Searching for New Luminescent Sensors: Synthesis and Photophysical Properties of a Tripodal Ligand Incorporating the Dansyl Chromophore and of Its Metal Complexes

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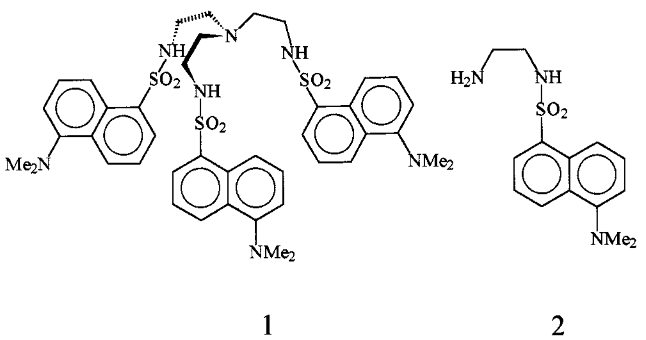
The new tripodal ligand **1** containing the dansyl chromophore has been synthesized and characterized. The intense luminescence characteristic of the chromophore is maintained in the ligand structure, showing that no intramolecular interactions are present. This ligand has been shown to complex in acetonitrile/water solutions only with Cu^{2+}, Co^{2+}, Zn^{2+}, and Cd^{2+} ions, with concomitant pronounced changes in the fluorescence spectra. The complexation is controlled by pH conditions: at neutral pH this ligand shows a remarkable selectivity towards Cu^{2+} ions, suggesting a possible use for **1** as a luminescent chemosensor for this ion.

Photoluminescence spectroscopy has recently attracted increasing attention in the scientific community as it has been finding applications in growing fields of great economic and social impact, such as medical diagnostics, environmental sciences, cell biology and molecular electronics.[1−5] In particular, the synthesis, characterization, and application of many luminescent sensors has opened up many opportunities for solving complex analytical problems. The sensitivity and versatility of luminescence spectroscopy make it a particularly suitable technique for analytical applications, giving for example the possibility of monitoring analyte concentrations in real-time and real-space.[2−5]

Of particular interest is the measurement of the concentrations of transition-metal ions, since many of these are also pollutants in environmental systems and essential trace elements in biological systems. For these reasons, many fluorescent sensors for these metal ions have been synthesized and characterized.[3−5] In this context, we have synthesized the ligand tris[2-(5-dimethylamino-1-naphthalenesulphonamido)ethyl]amine (**1**), a new tripodal ligand incorporating the dansyl chromophore. Its luminescent properties have been widely used in order to obtain fluorescent sensors and labels,[6−15] especially in the field of biochemistry for peptides and amino acids. We report here the synthesis and the luminescence properties of this ligand and its metal complexes, as well as luminescence studies of (dansylethylenediamine)metal complexes **2** to provide a more in-depth investigation of the photophysics of such a widely used chromophore.

Results

All the photophysical experiments were carried out in acetonitrile/water (1:1, v/v) solutions. The absorption spectrum of **1** (Figure 1) was very similar in shape to the absorption spectrum of **2**, but it was three times more intense, as would be expected given the presence of three chromophoric groups in **1**. As far as the fluorescence properties are concerned, as can be seen from Table 1, compounds **1** and **2** have very similar spectra and exhibit similar lifetimes and quantum yields. The absorption spectra and fluorescence properties of **1** and **2** do not depend on the pH conditions in the range 3−11.



1 2

Scheme 1

As can be seen from Figure 2 and Table 1, strong changes in the luminescence properties of **1** were indeed observed upon addition of Cu^{2+}, Co^{2+}, Zn^{2+}, and Cd^{2+} at pH = 9.5. In particular, for the first two metal ions, a strong quenching (I_{rel} = 1%, Table 1) of the fluorescence intensity was observed, while for Zn^{2+} and Cd^{2+} a blue shift, accompanied by an enhancement of the quantum yield, could be detected.

