A Cyclam Core Dendrimer Containing Dansyl and Oligoethylene Glycol Chains in the Branches: Protonation and Metal Coordination

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Abstract: We have synthesized a dendrimer (**1**) consisting of a 1,4,8,11-tetraazacyclotetradecane (cyclam) core, appended with four benzyl substituents that carry, in the 3- and 5-positions, a dansyl amide derivative (of type **2**), in which the amide hydrogen is replaced by a benzyl unit that carries an oligoethylene glycol chain in the 3- and 5-positions. All together, the dendrimer contains 16 potentially luminescent moieties (eight dansyl- and eight dimethoxybenzene-type units) and three distinct types of multivalent sites that, in principle, can be protonated or coordinated to metal ions (the cyclam nitrogen atoms, the amine moieties of the eight dansyl units, and the 16 oligoethylene glycol chains). We have studied the absorption and luminescence properties of **1**, **2**, and **3** in acetonitrile and the changes taking place upon titration with acid and a variety of divalent (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}), and trivalent (Nd^{3+}, Eu^{3+}, Gd^{3+}) metal ions as triflate and/or nitrate salts. The results obtained show that: 1) double protonation of the cyclam ring takes place before protonation of the dansyl units; 2) the oligoethylene glycol chains do not interfere with protonation of the cyclam core and the dansyl units in the ground state, but affect the luminescence of the protonated dansyl units; 3) the first equivalent of metal ion is coordinated by the cyclam core; 4) the interaction of the resulting cyclam complex with the appended dansyl units depends on the nature of the metal ion; 5) coordination of metal ions by the dansyl units follows at high metal-ion concentrations; 6) the effect of the metal ion depends on the nature of the counterion. This example demonstrates that dendrimers may exhibit complete functionality resulting from the integration of the specific properties of their component units.

Keywords: dansyl · dendrimers · fluorescence · metal coordination · protonation

Introduction

Dendrimers[1,2] constitute a class of multibranched molecules that can—by design—exhibit a high degree of order, but also a high degree of complexity. A most important feature of dendrimer chemistry is the possibility to insert selected chemical units in predetermined sites of the dendritic structure. It is thus possible to construct large nanometric molecules capable of performing complex functionality that derives from the integration of the specific properties of the constituent moieties.

Dendrimers that contain both luminescent units and coordination sites are particularly interesting, since they are capable of performing as luminescent ligands for metal ions.[3] Coupling luminescence with metal coordination can indeed be exploited for a variety of purposes, which include investigation of dendrimer structures,[4] encapsulated metal nanoparticles,[5] ion sensing,[6,7] light harvesting,[8] stepwise complexation,[9] and reversible metal complex assembly.[10] Metal ions have also been used to assemble luminescent dendrons[11] and as branching centres in the synthesis of luminescent dendrimers.[12]

In most cases, metal-ion coordination by a dendrimer takes place by units that are present along the dendrimer branches (e.g., amine,[6a,b,13] imine[9] or amide[6c,8a] groups) or appended at the dendrimer periphery (e.g., terpyridine,

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cathecolamide ligands).[14] Only a few examples of dendrimers with a well-defined metal-coordinating core have been reported so far,[15,16] exception being made for those based on porphyrins.[17]

1,4,8,11-Tetraazacyclotetradecane (cyclam) is one of the most extensively investigated macrocyclic ligands in coordination chemistry. In aqueous solution it can be protonated[18] and coordinated to a variety of metal ions with very large stability constants.[19,20] Cyclam and its derivatives have also been studied as carriers of metal ions in antitumor[21] and imaging[22] applications and, most recently, as anti-HIV agents.[23] In the last few years we have synthesized and studied several families of dendrimers with cyclam as a core.[16] Continuing our investigations in this field, we have synthesized a dendrimer (1) consisting of a cyclam core appended with four benzyl substituents that carry, in the 3- and 5-positions, a dansyl amide derivative (2) in which the amide hydrogen is replaced by a benzyl unit that carries an oligoethylene glycol chain in the 3- and 5-positions. Dendri-

16 oligoethylene glycol chains appended in the periphery) that, in principle, can be protonated or coordinated to metal ions. We hoped that this dendrimer might be soluble in water because of the oligoethylene glycol chains, but this was not the case. Therefore, we studied the absorption and luminescence properties of 1 and 2 in acetonitrile and the changes taking place upon titration with trifluoromethanesulfonic (triflic) acid and a variety of divalent (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) and trivalent (Nd^{3+}, Eu^{3+}, Gd^{3+}) metal ions as triflate or nitrate salts.

Results and Discussion

Absorption and emission spectra: Since the cyclam core does not show absorption bands above 240 nm, the chromophoric groups present in dendrimer 1 are those contained in its branches (2), namely eight dansyl- and eight dimethoxybenzene-type units. As shown in Figure 1, the spectrum of 2
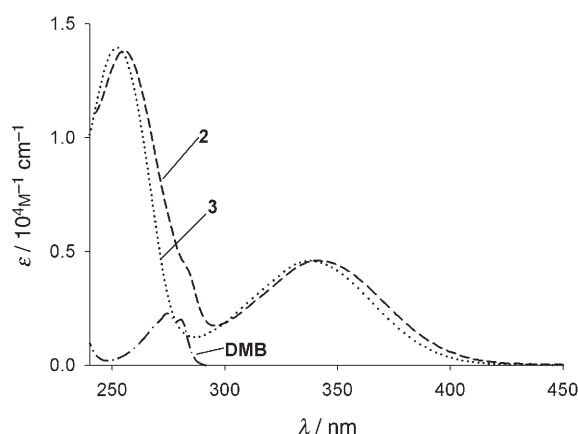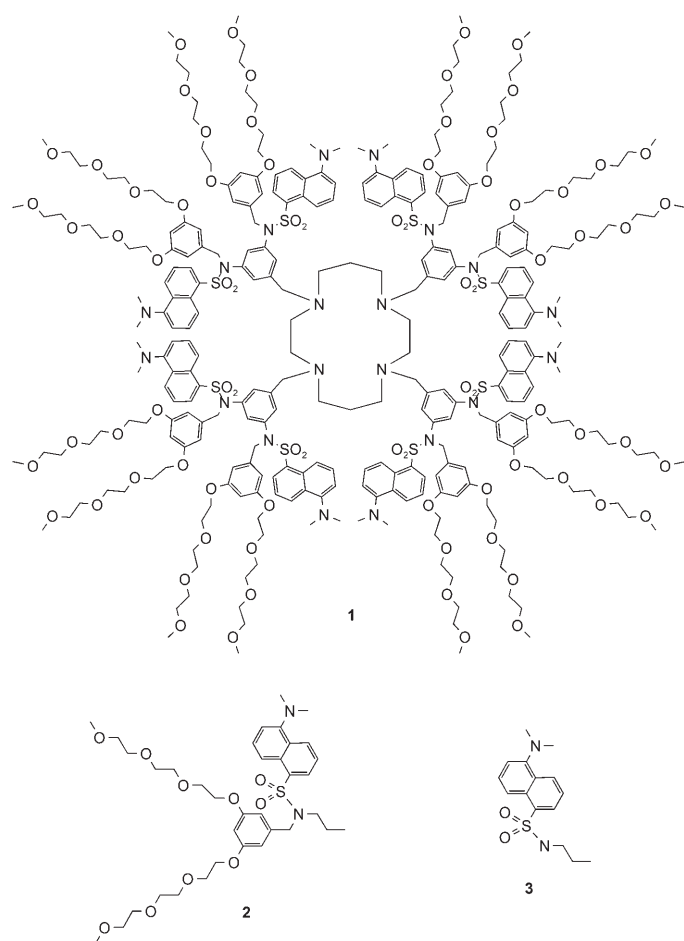

