Dendrimers based on a bis-cyclam core as fluorescence sensors for metal ions

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We have synthesized a novel dendrimer (**1**) based on two covalently linked cyclam units as a core appended to six branches, each one consisting of one dimethoxybenzene and two naphthyl units (cyclam = 1,4,8,11-tetraazacyclotetradecane). Such a dendrimer shows three fluorescence bands which can be assigned to naphthyl localized excited states (λ_{max} = 336 nm), naphthyl excimers (λ_{max} *ca.* 390 nm), and naphthyl–amine exciplexes (λ_{max} = 510 nm). Protonation or complexation of the bis-cyclam core with Zn^{2+} does not affect the absorption spectrum of the dendrimer, but causes noticeable changes in the fluorescence intensity of the three component bands. Complexation with Cu^{2+} not only causes changes in the relative intensities of the fluorescence bands, but also the appearance of a new absorption band in the near UV spectral region. Analysis of the titration curves has allowed us to obtain clear evidence for the formation of 1 : 1 (**1**(H^+), $[Zn(\mathbf{1})]^{2+}$, $[Cu(\mathbf{1})]^{2+}$) and 2 : 1 (**1**$(2H^+)$, $[Zn_2(\mathbf{1})]^{4+}$, $[Cu_2(\mathbf{1})]^{4+}$) species. Comparison with the behaviour of a previously investigated parent monocyclam dendrimer (**2**) suggests that in the 1 : 1 species of **1** both the cyclam units are involved in the complexation with Zn^{2+} and Cu^{2+}.

Introduction

Dendrimers[1] are well defined, iteratively branched compounds, with a high degree of order, rigid or flexible skeletons that can reach nanometric dimensions, and with the potential to contain selected chemical units at predetermined sites in their structure. Dendrimer chemistry is rapidly expanding both in fundamental research and in technological applications.[2]

Luminescent units can be easily incorporated in different regions of a dendritic structure. Indeed, in the last few years it has been shown that coupling luminescence with dendrimer chemistry can lead to systems capable of performing very interesting functions,[3] including (i) light harvesting,[4] (ii) changing the "colour" of light,[5] (iii) sensing with signal amplification,[6] (iv) quenching and sensitization processes,[7] and (v) fluorescence at the level of a single molecule.[8]

Fluorescent chemosensors[9] are usually made of a fluorescent unit connected with a receptor. Recognition of a substrate by the receptor affects the fluorescent properties of the fluorophore. For example, coordination of a metal ion with the receptor can cause quenching of the excited state of the fluorophore by energy or electron transfer, thereby switching off the fluorescent signal. In suitably designed dendrimers containing a great number of fluorescent units, coordination of a metal ion can lead to the quenching of the fluorescent excited state of a great number of fluorophores, thereby offering the possibility of signal amplification. For example, it has been shown[6] that in a fourth generation poly(propylene amine) dendrimer decorated with 32 dansyl units at the periphery and containing 30 aliphatic amine units in the interior, the strong fluorescence of all the dansyl units is quenched when a Co^{2+} ion is incorporated into the dendrimer.

In the above mentioned example, coordination of the metal ion takes place with some of the amine units of the dendrimer branches in a rather undefined way. The presence in the dendritic structure of a well defined metal coordinating unit could be useful to further develop opportunities for signal amplification offered by luminescent dendrimers. For this reason, we have recently synthesized dendrimers consisting of a 1,4,8,11-tetraazacyclotetradecane (cyclam) core appended with dimethoxybenzene and naphthyl units.[10] Cyclam is indeed one of the most extensively investigated ligands in coordination chemistry.[11,12]

