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Dendrimers with a cyclam core. Absorption spectra, multiple luminescence, and effect of protonation

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Abstract—We have synthesized two dendrimers (**4** and **5**) consisting of a 1,4,8,11-tetraazacyclotetradecane (cyclam) core appended with four dimethoxybenzene and eight naphthyl units (**4**) and 12 dimethoxybenzene and 16 naphthyl units (**5**). The absorption and luminescence spectra of these compounds and the changes taking place upon protonation of their cyclam core have been investigated. In acetonitrile-dichloromethane 1:1 v/v solution they exhibit three types of emission bands, assigned to naphthyl localized excited states (λ_{max}=337 nm), naphthyl excimers (λ_{max} ca 390 nm), and naphthyl-amine exciplexes (λ_{max}=480 nm). The tetraamine cyclam core undergoes only two protonation reactions, whose constants have been obtained by fitting the spectral changes. Protonation not only prevents exciplex formation for electronic reasons, but also causes strong nuclear rearrangements in the cyclam structure which affect excimer formation between the peripheral naphthyl units of the dendrimers. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

Dendrimers[1,2] are complex, but well defined chemical compounds, with a high degree of order and the possibility to contain selected chemical units in predetermined sites of their structure. These compounds are currently attracting the interest of a great number of scientists because of their unusual chemical and physical properties and the wide range of potential applications.

An important property of dendrimers is the presence of dynamic internal cavities.[3] This feature, coupled with the presence of coordinating moieties, has been exploited to host metal ions in the interior of dendrimers. Research on such host–guest systems has been performed for a variety of purposes which include investigation of the dendrimer structure,[4] preparation of encapsulated metal nanoparticles,[5] dioxygen binding,[6] ion transportation,[7] ion sensing,[8] light harvesting,[9] stepwise complexation,[10] and reversible metal complex assembly.[11] Metal ions have also been used to assemble coordinating dendrons[12] and as branching centres in dendrimer synthesis.[13] Perhaps surprisingly, only a few examples of dendrimers with a well defined metal-coordinating core have been reported so far.[14]

1,4,8,11-Tetraazacyclotetradecane (cyclam) is one of the most extensively investigated ligands in coordination chemistry. Both cyclam and its 1,4,8,11-tetramethyl derivative in aqueous solution can be protonated[15] and can coordinate metal ions such as Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) with very large stability constants.[16,17] Furthermore, cyclam and its derivatives have been studied as carriers of metal ions in antitumor[18] and imaging[19] applications and, most recently, as anti-HIV agents.[20] In most cases, the cyclam derivatives contain pendant functionalities to increase complex stabilities or to allow attachment of other chemical species to the macrocyclic structure. Protonated cyclam has recently been used to assemble two different metal complexes for energy transfer purposes.[21]

Continuing our investigations on photoactive dendrimers, we thought that cyclam could be a suitable core for constructing dendrimers capable of exhibiting luminescence switching properties upon acid–base or metal ion stimulation. Therefore we have synthesized two novel dendrimers (**4** and **5**, Scheme 1) consisting of a cyclam core appended with four dimethoxybenzene and eight naphthyl units (**4**) and 12 dimethoxybenzene and 16 naphthyl units (**5**). The absorption and luminescence spectra of these compounds have been investigated in acetonitrile–dichloromethane 1:1 v/v solution. For comparison purposes, the absorption and luminescence spectra of naphthalene (**1**), 2-naphthylmethyl-ethylamine (**2**), 1,4,8,11-tetrakis(naphthylmethyl)-cyclam (**3**), and dendrons **6** and **7** (Scheme 2) have also been studied. Dendrimers **4** and **5** have been found to exhibit three types of emission bands, that have been assigned to a naphthyl localized excited state, a naphthyl excimer, and a naphthyl-amine exciplex. Titration with trifluoroacetic acid has shown that the tetraamine cyclam core undergoes two

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Keywords: protonation; absorption spectra; dendrimers.