Figure 1. Absorption spectra of dendron 2 and reference compounds 3 and dimethoxybenzene (DMB) in acetonitrile at 298 K.

is almost exactly that expected on the basis of the spectra of the reference compound 3 and dimethoxybenzene. The small red shift of the dansyl band around 340 nm, which is due to a charge-transfer transition from the amine group to the aromatic moiety, suggests that in acetonitrile the dansyl unit of 2 experiences a slightly less polar environment than 3, presumably because of some wrapping by the oligoethylene glycol chains. Figure 2 shows that in 1 such a red-shift is more pronounced, indicating that in the dendrimer the dansyl unit indeed feels a less polar environment. As far the emission spectra are concerned (Figure 3), 3 shows the typical dansyl emission bands with $\lambda_{max} = 505$ nm, $\Phi = 0.30$, and $\tau = 12$ ns. Compound 2, which contains the fluorescent dansyl and dimethoxybenzene moieties ($\lambda_{max} = 310$ nm), shows only the dansyl band, slightly red-shifted ($\lambda_{max} = 522$ nm), with $\Phi = 0.30$, and $\tau = 13$ ns. These results indicate that the potentially fluorescent excited state of the dimethoxybenzene moiety is quenched by the nearby dansyl unit. Since the emission of the latter is not sensitized, the

mer 1 contains luminescent units (eight dansyl and eight dimethoxybenzene-type moieties) and three distinct types of multivalent basic sites (the cyclam core, the amine moieties of the eight dansyl units of the dendrimer branches, and the
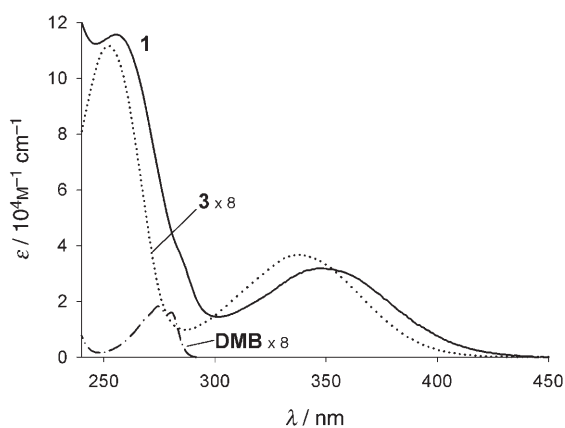
Figure 2. Absorption spectra of dendrimer **1** compared with those of its chromophoric units in acetonitrile at 298 K.

Figure 3. Emission spectra of the investigated compounds in acetonitrile at 298 K. The intensities are directly comparable since in all cases the excitation wavelength was 340 nm, the solution absorbance at the excitation wavelength was 0.20, and the same experimental set up was used.

quenching process most likely takes place by electron transfer.[24] In dendrimer **1**, the dansyl units maintain their strong fluorescence, slightly red-shifted (Figure 3; $\lambda_{max}=532$ nm, $\Phi=0.27$, and $\tau=15$ ns), and, as for **2**, no dimethoxybenzene emission is present.

Protonation: It is known that cyclam undergoes protonation in aqueous solution[18,25] as well as in other solvents.[26] In aqueous solution, the four successive pK_a values are 11.6, 10.6, 1.61, and 2.42,[18] showing that cyclam can be easily mono- and diprotonated, but further protonation is difficult. It is also interesting to note that the fourth pK_a value is larger than the third one, a result related to protonation-induced structural rearrangements. In dimethylformamide only two successive protonation steps have been observed with pK_a values of 9.3 and 7.5.[26] Studies performed on other dendrimers also showed that the cyclam core undergoes only two protonation reactions in a acetonitrile/dichloromethane 1:1 v/v solvent mixture.[16a,f]

It is also known that dansyl can be protonated at its amine moiety.[27] This process causes strong changes in the

absorption and emission spectra because of the charge-transfer nature of the dansyl bands. More specifically, protonation of model compound **3** causes the disappearance of the absorption bands with $\lambda_{max}=337$ and 252 nm, and of the emission band with $\lambda_{max}=505$ nm, and the concomitant appearance of the absorption ($\lambda_{max}=287$ nm) and emission ($\lambda_{max}=335$ nm, $\Phi=0.002$, $\tau<0.5$ ns) bands of protonated dansyl. We have found similar results for dendron **2**. Qualitatively, dendrimer **1** shows the same spectral changes (Figure 4), but the titration curves reveal a much more com-
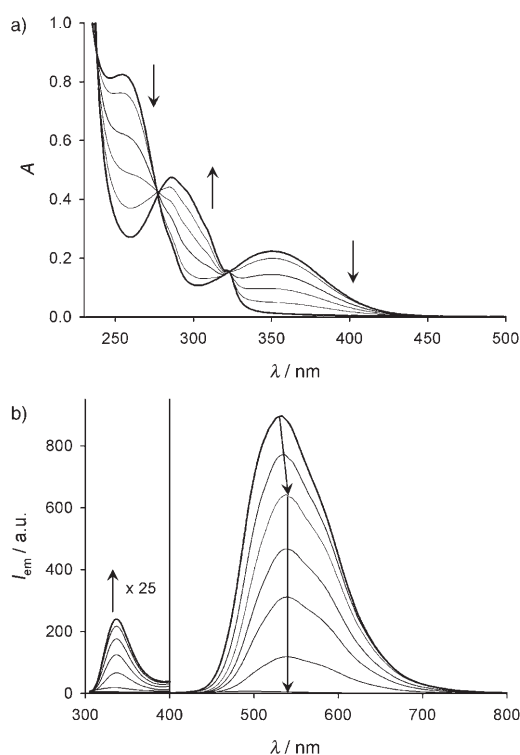

Figure 4. a) Absorption and b) emission spectra of **1** recorded during the titration with triflic acid in acetonitrile at 298 K. The final spectrum corresponds to the addition of 40 equivalents of acid. Excitation wavelength at an isosbestic point (270 nm).

plex behavior. In all cases, the initial spectrum could be obtained upon addition of a base (tributylamine).

