: $[Co(\mathbf{\mathit{n}D})_2]^{2+}$ for $n$ = 1, 2; $[Co(\mathbf{\mathit{n}D})]^{2+}$ for $n$ = 3, 4, 5.

**Quenching of the Dendrimer Fluorescence.** We have first examined the behavior of the monodansyl reference compound **I**, and we have found that addition of $Co^{2+}$ (up to $7.5 \times 10^{-4}$ M, as $Co(NO_3)_2$•$6H_2O$) to a $1.5 \times 10^{-4}$ M solution of **I** did not cause any change in the absorption and fluorescence properties (Figure 4).

Then, we have systematically investigated the behavior of the ***n*D** dendrimers upon addition of $Co(NO_3)_2$•$6H_2O$. In a first series of experiments, the concentration of each ***n*D** dendrimer was $(1.5/2^{(n+1)}) \times 10^{-4}$ M, to have in all cases the same concentration of dansyl units as in the experiments performed on the reference compound **I**. Under such conditions, we found that addition of $Co^{2+}$ ions caused a strong quenching on the fluorescence intensity of the dansyl units appended at the periphery of the dendrimers (Figure 4), without affecting their absorption spectra. A selection of the fluorescence quenching data obtained in these and other experiments is given in Table 1.

We have also found that, in all cases, if excess triflic acid is added to a metal-ion loaded dendrimer solution, full recovery of the fluorescence of the protonated dendrimer is observed,[26] showing that coordination of $Co^{2+}$ is a reversible process.[27]

At constant $Co^{2+}$ ($7.5 \times 10^{-6}$ M) and DANS ($1.5 \times 10^{-4}$ M) concentrations, corresponding to a 1:20 ratio between

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[24] Electrochemical studies performed in our laboratory on tributylamine in tetrabutylammonium hexafluorophosphate/tetrahydrofurane solution at room temperature.

[25] See, e.g.: (a) Schuster, M.; Sandor, M. *Fresenius' J. Anal. Chem.* **1996**, *356*, 326. (b) De Santis, G.; Fabbrizzi, L.; Licchelli, M.; Sardone, N.; Velders, A. H. *Chem. Eur. J.* **1996**, *2*, 1243. (c) Prodi, L.; Bolletta, F.; Montalti, M.; Zaccheroni, N. *Chem. Eur. J.* **1999**, *5*, 445. (d) Fabbrizzi, L.; Licchelli. M.; Parodi, L.; Poggi. A.; Taglietti, A. *Eur. J. Inorg. Chem.* **1999**, 35.

[26] The protonated dansyl units show a fluorescence band with $\lambda_{max}$ = 335 nm.[11f]

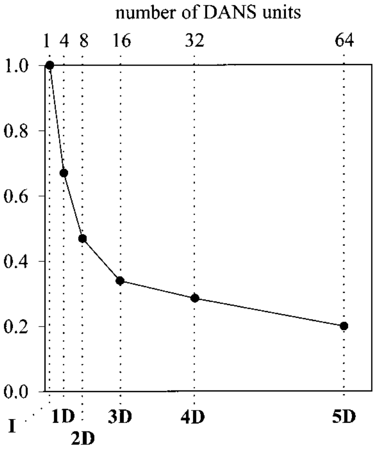

**Figure 5.** Effect on the fluorescence intensity caused by the addition of 7.5 × $10^{-6}$ M $Co^{2+}$ to solutions containing 1.5 × $10^{-4}$ M DANS in the form of reference compound **I** and of the ***n*D** dendrimers (for more details, see text).

the number of $Co^{2+}$ ions and DANS units, the efficiency of the fluorescence quenching (i.e., the fraction of DANS units quenched) increases with increasing dendrimer generation: 0.33 (**1D**), 0.53 (**2D**), 0.66 (**3D**), 0.71 (**4D**), 0.73 (**5D**) (Table 1, Figure 5). This shows that the quenching effect is magnified as the dansyl units are assembled in a smaller number of larger structures.

As shown in Figure 4, for each dendrimer the quenching efficiency increases with increasing $Co^{2+}$ concentration, until a plateau value is reached. In the case of **5D**, the maximum fluorescence quenching efficiency obtained at high $Co^{2+}$ concentrations is 0.86 (Table 1), which means that, as an average, 55 out of the 64 dansyl units appended to each dendrimer present in the solution can be quenched. At first sight, the quite similar behavior of **3D** and **4D** (Figure 4) could look surprising. This is likely related to the fact that in going from **3D** to **4D** there is not only a change in the generation number, but also a change in the core, which is a 1,2-diaminoethane group for **1D**, **2D** and **3D** and a 1,4-diaminobutane group for **4D** and **5D** (Figure 1). This difference in the core structure apparently plays a role in determining the coordination ability.