In a further effort to explore the potential of cyclam-based fluorescent dendrimers as ligands for metal ions (and thus as fluorescent sensors), we have synthesized a novel dendrimer (**1**, Scheme 1) based on two covalently linked cyclam units[13,14] as a core appended to six branches, each one consisting of a dimethoxybenzene and two naphthyl units. In this paper we report the changes caused by protonation and complexation with Zn^{2+} and Cu^{2+} on the fluorescent properties of this dendrimer. The results obtained are discussed by comparison with the properties of the parent monocyclam dendrimer **2**.[10,15]

Experimental

The bis-cyclam dendrimer **1** was synthesized starting from 1,1′-[1,4-phenylenebis(methylene)]bis(1,4,8,11-tetraazacyclotetradecane), which was synthesized as reported in the literature,[16,13] with the following modification:

1,4,8-tris(2,2,2-trifluoroacetyl)-1,4,8,11-tetraazacyclotetradecane (1.0 g, 2.05 mmol) was dissolved in DMF (25 ml) together with K_2CO_3 (0.708 g, 5.12 mmol). The mixture was

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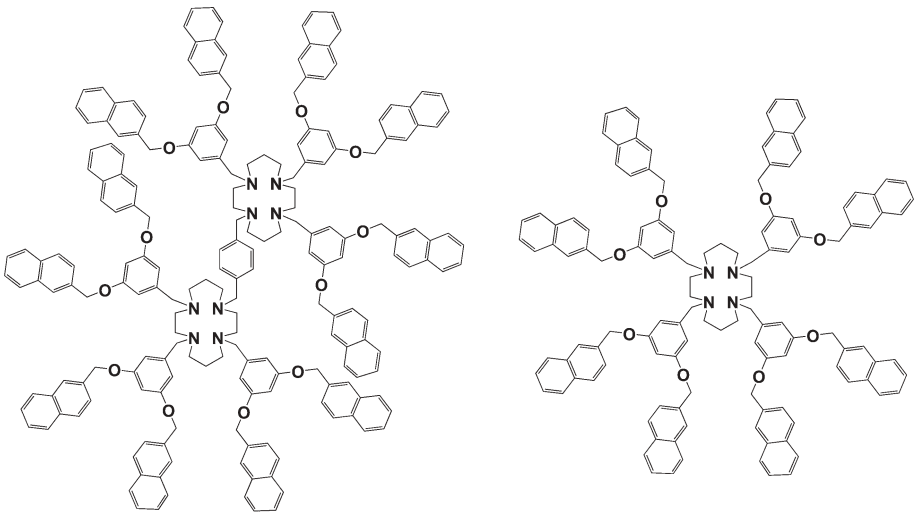

1 2

Scheme 1

then cooled to 0 °C before adding α,α-dibromoxylene (0.270 g, 1.02 mmol), dissolved in DMF (5 ml), dropwise. Stirring was continued for 4 d at RT after which the solvent was removed *in vacuo*. The rest was dissolved in CH_2Cl_2, washed with H_2O/sat. $NaHCO_3$-sol./H_2O, dried and removed *in vacuo*.

The rough product was then purified by column chromatography (SiO_2, 43–60 μm, CH_2Cl_2/EA/MeOH: 10/1/0,7) to give the pure product as a white foam, as shown by NMR and mass spectra.

The dendron 3,5-bis(2′-oxymethylnaphthyl)benzylbromide was synthesized as previously described.[17,18]

1,1′-[1,4-phenylenebis(methylene)]-4,4′,8,8′,11,11′-hexakis[3,5-bis (2′-oxymethylnaphthyl)benzyl]bis(1,4,8,11-tetraazacyclotetradecane): (=bis-cyclam dendrimer 1)

1,1′-[1,4-phenylenebis(methylene)]bis(1,4,8,11-tetraazacyclotetradecane) (0.150 g, 0.30 mmol) was taken up in DMF (35 ml) and K_2CO_3 (0.800 g, 5,79 mmol) was added. The resulting mixture was stirred for 10 min at RT under Ar, after which 3,5-bis(2′-oxymethylnaphthyl)benzylbromide (1.100 g, 2.276 mmol), dissolved in DMF (35 ml), was added dropwise. The resulting mixture was stirred at RT under Ar for 4 d. The solvent was then removed *in vacuo* and the rest was taken up in CH_2Cl_2. The organic layer was then washed with H_2O/sat. $NaHCO_3$-sol./H_2O, dried and removed *in vacuo*.