In the case of the simple dansyl unit **3**, the titration plot (Figure 5) shows that upon acid addition the decrease of the dansyl absorption band around 340 nm and emission band at 516 nm is accompanied by a concomitant increase of the protonated dansyl absorption band at 284 nm and emission band at 335 nm. After addition of slightly more than one equivalent of acid, the dansyl emission is completely quenched and the protonated dansyl emission reaches a plateau. The comparison between compounds **2** and **3** (Figure 5) seems to suggest that **2** is easier to protonate than **3**. In the case of dendron **2** (Figure 5), however, the decrease of the dansyl absorption and emission bands and the increase of the protonated dansyl absorption band are not accompanied by a symmetric and parallel increase of the pro-
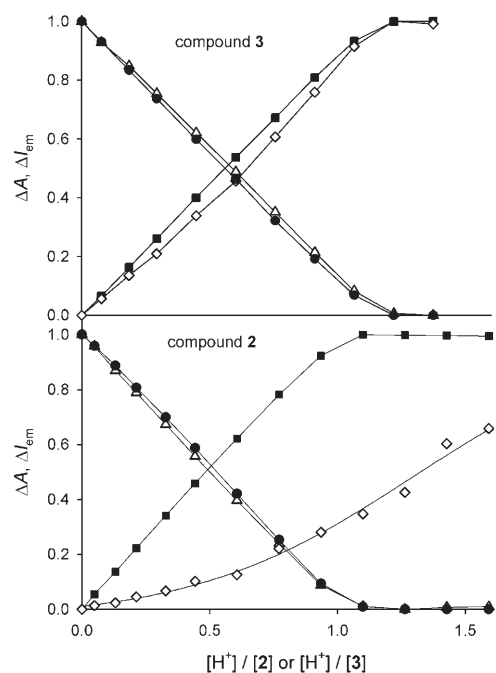
Figure 5. Normalized titration curves obtained for compounds **2** and **3** from absorption and emission measurements upon addition of triflic acid (acetonitrile, 298 K). Excitation at 270 nm in all cases. Absorbance values at 285 nm (full squares) and 342 nm (full circles). Emission intensity values at 335 nm (open rhombi), 505 nm (open triangles).
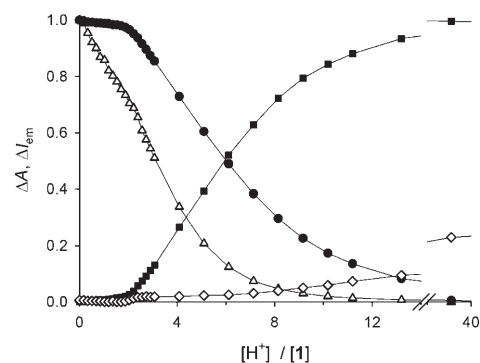

Figure 6. Normalized titration curves obtained for dendrimer **1** from absorption and emission measurements upon addition of triflic acid (acetonitrile, 298 K). Excitation at 270 nm in all cases. Absorbance values at 286 nm (full squares) and 348 nm (full circles). Emission intensity values at 335 nm (open rhombi), 532 nm (open triangles).

tonated dansyl emission. These results show that although protonation of the dansyl moiety does take place stoichiometrically also for dendron **2**, some process interferes with the emission of the excited state of the protonated species. Interestingly, such a process cannot be a simple quenching (regardless of the mechanism) by the moiety appended to the dansyl unit because all the quantities in Figure 5 are normalized to the values obtained at the end of the titration; in the case of the emission of protonated dansyl takes place after the addition of about one acid equivalent. The anomalous behavior of the emission of protonated dansyl could be accounted for by assuming that the excited state of protonated dansyl exhibits a lower proton affinity than the ground state. Since this is not the case for the simple dansyl unit **3**, the moiety appended to dansyl in **2** must be in some way responsible for the observed behavior. Our interpretation is that in **2** the protonated dansyl unit is partially enfolded by the oligoethylene glycol chains that can help the excited state deactivation by the known reversible proton-transfer mechanism.[28] As the concentration of acid increases, the oligoethylene glycol chains become more and more involved in ground-state proton interactions and their interference on the deactivation of the excited state of protonated dansyl decreases.

The titration plot of **1** (Figure 6) reveals an even more complex behavior. First of all, the absorbance at λ_{max} 348 nm of the dansyl units (Figure 2) is only slightly affected by acid addition until two protons have been added. In parallel, almost no increase at 286 nm is observed, showing that pro-

tonated dansyl units are not formed. These results can be straightforwardly explained by the fact that the first two added protons associate with the nitrogen atoms of the cyclam core (vide supra). The very small decrease of the dansyl absorbance at 348 nm caused by the first two protons (Figure 6) is actually due to a small red shift of the band, which can be ascribed to the effect of the positively charged core on the charge-transfer transition of the appended dansyl units. For more than two protons added, the parallel decrease at 348 nm and increase at 286 nm in absorption show that protonation of the eight dansyl units progressively takes place. It is worth noting that protonation of four out of eight dansyl units in the dendrimer (corresponding to 50% of absorbance change in Figure 6) is performed upon addition of six equivalents of acid. This result indicates that the first four dansyl units are protonated independently. As expected, protonation of the remaining dansyl units becomes more and more difficult as the overall charge of the dendrimer increases; complete protonation is obtained after addition of about 30 equivalents of acid, as mentioned above. The titration plots (Figure 6) also show that the decrease in intensity of the dansyl emission does not parallel the decrease of dansyl absorption. In fact, the emission intensity decreases even during the addition of the first two protons, that is, when protonation takes place at the cyclam core. Furthermore, the emission intensity becomes negligible after addition of about ten protons, that is, when, as shown by the absorption spectrum, 20% of the dansyl units are still unprotonated. The first result is ascribed to the influence of the positively charged core on the charge-transfer emission band, which actually undergoes a small red shift. As we will see later, a similar effect is also observed upon metal-ion coordination by the cyclam core. The larger than expected decrease of the dansyl emission intensity is due to electron-transfer quenching of the dansyl excited states by protonated dansyl units, as previously observed for other partially protonated polydansyl dendrimers.[29] Finally, it can be noted that the emission of the protonated dansyl units increases

very slowly on addition of acid. In fact, when, according to the changes in the absorption intensity, about 80% of the dansyl units are protonated, less than 5% of the protonated dansyl emission intensity is observed. As in the case of compound **2**, this effect can be ascribed to the fact that the protonated dansyl moieties of **1** are enfolded, presumably to a greater extent than in **2**, by the oligoethylene glycol chains, which can help the excited state deactivation by reversible proton transfer.