Smaller, but non-negligible changes could also be observed at these pH conditions in the absorption bands of **1** upon addition of Co^{2+}, Zn^{2+}, Cd^{2+}, and Cu^{2+} (Figure 1). A blue shift of the fluorescence band of **1** was also observed upon addition of Ag^{+} and Hg^{2+} metal ions; however, precipitation of the metal ions before reaching complete complexation prevented further investigations. Similar effects caused by addition of Cu^{2+} ions were observed in the absorption and luminescence spectra of compound **2**, while

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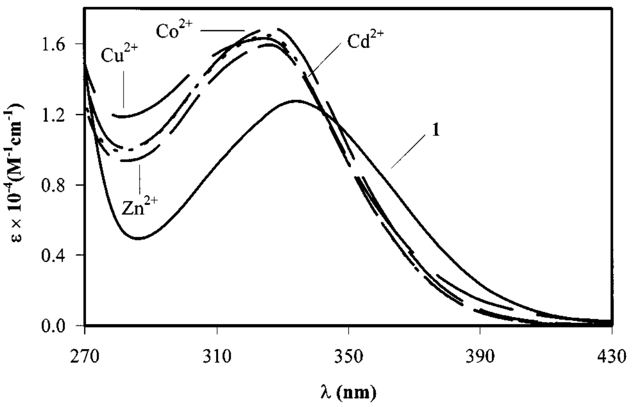

Figure 1. Absorption spectra of **1** and of its complexes with Cu^{2+}, Co^{2+}, Cd^{2+}, and Zn^{2+} in acetonitrile/water (1:1, v/v) solutions at pH = 9.5

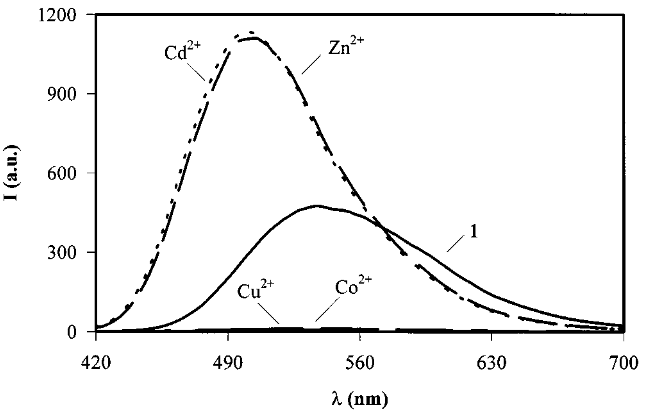

Figure 2. Fluorescence spectra (λ_{exc} = 340 nm) of **1** and of its complexes with Cu^{2+}, Co^{2+}, Cd^{2+}, and Zn^{2+} in acetonitrile/water (1:1, v/v) solutions at pH = 9.5

Table 1. Photophysical properties of ligands **1** and **2** and of their complexes with transition-metal ions in water/acetonitrile (1:1, v/v) at pH = 9.5

	Absorption		Luminescence				
			room temp.			77 K	
	λ_{max} [nm]	ε_{max} [$M^{-1}cm^{-1}$]	λ_{max} [nm]	τ [ns]	I_{rel}	λ_{max} [nm]	I_{rel}
1	334	12700	540	10	100	536	100
[Cu(**1**)]⁻	324	16300	540	10	1[a]	536	2[a]
[Co(**1**)]⁻	327	16900	540	10	1[a]	536	2.5[a]
[Zn(**1**)]⁻	326	16000	500	12	370	495	250
[Cd(**1**)]⁻	326	16500	500	12	370	495	250
2	334	4300	540	10	100	536	100
[Cu(**2**)$_2$]	325	5200	540	< 0.5	< 1	536	< 1

[a] This residual luminescence can be ascribed to an impurity of a luminescent dansyl derivative present in the sample. For more details, see text.