The resulting rough product was then purified by column chromatography (SiO_2, 43–60 μm, CH_2Cl_2/MeOH, 10/1) to give the pure product as a white foam (0.109 g, 0.065 mmol, 21,7%); ^{1}H-NMR:(400 MHz, $CDCl_3$, 25 °C), δ/ppm = 1.75–1.90 (m, 2 maxima, 8 H), 2.38–2.63 (m, 2 maxima, 32 H), 3.28–3.47 (m, 16H), 4.92–5.10 (m, 24H), 6.52–6.83 (m, 22H) 7.33 (s, 4H), 7.33–7.87 (m, 84H); ^{13}C-NMR: 100.6 MHz, $CDCl_3$, 25 °C), δ/ppm = 24.4, 70.0, 70.1, 70.2, 101.6, 106.0, 125.3, 125.4, 126.0, 126.1, 126.4, 127.7, 128.0, 128.2, 128.4, 133.0, 133.3, 134.6, 143.3, 143.6, 160.3; MALDI-TOF-MS: *m*/*z*: 2916.6 ($M + H^+$); MS calculated for $C_{202}H_{186}N_8O_{12}$: 2915,4.

The tetra-substituted cyclam (dendrimer **2**) was obtained as previously described.[10] Trifluoroacetic acid and $M(CF_3SO_3)_2$ salts ($M = Cu^{2+}$, Zn^{2+}) were purchased from Aldrich. Acetonitrile and dichloromethane Uvasol were purchased from Merck. All the absorption and emission spectra were carried out in air-equilibrated CH_3CN–CH_2Cl_2 1 : 1 v/v solution at 298 K, and in a rigid butyronitrile matrix at 77 K, with a Perkin Elmer λ 40 spectrophotometer and a Perkin Elmer LS50 spectrofluorimeter. The estimated experimental errors are: ±2 nm for the band maximum, ±5% for the molar absorption coefficient and ±10% for the relative intensities of the emission bands. Titration curves were obtained by submitting the spectra to the SPECFIT software.[19]

Absorption and emission spectra of the bis-cyclam dendrimer 1

The absorption spectra of dendrimers **1** and **2** are displayed in Fig. 1. The chromophoric groups present in the two

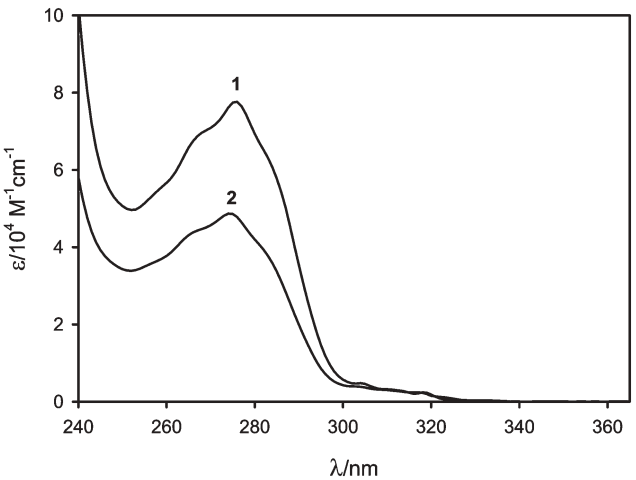

Fig. 1 Absorption spectra of dendrimers **1** and **2** in air-equilibrated CH_3CN–CH_2Cl_2 1 : 1 v/v solution at 298 K.

compounds (Scheme 1) are dimethoxybenzene (six and four, respectively) and 2-methylnaphthalene (twelve and eight, respectively). 2-Methylnaphthalene exhibits absorption bands at 275 nm ($S_0 \rightarrow S_2$ transition, $\varepsilon = 4800\ M^{-1}\ cm^{-1}$) and 310 nm ($S_0 \rightarrow S_1$ transition, $\varepsilon = 1100\ M^{-1}\ cm^{-1}$), and the dimethoxybenzene unit has an absorption maximum at 275 nm ($\varepsilon = 2200\ M^{-1}\ cm^{-1}$). The absorption spectra of the two compounds are those expected on the basis of the component units.