**Quenching Mechanism.** Since the addition of $Co^{2+}$ ions, even at higher concentrations, has no effect on the fluorescence of the monodansyl reference compound **I**, the quenching observed for the dendrimers (Figure 4) cannot be attributed to a dynamic[28] process, but it must originate from coordination of metal ions by the dendrimers. In this way, metal ions are within the interaction sphere of the excited dansyl units and cause a static quenching. It is well-known that the absorption and fluorescence bands of the dansyl chromophoric group are charge transfer in character; therefore, they should be affected if metal coordination by the dendrimer takes place at the amine units of the dansyl groups.[29] Since the positions of the band maxima do not change on addition of $Co^{2+}$, the ligand sites responsible for metal-ion coordination have to be the aliphatic amine groups which are present in the interior part of the dendrimers (Figure 1). Once metal coordination has occurred, quenching can take place by both energy- and electron transfer since the excited state of the dansyl unit is a good energy- and electron donor (vide supra) and Co(II) amine complexes have several low-energy excited states[30] and are easy to oxidize.[31]

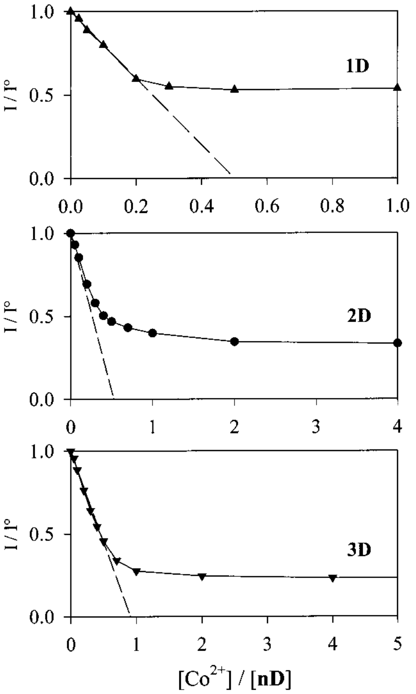

**Figure 6.** Effect of addition of $Co^{2+}$ ions on the fluorescence intensity of the **1D**, **2D** and **3D** dendrimers at constant concentration of the dansyl units ([DANS] = 1.5 × $10^{-4}$ M).

**Metal Ion Loading.** If the fluorescence quenching efficiencies are plotted against the $[Co^{2+}]/[\mathbf{\textit{n}D}]$ ratio (Figures 6 and 7), the results obtained throw light on the stoichiometry of the complexes of the small dendrimers and on the metal ion loading in the large dendrimers. In interpreting the results, it should be considered that there is a competition for metal ions between dendrimer coordinating sites, on one hand, and water molecules and nitrate counterions, that are added together with the metal ion, on the other hand. At very low $[Co^{2+}]/[\mathbf{\textit{n}D}]$ ratios, the number of dendrimer coordination sites is much larger than the number of water molecules and anions, but at high $[Co^{2+}]/[\mathbf{\textit{n}D}]$ ratios the reverse is true. Therefore, a change can be expected in the nature of the species containing the metal ion on increasing $Co^{2+}$ concentration.

The smallest dendrimer **1D** (Figure 1) can be viewed as a bidentate, ethylenediamine-type ligand with appended four fluorescent dansyl units. The plot of Figure 6 shows that for low $Co^{2+}$ concentrations ($[Co^{2+}]/[\mathbf{1D}] = 0.2$) the fluorescence intensity decreases linearly with increasing $[Co^{2+}]$. In this concentration range, each $Co^{2+}$ ion quenches 8 dansyl units, as it is also shown by the $[Co^{2+}]/[\mathbf{1D}] = 0.5$ value obtained by extrapolating the linear behavior observed for $[Co^{2+}]/[\mathbf{1D}] = 0.2$ to $I/I^0 = 0$. This result indicates that at low $Co^{2+}$ concentrations (i) **1D** is exclusively present as $[Co(\mathbf{1D})_2]^{2+}$, and (ii) in this complex each dansyl unit of the two **1D** ligands, when it is excited,[32] is quenched by the metal ion. At high $Co^{2+}$

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[27] For a recent example of pH-controlled release of a guest from poly(propylene amine) dendrimers, see: Pistolis, G. Malliaris, A.; Tsiourvas, D.; Paleos, C. M. *Chem. Eur. J.* **1999**, *5*, 1440.