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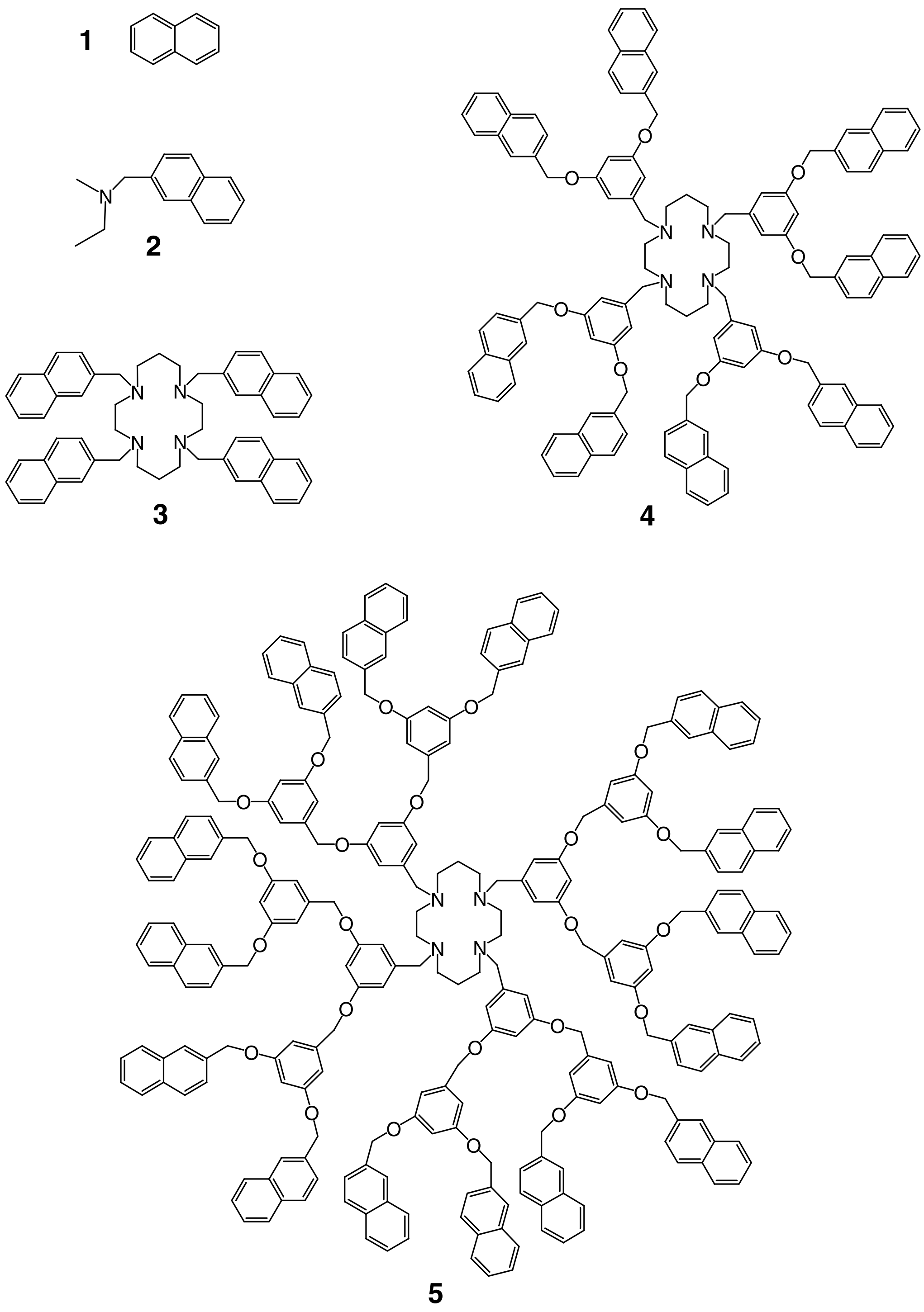


Scheme 1.