Metal-ion coordination: As mentioned in the introduction, dendrimer **1** contains three distinct types of multivalent, potentially coordinating sites: the cyclam core, the 16 oligoethylene glycol chains appended in the periphery, and the eight amine moieties of the dansyl units. Comparison with the behavior of dendron **2** and reference compound **3** can throw some light on the role played by each type of coordination sites. We have titrated **1**, **2**, and **3** in acetonitrile with Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Nd^{3+}, Eu^{3+}, and Gd^{3+}, as nitrate and/or triflate salts. In each experiment, the changes in the absorption and emission spectra of the dansyl moieties were monitored.

One can expect that coordination of the metal ion to the amine moiety of a dansyl chromophore has an effect similar to protonation, that is, a decrease in intensity of the absorption and emission bands at 337 and 505 nm, and the appearance of absorption and emission bands at 287 and 335 nm, respectively (vide supra). If the coordinated metal has low-lying metal-centered levels (e.g., Co^{2+}, Ni^{2+}, Cu^{2+}), and/or it is easy to reduce (e.g., Cu^{2+}), which implies the presence of low-energy ligand-to-metal charge-transfer levels, quenching of the coordinated dansyl emission band at 532 nm could also occur. Coordination of a metal ion to the cyclam core or the oligoethylene glycol chains of the dendrimer is also expected to affect the absorption and emission bands of dansyl. The vicinity of a charged metal ion could perturb the transition moments, thereby altering the intensities of the dansyl absorption and emission bands. Furthermore, oligoethylene glycol or cyclam complexes appended to the dansyl units could quench dansyl emission by energy and also by electron transfer, since dansyl can be easily oxidized ($E_{1/2} = 0.9$ V vs. SCE).[29]

The results obtained indeed show that titration of dendrimer **1** and reference compounds **2** and **3** with metal ions affects the dansyl absorption and emission bands in various ways. First of all it should be noted that in order to form metal complexes, ligands **1**–**3** must compete with solvent molecules and the counterions of the added metal ions. We have found indeed that the interaction of the metal ions with ligands **1**–**3** is much stronger when the counterion is triflate rather than nitrate (Figure 7). In fact, nitrate salts have been found to interact only with dendrimer **1**, not with compounds **2** and **3**.

Figure 8 shows the titration plots obtained on addition of Eu^{3+} (as triflate salt) to the "ligands" **1**, **2**, and **3**. These results show that each of the **1**–**3** ligands can coordinate Eu^{3+}. Analogous titration plots have been obtained in the case of
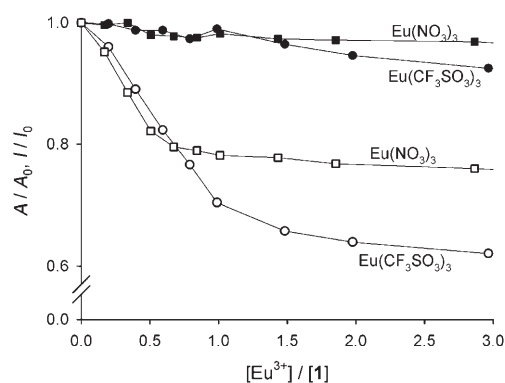

Figure 7. Changes in absorption (340 nm, full symbols) and emission (530 nm, open symbols) intensities observed for dendrimer **1** upon addition of Eu^{3+} triflate or nitrate (acetonitrile, 298 K). Excitation at 270 nm in all cases.
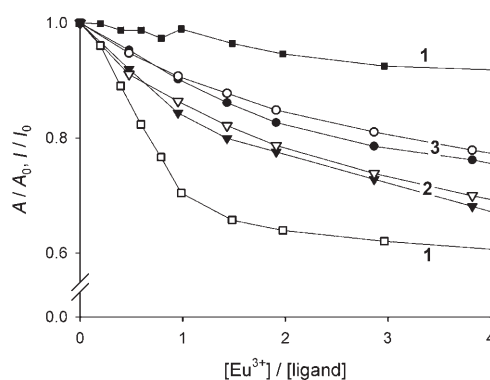

Figure 8. Changes in absorption (340 nm, full symbols) and emission (530 nm, open symbols) intensities observed for compounds **1**, **2**, and **3** upon addition of Eu^{3+} triflate (acetonitrile, 298 K). Excitation at 270 nm in all cases.

Nd^{3+} and Gd^{3+} and a qualitatively similar behavior was exhibited by Zn^{2+}.

For compounds **2** and **3**, metal-ion (as triflate salts) complexation causes parallel decrease in the intensities of the absorption and emission bands of dansyl as it happens upon dansyl protonation (vide supra). The appearance of an absorption band around 285 nm, and, in the case of **3**, also of an emission band at 335 nm, again similar to that found for protonated dansyl, is also observed. These results indicate that both **2** and **3** are able to coordinate metal ions by means of the amine moiety of the dansyl unit, albeit with a small association constant. Apparently, **2** is a slightly better ligand than **3**, presumably because the oligoethylene glycol chains help in keeping the metal ion coordinated to dansyl.