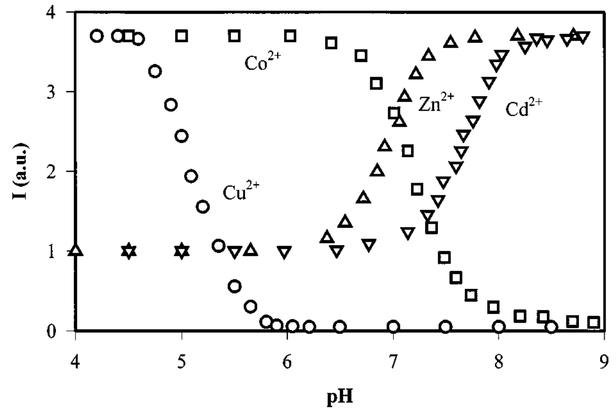

Figure 3. pH dependence of the fluorescence intensity (λ_{exc} = 340 nm) for solutions containing equimolar amounts (8 × 10^{-5} M) of **1** and (i) Cu^{2+} ions (λ_{em} = 540 nm), (ii) Co^{2+} ions (λ_{em} = 540 nm), (iii) Zn^{2+} ions (λ_{em} = 500 nm), and (iv) Cd^{2+} ions (λ_{em} = 500 nm); superimposable titration profiles have been obtained starting from pH = 11 upon addition of acid

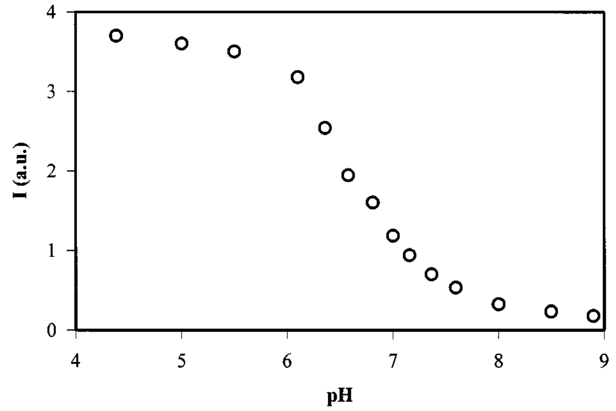

Figure 4. pH dependence of the fluorescence intensity (λ_{exc} = 340 nm, λ_{em} = 540 nm) for a solution containing equimolar (8 × 10^{-5} M) amounts of **2** and Cu^{2+}; superimposable titration profiles have been obtained starting from pH = 11 upon addition of acid

addition of Co^{2+} ions did not cause any change in its photophysical properties. An increase in the luminescence intensity of **2** was observed upon addition of Zn^{2+} and Cd^{2+}, but the formation of the metal hydroxide prevented the formation of the complex.

Addition to a 5 × 10^{-5} M solution of **1** and **2** of up to 10 molar equiv. of Na^{+}, K^{+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Eu^{3+}, Ni^{2+}, Mn^{2+}, Pb^{2+}, Fe^{2+}, Fe^{3+}, and Cr^{3+} did not lead to any change in the absorption and emission spectra of the dansyl derivatives in all the pH range examined (3−11). Furthermore, no effects were found on the absorption and luminescence spectra upon addition of up to 10 equiv. of the aforementioned metal ions to a solution containing equimolar amounts of **1** and Zn^{2+} or Cu^{2+} ions.

The observed changes for **1** and **2**, as can be seen from Figures 3 and 4, respectively, were very sensitive to the pH conditions: They were almost negligible at pH values lower than 4, and reached a plateau at higher pH, the pattern being characteristic for the ligand and the metal ion. This behavior is fully reversible; superimposable titration profiles have been obtained starting from pH = 11 upon addition of acid.

Titration experiments were performed in order to investigate the stoichiometry of the complexes formed, by adding the metal ion to a basic (pH = 9.5) solution of the ligand. Titrations of **1** and **2** with Cu^{2+} are shown in Figure 5. These experiments always indicate a 1:1 (metal/ligand) stoichiometry for **1**, while for **2** there is evidence of a 1:2 (metal/