[28] That dynamic quenching cannot account for the observed results was also expected on the basis of the Stern−Volmer equation (see, e.g., ref 23a): since the lifetime of the fluorescent excited state of the dansyl unit is around 12 ns, the metal ion concentration is too small to cause sizable effects even in the case of a diffusion controlled quenching process with $k_d = 1 \times 10^{10}$ $M^{-1}$ $s^{-1}$.

[29] Protonation of the amine units of the dansyl groups of the dendrimer is known to cause strong changes in the absorption and fluorescence spectra.[11f]

[30] Jorgensen, C. K. *Adv. Chem. Phys.* **1963**, *5*, 33.

[31] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley: New York, 1980.

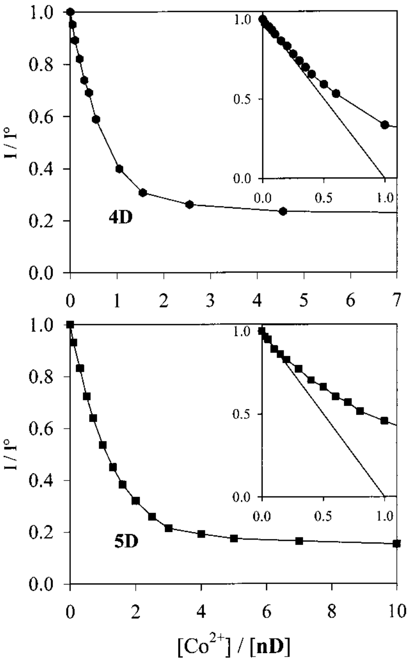

**Figure 7.** Effect of addition of $Co^{2+}$ ions on the fluorescence intensity of the **4D** and **5D** dendrimers at constant concentration of the dansyl units ([DANS] = $1.5 \times 10^{-4}$ M). Inset shows the results of a detailed investigation at low $Co^{2+}$ concentration.

concentrations the relative fluorescence intensity does not fall to zero, but reaches a plateau value of about 0.5. This may be due to incomplete complexation of the **1D** ligands which, at high $Co^{2+}$ concentrations, have to compete with a large number of water molecules and counterions.

In the case of **2D**, the $I/I^0$ vs $[Co^{2+}]/[\mathbf{2D}]$ plot (Figure 6) is similar to that found for **1D**. The straight line that interpolates the points obtained at low $Co^{2+}$ concentrations crosses again the $[Co^{2+}]/[\mathbf{2D}]$ axis at a $[Co^{2+}]/[\mathbf{2D}]$ value of about 0.5, which means that, under such conditions, complexes with 1:2 $Co^{2+}/\mathbf{2D}$ stoichiometry are mainly formed, and that in such complexes each one of the 16 dansyl units of the two **2D** ligands, when it is excited, is quenched by the metal ion. On increasing $Co^{2+}$ concentrations, it is likely that complexes of 1:1 $Co^{2+}/\mathbf{2D}$ stoichiometry are formed. The plateau value of about 0.70 for the quenching efficiency may again be due to incomplete complexation of **2D** in the presence of a large number of water molecules and counterions.

For the **3D** dendrimer, the straight line that interpolates the points at low $Co^{2+}$ concentrations crosses the $[Co^{2+}]/[\mathbf{3D}]$ axis at a value close to 1 (Figure 6). This suggests that 1:1 complexes are formed since the beginning, with practically complete quenching of each excited dansyl unit contained in the **3D** ligand. On increasing $Co^{2+}$ concentration, a non-zero plateau is reached, most likely for the above-mentioned interference by water molecules and counterions.

For the two larger dendrimers **4D** and **5D**, the $I/I^0$ vs $[Co^{2+}]/[\boldsymbol{n}\mathbf{D}]$ plot becomes smoother (Figure 7). At very low $Co^{2+}$ concentration (Figure 7, insets), the slope of the curve corresponds to the formation of 1:1 species in which practically each excited dansyl unit is quenched, regardless of its position in the dendritic structure. This suggests that upon metal coordination the dendrimer shrinks around the metal, thereby allowing all the dansyl units to be in the interaction sphere of the metal ion. Contrary to what happens for the smaller dendrimers (Figure 6), the quenching efficiency continues to increase for $[Co^{2+}]/[\mathbf{5D}]$ values higher than 1 (Figure 7). It seems likely that, on increasing $Co^{2+}$ concentration, species containing more than one metal ion per dendrimer are formed, as was recently found for poly(amidoamine) dendrimers.[2-4] The non-zero plateau value at high $Co^{2+}$ concentrations may be due again to the interference by water molecules and counterions. That the counterion can play a role at high $Co^{2+}$ concentrations is shown by the fact that when the titration is performed in the presence of an excess of nitrate ions (added as tetraethylammonium salt), the plateau $I/I^0$ value reached is higher, and the slope of the initial part of the plot is lower. Furthermore, the titration curve is somewhat different when the metal ion is added as a chloride salt.