In the case of **1**, completely different results have been obtained (Figure 8): 1) a discontinuity can be observed in the titration plots at one equivalent of added metal ion, whereas no such discontinuity is found in the case of **2** and **3**; 2) addition up to one equivalent of the metal ion has quite different effects on absorption and emission, which was not the case for **2** and **3**; 3) the effect on the absorption band in **1** is smaller than in **2** and **3**, whereas the reverse is

true for emission band; 4) after addition of one equivalent of metal ion, the slopes of the absorption and emission plots in the case of **1** become smaller than those found for **2** and **3**. All these results demonstrate that in the case of dendrimer **1** the first equivalent of added metal ion is not coordinated by the dansyl moieties as for **2** and **3**, but by the cyclam core. It seems likely that the access of metal ion to the cyclam core is facilitated by transient complexation with the oligoethylene glycol chains. The presence of the charged metal ion in the core has a small effect on the dansyl absorption band, but a strong influence on the emission band, which becomes weaker and slightly red-shifted. It can also be noted that once the cyclam core has hosted a metal ion, further addition of metal ions implies coordination to the dansyl units, as shown by the decrease in intensity of both the absorption and emission dansyl bands with approximately the same slopes (Figure 8). Such slopes at high metal-ion concentration are smaller than those found for **2** and **3**, presumably because the presence of a positively charged metal ion in the cyclam core makes more difficult coordination of another positively charged metal ion by the dansyl units of the branches.
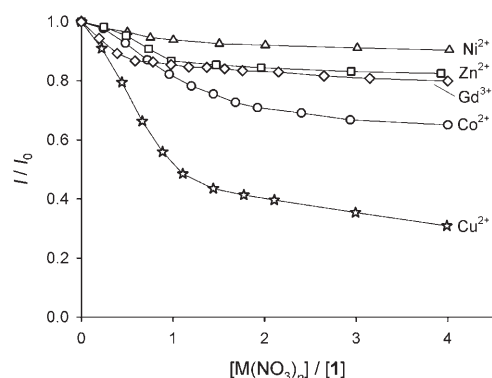

Figure 9. Changes in emission (530 nm) intensities observed for dendrimer **1** upon addition of nitrate salts (acetonitrile, 298 K). Excitation at 270 nm in all cases.

Figure 9 compares the results obtained monitoring the intensity of the dansyl emission band upon titration of dendrimer **1** with various metal ions as nitrate salts. Somewhat similar results were obtained upon titration with triflate salts. Clearly, there are effects strongly dependent on the chemical nature of the metal ion, with Cu^{2+} showing a quite distinct behavior that will be discussed below. In all cases, perhaps except for Co^{2+}, there is some discontinuity around one equivalent of added metal ion, as already discussed for the titration with triflate salts (see, e.g., the curve for **1** in Figure 8). This result suggests again that the first dendrimer site to be involved in metal coordination is the cyclam core. It should be pointed out that the slopes of the titration curves depend on two parameters, namely the association constant and the ability of the coordinated metal ion to quench, by any mechanism, the emission intensity of the dansyl units. As mentioned above, three quenching mecha-

nisms can be expected for metal ions coordinated to the cyclam core, namely 1) an effect of the positive charge of the metal ion on the emission transition moment, 2) an energy-transfer quenching when the metal ion has low-lying excited states, and 3) an electron-transfer quenching for metal ions that can be easily reduced (the oxidation potential of excited dansyl is ≈ -1.9 V vs. SCE).[6b] Energy- and electron-transfer quenching, of course, will play a role only if they can compete with the excited state lifetime of dansyl (ca. 15 ns). It should also be considered that the counterion, particularly in the case of nitrate salts, could play a role. Because so many parameters are involved, it is not easy to rationalize the results obtained. Among the metal ions used, Zn^{2+} and Gd^{3+} do not have low-lying metal-centered levels and are too difficult to oxidize or reduce. Therefore, when coordinated to the cyclam core, they should affect the dansyl emission only by a charge perturbation effect that is slightly stronger (Figure 9) for the metal carrying a higher charge (i.e., Gd^{3+}). The larger effect observed for Cu^{2+} could be attributed to either energy- or electron-transfer quenching. However, since Ni^{2+} and Co^{2+}, which have low-lying metal-centered excited states like the Cu^{2+} complexes, behave similarly to Zn^{2+}, we can conclude that the ability of Cu^{2+} to quench the dansyl excited state is related to the occurrence of an electron-transfer process. The lack of energy-transfer quenching is also apparent from the very similar behavior of Gd^{3+} and Nd^{3+}, and the fact that Eu^{3+} behaves like Gd^{3+} and Nd^{3+} suggests that quenching by electron transfer is not effective for Eu^{3+}. Other details of the observed results are difficult to interpret. For example, both Ni^{2+} and Co^{2+}, which have low-lying metal-centered levels, would be expected to exhibit a larger quenching effect that Zn^{2+}.

Conclusion

We have synthesized dendrimer **1** that contains 16 potentially luminescent moieties (eight dansyl- and eight dimethoxybenzene-type units) and three distinct types of multivalent sites (the cyclam nitrogen atoms, the amine moieties of the eight dansyl units, and the 16 oligoethylene glycol chains) that, in principle, can be protonated or coordinated to metal ions. We have investigated the absorption and luminescence properties of **1** in acetonitrile and the changes taking place upon titration with acid and a variety of divalent (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}), and trivalent (Nd^{3+}, Eu^{3+}, Gd^{3+}) metal ions as triflate and/or nitrate salts. The first site to be involved in the protonation (two equivalents of H^+) and metal coordination (one equivalent of metal ion) is the cyclam core, followed by the dansyl units. Once hosted by cyclam, the metal ion interacts with the appended dansyl units. The nature and extent of interaction depend in a complex way on the nature of the metal ion and of the counterion.

The results obtained show that: 1) cyclam is an ideal core for obtaining dendrimers capable of associating protons and

metal ions; 2) the dansyl chromophoric group is a useful unit to construct dendrimers sensitive to environment perturbations; 3) it is possible to design and construct dendrimers that, thanks to the integration of the properties of suitable components, can perform complex functions that derive from the integration of the specific properties of the constituent moieties. Therefore, such design is interesting for understanding relations between complex structure and multiple functionality.
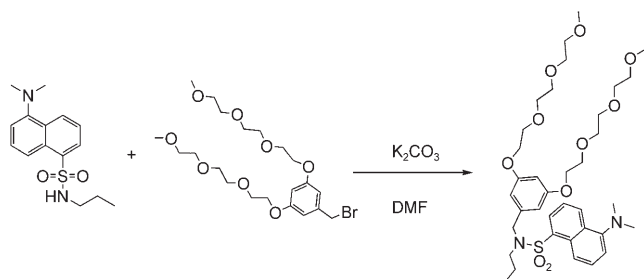
Experimental Section