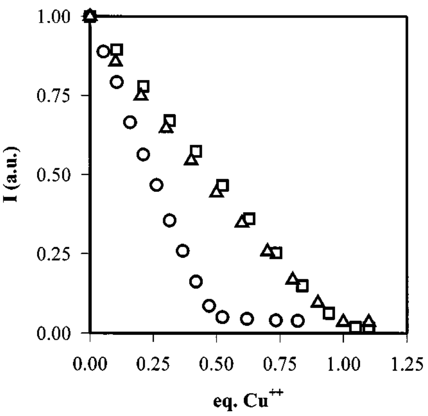

Figure 5. Dependence of the fluorescence intensity (λ_{exc} = 340 nm, λ_{em} = 540 nm) of a solution (i) containing **2** (8 × 10^{-5} M) at pH = 9.5 (open circles), (ii) containing **1** (8 × 10^{-5} M) at pH = 9.5 (open triangles), and (iii) containing **1** (8 × 10^{-5} M), Zn^{2+}, Co^{2+}, and Cd^{2+} (1.6 × 10^{-4} M) at pH = 6.5 (open squares) upon addition of Cu^{2+}

ligand) stoichiometry. On adding up to 2 equiv. of Co^{2+}, Zn^{2+}, and Cd^{2+} ions to a solution of **1** at pH = 6.5 no changes in the luminescence properties of the ligand were observed. Titration of the same solution containing the aforementioned ions with Cu^{2+} ions led to the same pattern as shown for the titration at pH = 9.5 (Figure 5). These results clearly indicate that under these conditions only the copper ions can induce changes in the luminescence properties of **1**, and no interferences come from the other metal ions.

Addition of NaOH to a solution containing an equimolar amount of metal ion and ligand **1** (Figure 6) showed that for Co^{2+}, Zn^{2+}, and Cd^{2+} the plateau of the luminescence intensity vs. added base is reached after addition of 3 equiv. of base. For Cu^{2+}, the complete quenching of the luminescence was observed after addition of 2 equiv. of base while further changes were observed in the absorption bands of the dansyl chromophores until the addition of 3 equiv. (Figure 7). Strong changes were also observed for the metal-centered absorption bands of the copper ion in the 450–1100 nm region (Figure 8). Addition of up to 2 equiv. of base to an equimolar (1 × 10^{-3} M) solution of **1** and Cu^{2+} led to the appearence of a band with maximum at 620 nm, while addition of a third equivalent caused the disappearence of such a band with the concomitant formation of a band centered at 1050 nm.

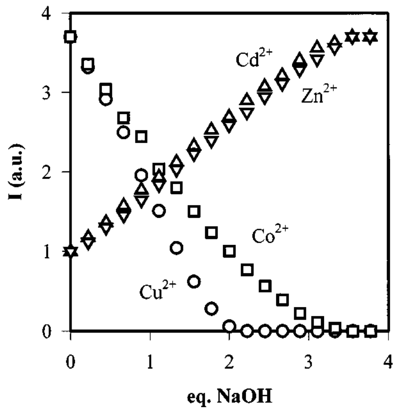

Figure 6. Dependence of the fluorescence intensity (λ_{exc} = 340 nm) for solutions containing equimolar amounts (8 × 10^{-5} M) of **1** and (i) Cu^{2+} ions (λ_{em} = 540 nm), (ii) Co^{2+} ions (λ_{em} = 540 nm), (iii) Zn^{2+} ions (l_{em} = 500 nm), and (iv) Cd^{2+} ions (λ_{em} = 500 nm) upon addition of NaOH

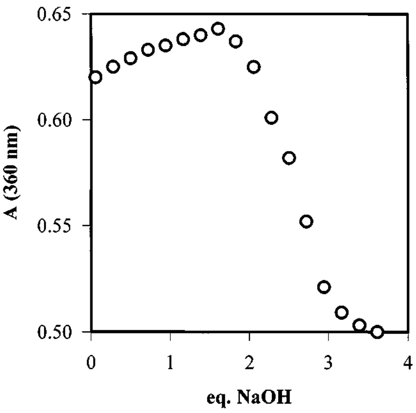

Figure 7. Dependence of the absorbance at 360 nm of a solution containing **1** and Cu^{2+} (8 × 10^{-5} M) upon addition of NaOH