The emission spectrum of **1** in acetonitrile–dichloromethane 1 : 1 v/v at 298 K shown in Fig. 2 is quite similar to that of **2**.[10] Both 2-methylnaphthalene ($\lambda_{max} = 335$ nm, $\Phi = 6.6 \times 10^{-2}$) and dimethoxybenzene ($\lambda_{max} = 300$ nm, $\Phi = 1.1 \times 10^{-2}$) are known to exhibit fluorescence. Since the fluorescent excited state of dimethoxybenzene is higher in energy than that of 2-methylnaphthalene, excitation of dimethoxybenzene should be followed by energy transfer to the naphthyl unit. In order to elucidate this point, we have compared the emission intensities observed for compound **1** upon excitation at 275 nm (where 23% of the light is absorbed by the dimethoxybenzene units) and 305 nm (where absorption is only due to the naphthyl units). The results obtained show that dimethoxybenzene emission is almost completely quenched and that energy transfer does occur with an efficiency $\geqslant 0.5$.

In Fig. 2, the fluorescence spectrum of 2-methylnaphthalene is also reported for comparison purposes. Since excitation has been performed at the same wavelength (310 nm) on solutions showing the same absorbance (0.50), the emission intensities are directly comparable. As in the case of **2**, the emission intensity of **1** at 336 nm is less than 10% of that exhibited by 2-methylnaphthalene, and other bands clearly contribute to the spectrum at longer wavelengths.

The quenching of naphthyl excited states by amine units is a well known phenomenon, usually ascribed to photoinduced electron transfer (PET) processes.[20] In several cases, quenching occurs *via* formation of intramolecular exciplexes between excited naphthyl units and amines.[21–24] The broad band exhibited by **1** with a maximum at about 510 nm can indeed be assigned to such exciplexes. A further indication of this assignment is the disappearance of this band in the emission spectrum of compound **1** in butyronitrile at 77 K, where formation of exciplexes is prevented by the lack of solvent repolarisation. Careful examination of the emission spectrum of **1** shows, in fact, that it receives a contribution from a third component band in the 400 nm region, which overlaps the other two bands. Such an emission, previously observed for macrocyclic ligands bearing naphthyl chromophores,[25,26] can be assigned to naphthyl excimers. As expected, such an excimer band is almost completely absent in a butyronitrile rigid matrix at 77 K.

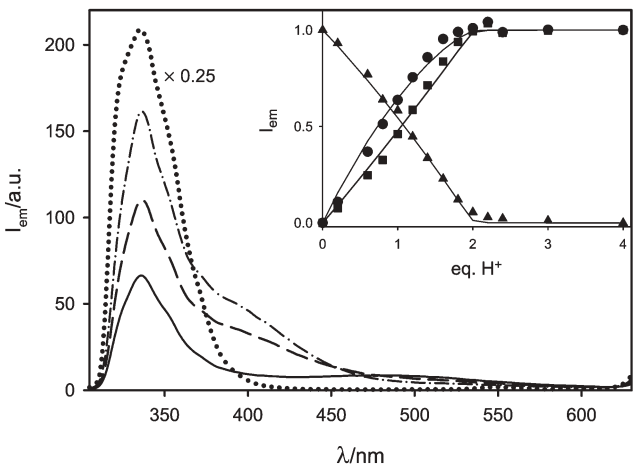

Fig. 2 Emission spectra of **1** (full line) and 2-methylnaphthalene (dotted line). The dashed and dotted-dashed lines are the spectra of **1** after addition of one and two equivalents of trifluoroacetic acid. The inset shows the normalized fluorescence intensity changes at 336 (■), 390 (●), and 510 (▲) nm. Experimental conditions: acetonitrile–dichloromethane 1 : 1 v/v solution, 298 K, $\lambda_{exc} = 275$ nm, absorbance = 0.50.