General remarks: $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, and $Co(NO_3)_2 \cdot 6H_2O$ were commercial, high purity reagents. High purity triflic (CF_3SO_3H) acid and tributylamine were bought from Aldrich and used without further purification. Titration experiments of the studied compounds were performed in acetonitrile. Compound **3** was synthesized according to literature procedures.[30]
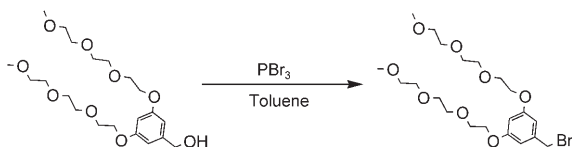
3,5-Bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzylbromide: Tribromophosphine (513 mg, 1.9 mmol, 0.18 mL) was added dropwise to a solution of 3,5-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzyl alcohol (2.0 g, 4.6 mmol) in toluene (30 mL) at 0°C and the resulting mixture was stirred for 3 h at RT. The reaction mixture was then poured on an equi-volumetric amount of ice–water and the resulting mixture was extracted three times with chloroform. The combined organic phases were dried over sodium sulphate and removed in vacuo. Purification by column chromatography (SiO_2: ethylacetate/methanol 20:1) yielded a colourless oil (1.6 g, 68%). ^{1}H NMR: (400 MHz, $CDCl_3$, 25°C): $\delta = 3.37$ (s, 6H; OCH_3), 3.53–3.74 (m, 16H; OCH_2), 3.83 (t, $^3J_{HH} = 5.09$ Hz, 4H; Ar-OCH_2CH_2O), 4.10 (t, $^3J_{HH} = 5.09$ Hz, 4H; Ar-OCH_2CH_2O), 4.39 (s, 4H; CH_2Br), 6.42 (t, $^4J_{HH} = 2.26$ Hz, 1H; Ar-H), 6.54 ppm (d, $^4J_{HH} = 2.26$ Hz, 2H; Ar-H); ^{13}C NMR: (100.6 MHz, $CDCl_3$, 25°C): $\delta = 33.52$ (Ar-CH_2Br), 59.02 (OCH_3), 67.60, 69.65, 70.59, 70.67, 70.85, 71.97 (OCH_2), 101.81, 107.93, 139.63, 160.04 ppm (C_{ar}).
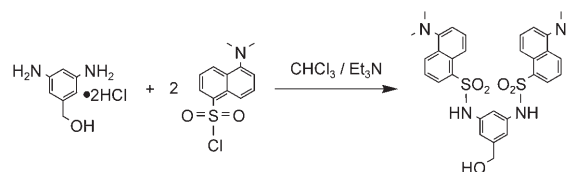
***N*-(3,5-Bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzyl)-*N*-propyl-(5′-dimethylaminonaphthalene-1′-sulfonic acid)amide (2)**: *N*-Propyl-(5′-di-

methylaminonaphthalen-1′-sulfonic acid)amide (292 mg, 1 mmol) was dissolved in DMF (30 mL) and potassium carbonate (571 mg) was added. To this solution, a solution of 3,5-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzylbromide (499.5 mg, 1 mmol) in DMF (60 mL) was added

dropwise. The resulting mixture was stirred for 1 day at RT and filtered, and the solvent was removed in vacuo. The residue was dissolved in dichloromethane and washed three times with water and saturated sodium hydrogen carbonate solution. The organic phase was then dried over sodium sulphate and removed in vacuo. The crude product was purified by column chromatography (SiO_2; dichloromethane/methanol 25/1) yielding a yellow foam (396 mg, 56%). ^{1}H NMR: (400 MHz, $CDCl_3$, 25°C): $\delta = 0.70$ (t, $^3J_{HH} = 7.33$ Hz, 3H; $CH_2CH_2CH_3$), 1.44 (sext, $^3J_{HH} = 7.33$ Hz, 2H; $^3J_{HH} = 7.58$ Hz, $CH_2CH_2CH_3$), 2.84 (s, 6H; N(CH_3)$_2$), 3.18(t, $^3J_{HH} = 7.58$ Hz, 2H; NHCH_2CH$_2$CH$_3$), 3.33 (s, 6H; OCH_3), 3.51–3.75 (m, 24H; OCH_2), 4.29 (s, 2H; ArCH_2N), 6.14 (s, 2H; Ar-H), 6.27 (s, 1H; Ar-H), 7.13 (d, $^3J_{HH} = 7.45$ Hz, 2H; dansyl-H), 7.46 (t, $^3J_{HH} = 8.46$ Hz, 2H; dansyl-H), 7.52 (t, $^3J_{HH} = 8.46$ Hz, 2H; dansyl-H), 8.22 (d, $^3J_{HH} = 7.33$ Hz, D2H; ansyl-H), 8.28 (d, $^3J_{HH} = 8.57$ Hz, 2H; dansyl-H), 8.48 ppm (d, $^3J_{HH} = 8.46$ Hz, 2H; dansyl-H); ^{13}C NMR: (100.6 MHz, $CDCl_3$, 25°C): $\delta = 11.1$ (CH_3), 22.0 (N-CH_2), 45.4 (N(CH_3)$_2$), 48.0 (NCH_2), 50.4 (Ar-CH_2N), 59.0, 67.2, 69.6, 70.6, 70.8, 71.9 (CH_2O), 101.2, 106.6, 115.0, 120.0, 123.2, 128.1, 130.0 130.1, 130.2, 135.1, 138.3, 151.9, 160.0 ppm (C_{Ar}); FAB-MS: m/z (%): 707.4 (100) [M+H]$^+$.

3,5-Bis(5′-dimethylaminonaphthalene-1′-sulfonamido)benzylalcohol: 3,5-Diaminobenzylalcohol dihydrochloride (1.6 g, 7.2 mmol) and triethyl-