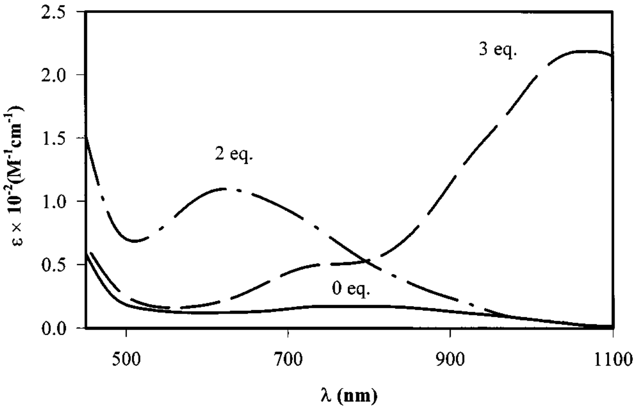

Figure 8. Cu^{2+}-centered absorption bands in the presence of one equiv. of **1** in acetonitrile/water (1:1, v/v) after the addition of various amounts of NaOH

By contrast, for **2** and Cu^{2+} complete quenching of the luminescence was observed after addition of 1 equiv. of base relative to the ligand.

Discussion

Dansylamide and its derivatives typically show intense and large luminescence bands in the 400–600-nm region. These bands are very sensitive to the polarity of the solvent and have considerable charge-transfer character, caused by mixing of the ^1L_a and ^1L_b states of naphthalene with a charge-transfer state arising from the promotion of a lone-pair electron on the amino group into a π antibonding orbital of the naphthalene ring.[16] The photophysical behavior of **1** and **2** is in agreement with the data obtained with other dansyl derivatives.[6–16] The constancy of the photophysical properties on passing from compound **1** to dansylamide and the ligand **2** shows that intramolecular interactions between the three chromophores in **1** are negligible.

Complexes with Cu^{2+}

Addition of Cu^{2+} ions to a neutral water/acetonitrile (1:1, v/v) solution of **1** and **2** caused a strong decrease in the fluorescence intensity and lifetime of the ligands. The quenching observed for **2** has been explained, as already reported for other dansyl derivatives, as being due to the complex formation by the amino group, followed by abstraction of the sulphonamide hydrogen atom.[9−10,17] For compound **2** (Figure 5) evidence for the formation of a complex with a 2:1 (ligand/metal ion) stoichiometry could be seen, although a 1:1 stoichiometry at higher metal concentration cannot be ruled out.[11] The observation of a plateau after addition of an equimolar amount of base in respect to the ligand is further evidence for the mechanism involving the deprotonation of the sulphonamide group for obtaining the quenched species.

A similar complexation/deprotonation mechanism can also be invoked for **1**, but with some differences. The first one is the evidence, from titration experiments, of the formation of a complex with 1:1 stoichiometry between **1** and Cu^{2+}. In addition, the pattern shown by the fluorescence spectra clearly indicates that an almost complete quenching is reached after addition of two equiv. of base (Figure 6), i.e. with the formation of a neutral complex obtained with the deprotonation of only two dansyl moieties. Under these conditions a residual luminescence with a relative intensity of 1% is observed that has an unquenched lifetime. This residual luminescence can be ascribed to an impurity of a luminescent dansyl derivative present in the sample. The further deprotonation of the third side arm, demonstrated by the changes in the absorption spectra (Figures 7 and 8), is obtained only in a second step at $pH > 7.5$ with the addition of the third equivalent of base.

In principle, the quenching effect after the formation of the complex can be ascribed for both **1** and **2** to either a dansyl-to-metal energy-transfer (ET) or a metal-to-dansyl electron-transfer (eT) mechanism. From the intensity data obtained, lower limits of the quenching rate constants at room temperature and at 77 K can be calculated for **1** by using Equation 1, and are $1 \times 10^{-10}\ s^{-1}$ and $5 \times 10^{-9}\ s^{-1}$, respectively. The high value of the estimated quenching rate constant at 77 K suggests at least a contribution from the ET mechanism.

$$k_q = 1/\tau^\circ(I^\circ/I - 1) \qquad (1)$$

The almost complete quenching of **1** after deprotonation of only two dansyl derivatives suggests that under these conditions the third side arm lies in close contact to the metal ion.

It is important to note that the formation of the Cu complex occurs at lower pH values for **1** than for **2**. This observation, together with the different stoichiometry observed for the two ligands, confirms the co-operative effect of the three side arms of the tripodal ligand **1**.