We would like to note that the very low intensity of the naphthyl band of **1**, compared to the intensity of 2-methylnaphthalene, can be due not only to the direct engagement of excited naphthyl units in exciplexes and excimers, but also to the deactivation of such excited units by energy transfer to the lower lying exciplex and excimer levels.

Before studying the effect of addition of acid or metal ions to solutions containing **1**, we have performed experiments on its dimethoxybinaphthyl dendron and we have found that neither protons nor metal ions cause any change in the absorption and emission spectra.

Effects of protonation

It is well known that cyclam undergoes protonation in aqueous solution[27,28] as well as in other solvents.[29] In aqueous solution, the four successive pK_a values are 11.6, 10.6, 1.61, and 2.42,[28] showing that cyclam can be easily mono- and di-protonated, 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.

Protonation of amines engages the lone pair of the nitrogen atoms and therefore moves the n(N) $\rightarrow$ π^* charge-transfer (CT) transitions to higher energy.[20] The lack of any change in the absorption spectrum upon addition of trifluoroacetic acid to a 1.1×10^{-5} M solution of **1** shows that CT transitions do not contribute to the absorption spectrum. This finding shows that there is no appreciable interaction between amine and aromatic moieties in the ground state.

Addition of trifluoroacetic acid, however, causes strong changes in the emission spectrum of **1** (Fig. 2), which are similar but not identical to those previously observed for **2**.[10] As shown in the inset of Fig. 2, no further change was observed after addition of two equivalents of protons per dendrimer, *i.e.*, after formation of a **1**($2H^+$) species; the same 2 : 1 proton : dendrimer ratio was observed[10] at the end of the titration of **2** which, however, contains only one cyclam unit (Scheme 1). These results suggest that the two cyclam units of **1** do not behave independently and that in the **1**($2H^+$) species the two protons are likely shared by the two cyclam units in a sandwich-type structure.

The spectra reported in Fig. 2 show that protonation of **1** causes: (i) a linear increase in the intensity of the naphthyl localized band with $\lambda_{max} = 336$ nm that, however, remains much weaker than the band of 2-methylnaphthalene; (ii) a

decrease, but not the disappearance, of the exciplex band with maximum at around 510 nm; (iii) a moderate, slightly non-linear increase in intensity of the excimer band around 390 nm. The non-linear increase in intensity of the excimer band suggests that protonation causes a rearrangement in the structure of the dendrimer and the relatively small recovery of the intensity of the naphthyl fluorescence on protonation is likely related to the lack of disappearance of exciplexes and the further formation of excimers. From a SPECFIT analysis of the observed spectral changes the following values were obtained for the first and second protonation constants: log $\beta_{1:1}$ = 8.1 ± 0.6, and log $\beta_{2:1}$ = 14.1 ± 0.6.

Complex formation with Zn^{2+}

Upon addition of $Zn(CF_3SO_3)_2$ (up to three equivalents) to a 1.1×10^{-5} M solution of **1** no change was observed in the absorption spectrum, whereas strong changes were observed in the emission spectrum (Fig. 3). Such changes are qualitatively similar to those caused by protonation, but there are some important differences: (i) the titration plot of the naphthyl fluorescence clearly shows a discontinuity after addition of one equivalent of Zn^{2+} per dendrimer and at the end of the titration, which occurs after addition of about two equivalents of metal ion, the naphthyl band is more intense than in the case of protonation; furthermore, most of the increase in intensity of the naphthyl fluorescence band takes place after addition of one equivalent of Zn^{2+}; (ii) the exciplex band with a maximum at around 510 nm decreases in intensity, shows a discontinuity, and does not disappear; (iii) the increase in intensity of the excimer band at 390 nm, once corrected for the contribution of the naphthyl fluorescence, reaches a plateau after addition of one equivalent of metal ion.