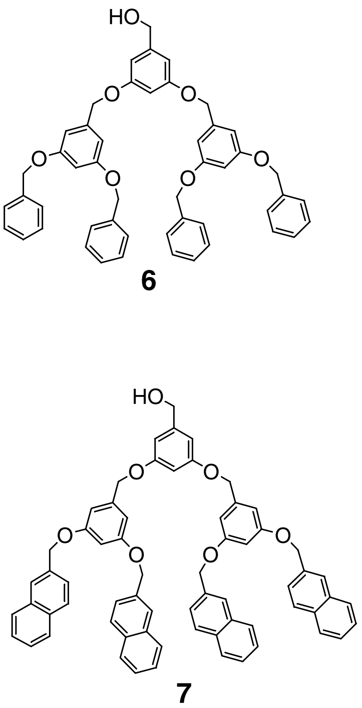
successive protonation reactions that have dramatic effects on the luminescence properties.

2. Results and discussion

2.1. Unprotonated species

All the compounds are soluble in acetonitrile–dichloromethane 1:1 v/v, which has therefore been chosen as the solvent for our experiments. The X-ray structure of cyclam[17] shows that the macrocycle adopts an endodentate, centrosymmetric conformation with two three-centre hydrogen bonds. In compounds **3**–**5**, of course, hydrogen bonds cannot be present because the hydrogens have been replaced by substituents.

The absorption spectra of compounds **2**–**5** are shown in Figure 1. The only chromophoric group present in compounds **2** and **3** is naphthalene. Accordingly, the spectra of these compounds show the well known naphthalene bands around 270 nm ($S_0 \rightarrow S_2$ transition) and 310 nm



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Scheme 2.

($S_0 \rightarrow S_1$ transition).[22] Dendrimers **4** and **5** contain both naphthalene and dimethoxybenzene chromophoric groups. The dimethoxybenzene unit present in the dendrimers has an absorption maximum at 275 nm with $\varepsilon=2200\ M^{-1}\ cm^{-1}$,[†] much smaller than that of the naphthalene unit at the same wavelength ($6000\ M^{-1}\ cm^{-1}$ for compound **2**). As shown in the inset of Figure 1, the molar absorption coefficient at 275 nm of compounds **4** and **5** is higher than expected from the number of their naphthyl units because of the contribution of the dimethoxybenzene groups. If such a contribution is subtracted, the molar absorption coefficients for **4** and **5** become slightly smaller than expected on the basis of the data obtained for **2** and **3**, most likely because the naphthyl unit of **2** and **3** is not a perfect model for the naphthyl unit of **4** and **5**, owing to the different substituents. We can conclude that the absorption spectra of the examined compounds are roughly those expected from the spectra of the component chromophoric units.

Both naphthalene and dimethoxybenzene are known to exhibit fluorescence. The fluorescent excited state of dimethoxybenzene is slightly higher in energy than that of naphthalene. Therefore excitation of dimethoxybenzene can be expected to be followed by energy transfer to the naphthalene unit. In order to elucidate this point, we have compared the emission intensities observed for compound **5** 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 naphthalene units).[‡]

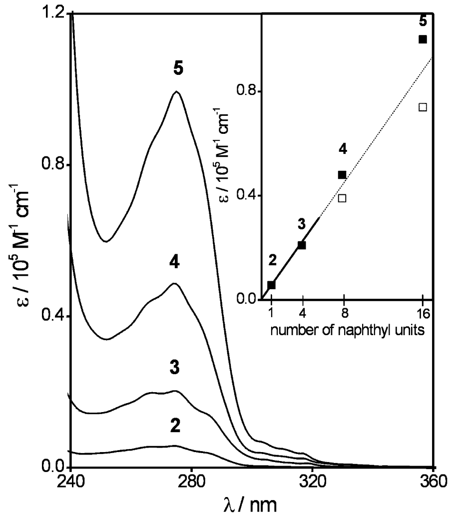

Figure 1. Absorption spectra of the investigated compounds in acetonitrile–dichloromethane 1:1 v/v solution at 298 K. The inset shows the molar absorption coefficients at 275 nm (dark squares). The empty squares represent the molar absorption coefficients of dendrimers **4** and **5** after subtraction of the expected contribution of their dimethoxybenzene chromophoric units.