amine (3.0 g, 4.1 mL, 30 mmol) were suspended in absolute chloroform (40 mL) and a solution of dansyl chloride (4.2 g) in chloroform (100 mL) was added dropwise over a period of 2.5 h. The reaction mixture was then stirred for 2 days at RT. The organic phase was then washed with water (2×), saturated sodium hydrogen carbonate, and water, and was dried over sodium sulphate and the solvent was removed in vacuo. The crude product is purified by column chromatography (SiO_2; dichloromethane/ethyl acetate : 1/1) yielding a yellow solid (2.4 g, 55%). ^{1}H NMR: (400 MHz, $CDCl_3$, 25°C): $\delta = 2.79$ (s, 12H; N(CH_3)$_2$), 4.13 (s, 2H; Ar-CH_2OH), 6.45 (d, $^4J_{HH} = 1.89$ Hz, 2H; Ar-H), 6.72 (t, $^4J_{HH} = 1.89$ Hz, 1H; Ar-H), 7.07 (d, $^3J_{HH} = 7.45$ Hz, 2H; dansyl-H), 7.25 (t, $^3J_{HH} = 8.46$ Hz, 2H; dansyl-H), 7.41 (t, $^3J_{HH} = 8.46$ Hz, 2H; dansyl-H), 7.52 (br s, 2H; N-H), 8.00 (d, $^3J_{HH} = 7.33$ Hz, 2H; dansyl-H), 8.23 (d, $^3J_{HH} = 8.57$ Hz, 2H; dansyl-H), 8.41 ppm (d, $^3J_{HH} = 8.46$ Hz, 2H; dansyl-H); ^{13}C NMR: (100.6 MHz, $CDCl_3$, 25°C): $\delta = 45.37$ (N(CH_3)$_2$), 63.95 (Ar-CH_2OH), 110.48, 114.45, 115.30, 118.59, 123.18, 128.62, 129.48, 129.72, 130.34, 130.87, 133.99, 137.69, 143.20, 151.88 ppm (C_{Ar}); FAB-MS: m/z (%): 604.1 (100) [M+H]$^+$.
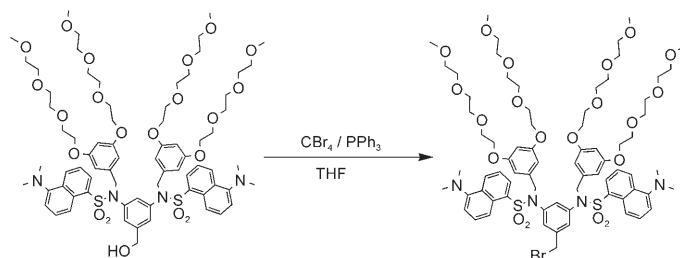
3,5-Bis(*N*-3′,5′-bis{2″-[2″-(2″-methoxyethoxy)ethoxy]ethoxy}benzyl-5′-dimethylamino-naphthalene-1′-sulfonamido)benzyl alcohol: A solution of
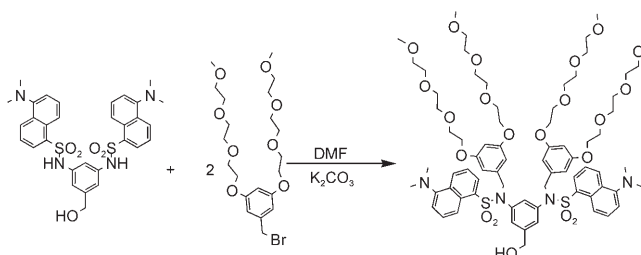
3,5-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzylbromide (1.5 g) in DMF (20 mL) was added dropwise to a solution of 3,5-bis(5′-dimethyl-

aminonaphthalene-1′-sulfonamido)benzyl alcohol (830 mg, 1.4 mmol) and potassium carbonate (950 mg, 6.9 mmol) in DMF (30 mL) and stirred for 3 days at RT. The solvent is removed in vacuo and the rest was dissolved in chloroform washed multiple times with water and saturated sodium hydrogen carbonate solution. The combined organic phases are dried over sodium sulphate and removed in vacuo. Purification by column chromatography (SiO$_2$: ethylacetate/methanol 7:1) yielded a yellow oil (1.5 g, 77%). ^{1}H NMR: (300 MHz, CDCl$_3$, 25°C): $\delta = 2.86$ (s, 12H; N-(CH$_3$)$_2$), 3.34 (s, 12H; OCH$_3$), 3.53–3.66 (m, 32H; OCH$_2$), 3.73 (t, $^3J_{HH} =$ 5.07 Hz, 8H; Ar-OCH$_2$CH$_2$O), 3.94 (t, $^3J_{HH} = 4.33$ Hz, 8H; Ar-OCH$_2$CH$_2$O), 4.10 (s, 2H; Ar-CH$_2$OH), 4.52 (s, 4H; CH$_2$N), 6.27 (d, $^4J_{HH} = 2.07$ Hz, 4H; Ar-H), 6.33 (t, $^4J_{HH} = 1.88$ Hz, 2H; Ar-H), 6.66 (d, $^4J_{HH} = 1.70$ Hz, 2H; Ar-H), 6.92 (s, 1H; Ar-H), 7.08 (d, $^3J_{HH} = 7.16$ Hz, 2H; dansyl-H), 7.17 (t, $^3J_{HH} = 7.54$ Hz, 2H; dansyl-H), 7.36 (t, $^3J_{HH} =$ 8.29 Hz, 2H; dansyl-H), 7.94 (d, $^3J_{HH} = 7.72$ Hz, 4H; dansyl-H), 8.49 ppm (d, $^3J_{HH} = 8.29$ Hz, 2H; dansyl-H); ^{13}C NMR: (100.6 MHz, CDCl$_3$, 25°C): $\delta = 45.43$ (N(CH$_3$)$_2$), 54.53 (NCH$_2$), 58.97 (OCH$_3$), 63.61 (CH$_2$OH), 67.39, 69.57, 70.51, 70.59, 70.70, 71.91 (OCH$_2$), 101.58, 107.26, 115.11, 119.69, 123.14, 126.73, 127.91, 128.56, 129.81, 130.17, 130.73, 130.92, 133.80, 137.92, 139.38, 142.64, 151.63, 159.85 ppm (C$_{Ar}$); FAB-MS: m/z (%): 1433.7 (35) [M+H]$^+$.

3,5-Bis(N-3′,5′-bis{2″-[2″-(2″-methoxyethoxy)ethoxy]ethoxy}benzyl-5′-dimethylaminonaphthalene-1′-sulfonamido)benzyl bromide: 3,5-bis(N-3′,5′-bis{2″-[2″-(2″-methoxyethoxy)ethoxy]ethoxy}benzyl-5′-dimethylamino-