These results clearly indicate that a 1 : 1 complex, $[Zn(\mathbf{1})]^{2+}$, is first formed and then replaced by a 2 : 1 species, $[Zn_2(\mathbf{1})]^{4+}$. SPECFIT analysis yielded values of log $\beta_{1:1}$ = 9.7 ± 0.7, and log$\beta_{2:1}$ = 16.1 ± 0.8 for these two species, respectively. In the 1 : 1 complex $[Zn(\mathbf{1})]^{2+}$, both the cyclam units are likely to be coordinated to Zn^{2+}, as suggested by the formation of a 1 : 2 compound, $[Zn(\mathbf{2})_2]^{2+}$, on titration of the monocyclam dendrimer **2** with Zn^{2+}.[30] In the 1 : 1 complex of Zn^{2+} with **1**, $[Zn(\mathbf{1})]^{2+}$, the metal ion is likely to be sandwiched between the two cyclam units, as is thought to happen in the $[Zn(\mathbf{2})_2]^{2+}$ compound. All the metal complexes of cyclam and of non-dendritic cyclam derivatives reported so far have a 1 : 1 stoichiometry.[11] Apparently, the dendrimer branches not only do not hinder, but in fact favour coordination of cyclam units to metal ions with respect to solvent molecules and counter ions; indeed, even evidence for formation of $[Eu(\mathbf{2})_3]^{3+}$ has also been reported.[31] Presumably, the dendritic branches force the cyclam cores to adopt a structure in which only three N atoms are available for metal complexation. As in the case of $[Zn(\mathbf{2})_2]^{2+}$,[30] two limiting structures can be proposed for $[Zn(\mathbf{1})]^{2+}$: (i) an "inward" structure, in which the branches of the two coordinated cyclam units are intermeshed, or (ii) an "outward" structure, in which the branches of the two coordinated moieties do not interact. An inward structure with intermeshed branches should favour the formation of excimers. The results obtained, however, show that in going from $[Zn(\mathbf{1})]^{2+}$ to $[Zn_2(\mathbf{1})]^{4+}$ the intensity of the excimer band does not change. It seems, therefore, more likely that in these sandwich-type complexes the dendrimer branches extend outward and maintain the same structure in the $[Zn_2(\mathbf{1})]^{4+}$ species.

Complex formation with Cu^{2+}

Quite different results were obtained upon titration of a 1.1×10^{-5} M solution of **1** with $Cu(CF_3SO_3)_2$. The absorption spectrum (Fig. 4) showed the appearance of a broad tail in the 300–400 nm region. The absorbance values increase almost linearly up to the addition of two equivalents of metal ion per dendrimer (Fig. 4, inset). A quite similar absorption band, assigned to ligand-to-metal charge-transfer (MLCT) transitions, is obtained when a 2.2×10^{-5} M cyclam solution is