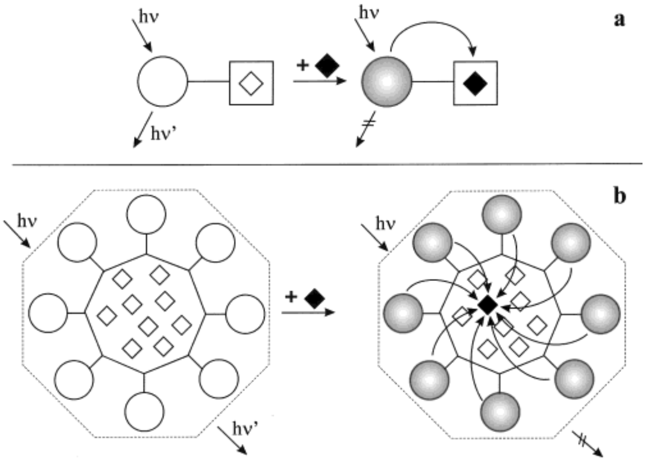

**Figure 8.** Schematic representation of (a) a conventional fluorescent sensor and (b) a fluorescent sensor with signal amplification. Open rhombi indicate coordination sites and black rhombi indicate metal ions. The curved arrows represent quenching processes. In the case of a dendrimer, the absorbed photon excites a single fluorophore component, that is quenched by the metal ion, regardless of its position. For **5D**, a $Co^{2+}$ ion quenches each one of the 64 dansyl units of the dendrimer (Figure 7).

**Sensory Signal Amplification.** In the past few years there has been a great development in the field of fluorescent chemosensors.[33] These compounds are usually made of a fluorescent unit connected with a receptor. Coordination of a substrate by the receptor affects the fluorescent properties of the fluorophore. For example (Figure 8a), the substrate can cause quenching of the excited state of the fluorophore by energy or electron transfer, switching off the fluorescent signal. Because of its strong fluorescence, the dansyl group is often used as a fluorophore for sensory purposes.[25]

A most important property of a fluorescent sensor is, of course, sensitivity. We have seen that in the dendrimers studied in this paper coordination of a metal ion can cause the quenching of a great number of dansyl units, as schematized in Figure 8b.[32] This leads to a strong amplification of the sensory signal. In the case of **5D**, at low $Co^{2+}$ concentrations a $Co^{2+}$ ion quenches each one of the 64 dansyl units of the dendrimer. Such

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(32) It should be noted that under the experimental condition used, simultaneous multiexcitation processes are unlikely to occur. Therefore, even in the larger dendrimers, the dansyl units are excited (and quenched) one at a time.

(33) (a) Bissell, R. A.; de Silva, A. P.; Gunaratne, H. Q. N.; Lynch, P. L. M.; Maguire, G. E. M.; McCoy, C. P.; Sandanayake, K. R. A. S. *Top. Curr. Chem.* **1993**, *168*, 223. (b) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515. (c) Desvergne, J. P., Czarnik, A. W., Eds. *Chemosensors of Ion and Molecule Recognition*; Kluwer: Dordrecht, 1997. (d) Beer, P. D. *Acc. Chem. Res.* **1998**, *31*, 71. (e) Fabbrizzi, L.; Licchelli, M.; Pallavicini, P. *Acc. Chem. Res.* **1999**, *32*, 846. (f) Prodi, L.; Bolletta, F.; Montalti, M.; Zaccheroni, N. *Coord. Chem. Rev.*, in press.

a signal amplification effect is similar to that previously observed for polymeric chains of sensors.[34] The problem of designing dendrimers capable of coupling sensitivity with metal ion selectivity is currently under investigation in our laboratories.

## Conclusions

We have shown that poly(propylene amine) dendrimers functionalized in the periphery with dansyl units can reversibly coordinate $Co^{2+}$ ions. Complexation of the metal ions causes the quenching of the fluorescence of the dansyl units appended to the dendrimers. The increase in the fluorescence quenching efficiency with increasing size of the dendrimer is related to the assembly of large numbers of dansyl units around the coordination sites. This effect leads to a strong amplification of the fluorescence quenching signal (Figure 8b), a phenomenon previously observed for polymeric chains of sensors (sensory signal amplification). In the case of **5D**, at low $Co^{2+}$ concentrations a $Co^{2+}$ ion quenches each one of the 64 dansyl units of the dendrimer. Optimization of these systems requires the coupling of sensitivity with selectivity. We are currently designing dendritic structures where only one selective coordination site is present.

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[34] Swager, T. M. *Acc. Chem. Res.* **1998**, *31*, 201.