naphthalene-1′-sulfonamido)benzyl alcohol (1.0 g, 0.7 mmol) and tetrabromomethane (350 mg, 1.1 mmol) were dissolved in THF (10 mL). Triphenylphosphine (275 mg, 1.1 mmol) were added in portions. The reaction mixture was then poured on an equi-volumetric amount of ice–water and the resulting mixture was extracted three times with chloroform. The combined organic phases were dried over sodium sulphate and the solvent was removed in vacuo. Purification by column chromatography (SiO$_2$: ethylacetate/methanol 10:1) yielded a yellow oil (640 mg, 59%). ^{1}H NMR: (400 MHz, CDCl$_3$, 25°C): $\delta = 2.88$ (s, 12H; N(CH$_3$)$_2$), 3.37 (s, 12H; OCH$_3$), 3.49–3.68 (m, 32H; OCH$_2$), 3.75 (t, $^3J_{HH} = 5.07$ Hz, 8H; Ar-OCH$_2$CH$_2$O), 3.87 (s, 2H; Ar-CH$_2$Br), 3.96 (t, $^3J_{HH} = 4.33$ Hz, 8H; Ar-OCH$_2$CH$_2$O), 4.54 (s, 4H; CH$_2$N), 6.27 (d, $^4J_{HH} = 2.07$ Hz, 4H; Ar-H), 6.35 (t, $^4J_{HH} = 1.88$ Hz, 2H; Ar-H), 6.57 (d, $^4J_{HH} = 1.70$ Hz, 2H; Ar-H), 6.99 (s, 1H; Ar-H), 7.09 (d, $^3J_{HH} = 7.16$ Hz, 2H; dansyl-H), 7.25 (t, $^3J_{HH} =$ 7.54 Hz, 2H; dansyl-H), 7.36 (t, $^3J_{HH} = 8.29$ Hz, 2H; dansyl-H), 7.87 (d, $^3J_{HH} = 7.35$ Hz, 4H; dansyl-H), 7.97 (d, $^3J_{HH} = 8.66$ Hz, 4H; dansyl-H), 8.49 ppm (d, $^3J_{HH} = 8.47$ Hz, 2H; dansyl-H); ^{13}C NMR: (100.6 MHz, CDCl$_3$, 25°C): $\delta = 31.50$ (CH$_2$Br), 45.46 (N(CH$_3$)$_2$), 54.46 (NCH$_2$), 59.01 (OCH$_3$), 67.43, 69.64, 70.55, 70.62, 70.74, 71.95 (OCH$_2$), 101.59, 107.20, 115.27, 119.52, 123.19, 128.16, 128.61, 129.71, 129.82, 130.08, 130.86, 131.03, 133.56, 137.77, 138.52, 139.67, 151.99, 159.97 ppm (C$_{Ar}$); FAB-MS: m/z (%): 1497.7 (20) [M+H]$^+$.

1,4,8,11-Tetra[3,5-bis(N-3′,5′-bis{2″-[2″-(2″-methoxyethoxy)ethoxy]ethoxy}benzyl-5″-dimethylaminonaphthalene-1″-sulfonamido)benzyl]-1,4,8,11-tetraazacyclotetradecane (1): Cyclam (11 mg, 5.5×10^{-5} mol), 3,5-bis(N-3′,5′-bis{2″-[2″-(2″-methoxyethoxy)ethoxy]ethoxy}benzyl-5′-dimethylaminonaphthalen-1′-sulfonamido)benzyl bromide (411 mg, 27.5×10^{-5} mol) and potassium carbonate (91 mg, 66×10^{-5} mol) were dissolved in acetonitrile (30 mL) and stirred for 5 days at RT. The solvent was removed in vacuo and the residue was dissolved in chloroform (30 mL). The organic
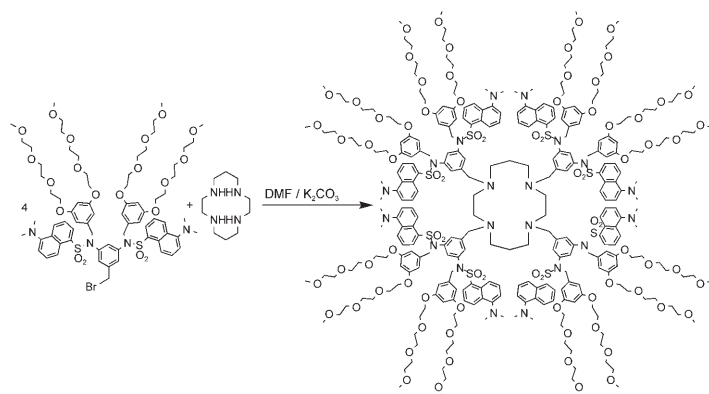
phase was then washed with water and saturated sodium hydrogen carbonate, and dried over sodium sulphate; the solvent was then removed in vacuo. The crude product was purified by column chromatography (SiO$_2$; ethyl acetate/methanol 2:1) yielding a fluorescent yellow oil (140 mg, 44%). ^{1}H NMR:(400 MHz, CDCl$_3$, 25°C): $\delta = 1.28$ (s, 4H; CH$_2$), 2.01 (s, 8H; CH$_2$N), 2.13 (s, 8H; CH$_2$N), 2.75 (s, 48H; N(CH$_3$)$_2$), 3.08 (s, 8H; Ar-CH$_2$N), 3.32 (s, 48H; OCH$_3$), 3.47–3.62 (m, 160H; OCH$_2$), 3.76 (t, $^3J_{HH} =$ 5.18 Hz, 32H; Ar-OCH$_2$CH$_2$O), 4.45 (s, 16H; CH$_2$N-SO$_2$), 6.14 (d, $^4J_{HH} =$ 1.89 Hz, A16H; r-H), 6.22 (s, 8H; Ar-H), 6.88 (s, 4H; Ar-H), 6.91 (s, 8H; Ar-H), 6.99 (d, $^3J_{HH} = 7.40$ Hz, 8H; dansyl-H), 7.18 (t, $^3J_{HH} = 8.46$ Hz, 8H; dansyl-H), 7.23 (t, $^3J_{HH} = 8.21$ Hz, 8H; dansyl-H), 7.88 (d, $^3J_{HH} = 7.20$ Hz, 8H; dansyl-H), 7.97 (d, $^3J_{HH} = 8.72$ Hz, 8H; dansyl-H), 8.36 ppm (d, $^3J_{HH} = 8.46$ Hz, 8H; dansyl-H); ^{13}C NMR: (100.6 MHz, CDCl$_3$, 25°C): $\delta =$ 45.60 (N(CH$_3$)$_2$), 55.34 (NCH$_2$), 59.21 (OCH$_3$), 67.45, 69.76, 70.73, 70.78, 70.86 (OCH$_2$), 101.38, 106.97, 115.32, 119.83, 123.33, 128.14, 128.37, 129.90, 130.34, 130.93, 134.45, 138.66, 140.10, 142.08, 151.81, 160.01 ppm (C$_{Ar}$); MALDI-TOF-MS: m/z (%): 5864.1 (20) [M+H]$^+$.

Photophysical experiments: The experiments were carried out in air-equilibrated acetonitrile at 298 K. UV/Vis absorption spectra were recorded with a Perkin Elmer λ40 spectrophotometer, using quartz cells with a path length of 1.0 cm. Fluorescence spectra were obtained with a Perkin Elmer LS-50 spectrofluorimeter, equipped with a Hamamatsu R928 phototube, on air-equilibrated solutions. Excitation was performed at 270 nm, which corresponds to an isosbestic point both in the protonation and metal-coordination experiments. Fluorescence lifetime measurements were performed by time-correlated single-photon counting (0.5 ns time resolution) with a D$_2$ lamp. The estimated experimental errors are: ± 2 nm on the band maximum, ± 5% on the molar absorption coefficient, and ± 5% on the pK values.

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