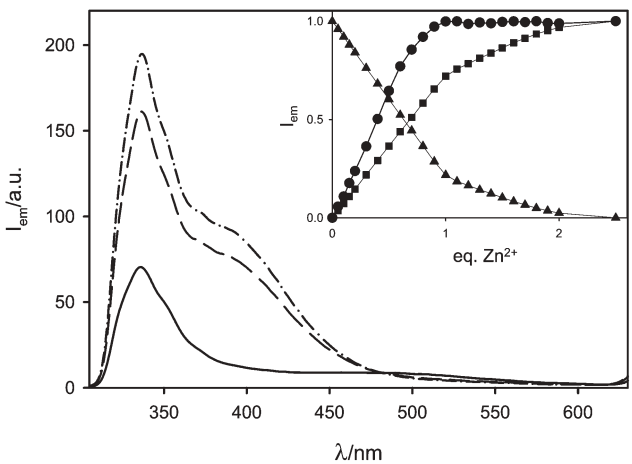

Fig. 3 Emission spectrum of **1** before (full line) and after the addition of one (dashed line) and two (dotted–dashed) equivalents of $Zn(CF_3SO_3)_2$. Inset shows the normalized fluorescence intensity changes at 336 (■), 390 (●), and 510 (▲) nm. Experimental conditions: acetonitrile-dichloromethane 1 : 1 v/v solution, 298 K, λ_{exc} = 275 nm, absorbance = 0.50.

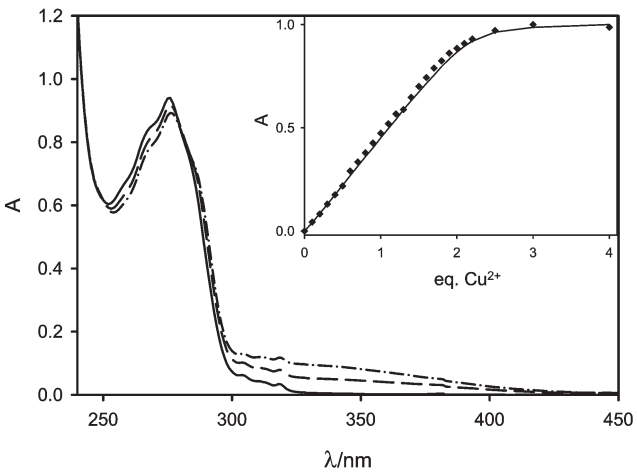

Fig. 4 Absorption spectrum of **1** before (full line) and after the addition of one (dashed line) and two (dotted–dashed) equivalents of $Cu(CF_3SO_3)_2$. Inset shows the normalized absorption changes at 319 nm. Experimental conditions: acetonitrile–dichloromethane 1 : 1 v/v solution, 298 K.

titrated by $Cu(CF_3SO_3)_2$. Therefore we can conclude that upon addition of $Cu(CF_3SO_3)_2$ to **1**, both the cyclam units of the dendrimer coordinate a Cu^{2+} ion. SPECFIT analysis based on the changes in the absorption spectrum yielded a value of $\log \beta_{2:1} = 11.9 \pm 0.3$.

More details were obtained from the changes observed in the emission spectrum (Fig. 5), which can be summarized as follows: (i) the intensity of the naphthyl band is almost constant up to the addition of one equivalent of metal ion and then decreases slightly; (ii) the intensity of the exciplex band decreases linearly and disappears after addition of two equivalents of metal ions; (iii) the intensity of the excimer band increases at the beginning of the titration, and reaches a maximum value after addition of one equivalent of metal ion and then decreases. SPECFIT analysis was not performed in the case of the emission spectrum because of the too complex behaviour and the relatively small intensity changes.

We would like to emphasise an important difference in the behaviour of the emission spectrum of **1** upon titration with H^+ or Zn^{2+} (Figs. 2 and 3), and titration with Cu^{2+} (Fig. 5). In the case of H^+ or Zn^{2+}, the decrease in the intensity of the exciplex emission, caused by the engagement of the cyclam N atoms by protons or metal ions, is accompanied, as expected, by an increase in the intensity of the naphthyl emission. This does not happen, however, when titration is performed with Cu^{2+}; in particular, at the end of the titration, when $[Cu_2(\mathbf{1})]^{4+}$ is formed, although exciplex formation is fully prevented by coordination of two metal ions, the naphthyl emission is clearly *less* intense than in the free dendrimer **1**. This result can be easily rationalized considering that coordination of Cu^{2+}, while preventing deactivation of the excited naphthyl units *via* exciplex formation, introduces another deactivation channel related to the presence of the low energy MLCT state.