Complexes with Co^{2+}

As reported above, no changes in absorption and fluorescence spectra were observed on adding Co^{2+} ions to a solution of **2**. In contrast, at pH values higher than 7, a quenching ($I_{rel} = 1\%$, Table 1) of the fluorescence intensity of **1** is observed, and titration experiments revealed a 1:1 (ligand/metal) stoichiometry of the complex. In this case, a simultaneous deprotonation of all the three dansyl moieties is observed from titration experiments (Figure 6). As discussed previously, a dansyl-to-Co energy-transfer (ET) or a Co-to-dansyl electron-transfer (eT) mechanism can be invoked to explain the observed fluorescence quenching, although its high efficiency at 77 K (Table 1) again suggests a contribution from the energy-transfer mechanism. As proposed for the Cu^{2+} complex, a co-operative effect of the three arms of the ligand **1** has to be invoked in order to explain the different behaviour of the two ligands examined.

Complexes with Zn^{2+} and Cd^{2+}

As reported above, addition of Zn^{2+} and Cd^{2+} ions to basic water/acetonitrile solutions of **1** caused a noticeable blue-shift in their fluorescence bands, with a concomitant increase in the quantum yield and lifetime. This effect can also be explained in terms of the formation of a complex by the amino group, followed by the deprotonation of the sulphonamide hydrogen atoms. As already known, complexation with d^{10}-Zn^{2+} and -Cd^{2+} ions does not usually introduce low-energy metal-centered or charge-separated excited states into the molecule, so that ET and eT processes cannot usually occur. However, the deprotonation/complexation process increases the electronic density on the naphthalene ring, moving towards higher energy the amine-to-naphthalene charge-transfer state present in the dansyl chromophore. A hypsochromic shift with a concomitant increase of the luminescence intensity is also observed for dansyl derivatives upon raising the energy of this excited state using low-polar solvents.[16] Complexes with a 1:1 (ligand/metal ions) stoichiometry are obtained for **1** with both Zn^{2+} and Cd^{2+}, and as observed for the Co^{2+} ions, a simultaneous deprotonation of all the three dansyl groups takes place (Figure 6). For ligand **2**, formation of the complexes occurs at higher pH values, but the competitive formation and precipitation of the metal hydroxide prevents the complete formation of the complexes.

The results obtained with Na^+, K^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Eu^{3+}, Ni^{2+}, Mn^{2+}, Pb^{2+}, Fe^{2+}, Fe^{3+}, and Cr^{3+}, both by direct and by competition experiments, indicate that these metal ions do not interfere with the complexation of Cu^{2+}, Co^{2+}, Zn^{2+} and Cd^{2+} ions. Finally, it is worth noting that among the latter ions, **1** shows a remarkable affinity and selectivity towards the Cu^{2+} ions, as can be seen from the titration experiment performed in the presence of the other possible interfering metal ions (Figure 5). The pH window in which the complete quenching occurs is quite large (Figure 3) compared with that of other chemosensors for Cu^{2+}.[18−20] All these features make **1** a good candidate for a possible use as chemosensor for copper ions.

Conclusions

Tris[2-(5-dimethylamino-1-naphthalenesulphonamido)-ethyl]amine (**1**), a new tripodal ligand, has been synthesized and characterized, and the results compared with dansylethylenediamine (**2**), a compound that has been widely used as a reference for many other dansyl derivatives. The fluorescence properties of **1** are not unexpected considering the presence of three non-interacting dansyl moieties. Strong changes were observed upon addition of Cu^{2+}, Co^{2+}, Zn^{2+}, and Cd^{2+}, indicating a strong complexation leading to deprotonation of the sulphonamide groups of the dansyl moieties for all of them. For Cu^{2+} and Co^{2+}, a strong quenching was observed both at room temperature and at 77 K, that can be ascribed to energy- or electron-transfer processes, although the first possibility seems to be the most likely. For Zn^{2+} and Cd^{2+}, a shift of the fluorescence band toward lower wavelengths was observed with a concomitant increase of fluorescence quantum yield and lifetime. This phenomenon can be explained by a higher electronic density on the naphthalene ring of the dansyl groups after the deprotonation/complexation process. For all the metal ions, **1** was found to form stronger complexes than **2**, indicating a co-operative effect of the three arms of the tripodal ligand. Furthermore, **1** shows a remarkable affinity and selectivity towards the Cu^{2+} ions at pH > 4, suggesting a possible use of this ligand as luminescent chemosensor for these ions.

Experimental Section

General: The following materials were used: dansyl chloride (Aldrich), tris(2-aminoethyl)amine, “TREN” (Aldrich), triethylamine (Aldrich); sodium hydroxide, copper(II) nitrate hemipentahydrate, cobalt(II) and zinc(II) hexahydrate, and cadmium(II) nitrate tetrahydrate were obtained from Fluka. − Dansylethylenediamine (**2**) was a gift from Prof. Marchelli and Dr. Corradini of the University of Parma, and was available from previous work.[9] − Thin-layer-chromatographic analysis was performed using precoated TLC silica gel plates (60 F-254, Merck). − ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 20°C with a Varian 500 FT spectrometer.

Tris[2-(5-dimethylamino-1-naphthalenesulphonamido)ethyl]amine (1): To a stirred solution of dansyl chloride (0.2 g, 0.74 mmol) in anhydrous $CHCl_3$ (8 ml) was added triethylamine (0.1 ml, 0.75 mmol) and TREN (35 ml, 0.25 mmol); the solution turned from dark yellow to fluorescent in less than 2 min. After stirring for another 2 h, the reaction mixture was quenched (ethyl acetate, 0.1 M in water) and extracted (CH_2Cl_2, 3 × 30 ml). Purification by flash chromatography on silica gel (CH_2Cl_2/diethyl ether, 1:1) allowed the isolation of **1** (120 mg, 59%) as a highly fluorescent yellow dense oil. − ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.51$ (d, 3 H, $J = 8.5$ Hz), 8.44 (d, 3 H, $J = 8.5$ Hz), 8.26 (d, 3 H, $J = 7.0$ Hz), 7.52 (m, 6 H), 7.05 (d, 3 H, $J = 7.5$ Hz), 6.56 (br. s, 3 H, NH), 2.84 (m, 24 H, NCH_3, NCH_2CH_2NH), 2.42 (br. s, 6 H, NCH_2CH_2NH). − ^{13}C NMR ($CDCl_3$): $\delta = 152.19$, 130.58, 130.31, 130.07, 129.55, 129.06, 123.74, 119.98, 115.75, 53.14 (NCH_2CH_2NH), 45.93 (NCH_3), 42.02 (NCH_2CH_2NH).

Spectroscopic Measurements: The solvents used for photophysical measurements were acetonitrile (Merck UVASOL) and Millipore grade water, both without further purification. The solutions of the ligands were prepared in a concentration range between 4×10^{-5} M and 1×10^{-4} M unless otherwise noted. Absorption spectra were recorded with Perkin−Elmer lambda 16 and lambda 40 spectrophotometers. Corrected emission and excitation spectra were obtained with a Perkin−Elmer LS50 spectrofluorimeter. The fluorescence lifetimes (uncertainty, ± 5%) were obtained with an Edinburgh single-photon-counting apparatus (D_2-filled flash lamp). Luminescence quantum yields (uncertainty ± 15%) were determined using quinine sulphate ($\Phi = 0.546$[21] in 1 N H_2SO_4 aqueous solution) as standard. Emission spectra in a rigid matrix at 77 K were recorded using quartz tubes immersed in a quartz Dewar filled with liquid nitrogen. In order to allow comparison of emission intensities, corrections for instrumental response, inner filter effects, and phototube sensitivity were performed.[22]

Metal-Ion Binding: Titration experiments of **1** and **2** with the different metal ions were carried out on 3 ml of 5×10^{-5} M solutions, adding 10 ml each time of a 2.5×10^{-3} M solution of the metal ion. These experiments were performed at pH = 6.5 using a 10^{-2} M lutidine buffer and at pH = 9.5 using a 10^{-2} M borate buffer. The pH dependence of the complexation processes were followed by adding 10 ml each time of a 5×10^{-3} M solution of NaOH to a solution containing **1** or **2** (5×10^{-5} M) and the metal ion (5.2×10^{-5} M).

Acknowledgments

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