Fig. 4 shows that from the view point of the interaction between cyclam and metal ion (*i.e.*, from the behaviour of the MLCT absorption band), there are minor (if any) differences between the 1 : 1 and 2 : 1 species. In other words, the two cyclam units behave independently as far as the MLCT absorption is concerned. From the view point of the naphthyl units (Fig. 5), however, it is clear that a 1 : 1 complex, $[Cu(\mathbf{1})]^{2+}$, is first formed, as suggested by the formation of a 1 : 2 compound, $[Cu(\mathbf{2})_2]^{2+}$ on titration of the monocyclam dendrimer 2 with Cu^{2+},[32] and then replaced by a 2 : 1 species, $[Cu_2(\mathbf{1})]^{4+}$.

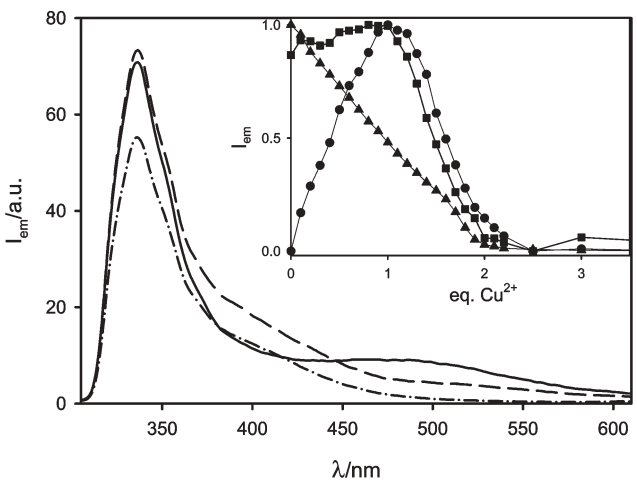

Fig. 5 Emission spectrum of **1** before (full line) and after the addition of one (dashed line) and two (dotted–dashed) equivalents of $Cu(CF_3SO_3)_2$. Inset shows the normalized fluorescence intensity changes at 336 (■), 390 (●), and 510 (▲) nm. Experimental conditions: acetonitrile–dichloromethane 1 : 1 v/v solution, 298 K, $\lambda_{exc} = 275$ nm, absorbance = 0.50.

Conclusions

We have prepared for the first time a dendrimer with a bis-cyclam core. Such a dendrimer (**1**) contains in its branches 12 naphthyl units and exhibits three fluorescence bands assigned to naphthyl localized excited states ($\lambda_{max} = 336$ nm), naphthyl excimers (λ_{max} *ca.* 390 nm), and naphthyl-amine exciplexes ($\lambda_{max} = 510$ nm). Titration with H^+, Zn^{2+}, and Cu^{2+} causes strong changes in the emission spectrum and, in the case of Cu^{2+}, also in the absorption spectrum. Clear evidence for formation of 1 : 1 ($\mathbf{1}\cdot(H^+)$, $[Zn(\mathbf{1})]^{2+}$, $[Cu(\mathbf{1})]^{2+}$) and 2 : 1 ($\mathbf{1}\cdot(2H^+)$, $[Zn_2(\mathbf{1})]^{4+}$, $[Cu_2(\mathbf{1})]^{4+}$) species has been obtained. The three luminescence bands and, in the case of Cu^{2+}, also an absorption band, offer a way to monitor not only the metal–ligand coordination process, but also its effect on the interaction between the naphthyl units contained in the dendritic branches. The spectral changes are probably too weak and too complex to be used for sensory purposes. We would like to note, however, that while the availability of dendrimers possessing a well defined ligand unit, like cyclam, opens the way for the construction of mixed dendritic-ligand complexes, dendrimers containing two cyclam units can be used, in principle, to construct dendrimers containing two different types of metal ions.

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