The results obtained show that dimethoxybenzene emission is almost completely quenched and the energy transfer does occur with efficiency >0.5.

The emission spectra of compounds **2**–**5** in acetonitrile–dichloromethane 1:1 v/v at 298 K are shown in Figure 2. In the same figure, the fluorescence spectrum of naphthalene (**1**) is also reported for comparison purposes. Since excitation has been performed at the same wavelength (275 nm) on solutions having the same absorbance (0.50), the intensities of the various bands are directly comparable. It can be noticed that the emission intensity of compounds **2** and **3** at 337 nm is only 1 or 2% that of the naphthalene,[§] and that these compounds exhibit a broad emission with maximum at about 480 nm. The quenching of naphthalene excited states by appended amine units is a well known phenomenon, usually ascribed to photoinduced electron transfer (PET) processes.[23] In several cases, the quenching occurs via formation of an intramolecular exciplex between the excited naphthyl unit and amine.[24–27] The broad band with maximum at about 480 nm can indeed be assigned to such an exciplex. A further indication of this assignment is the disappearance of this band in the emission spectrum of compound **5** in butyronitrile at 77 K, where formation of exciplexes is prevented by the lack of solvent repolarisation. As shown in Figure 2, dendrimers **4** and **5** display complex emission spectra which include (i) the locally excited naphthalene band exhibiting the characteristic vibrational structure, (ii) the exciplex band shown by **2** and **3**, slightly displaced to higher energies, and (iii) an emission band in the 400 nm region, overlapped with the other two bands, which is not present in **1**, **2**, and **3**. Such an emission, which is particularly evident in the case of **5**, was previously observed for other macrocyclic ligands bearing naphthyl chromophores[28,29] and can be assigned to naphthyl excimers. As could be expected, this excimer band is

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[†] The value of the molar absorption coefficient for the dimethoxybenzene unit was obtained from the absorption spectrum of dendron **6**.

[‡] The fraction of light absorbed by the two chromophores at 275 nm was obtained from the comparison of the molar absorption coefficients of the dendrons **6** and **7**. Correction for the different number of photons emitted by the lamp at the two different excitation wavelengths was performed using a naphthalene solution as a reference.

[§] It cannot be excluded that such a weak emission is due to small amounts of impurities of strongly emitting naphthalene-type compounds.

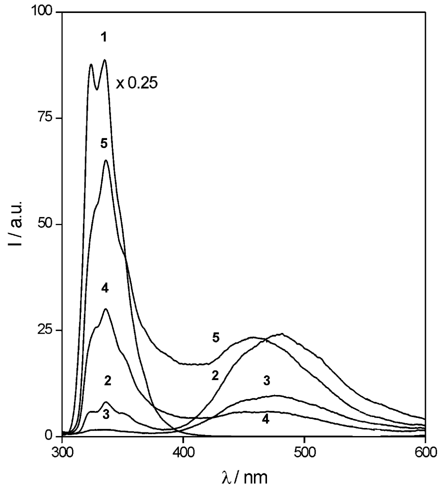

Figure 2. Emission spectra of the investigated compounds in acetonitrile–dichloromethane 1:1 v/v solution at 298 K. The intensities are directly comparable since in all cases the excitation wavelength was 275 nm, the solution absorbance at the excitation wavelength was 0.50, and the same experimental set up was used.

almost completely absent in a butyronitrile rigid matrix at 77 K. The three different types of excited states responsible for the observed emissions are schematically shown in Figure 3(a).

2.2. Effects of protonation

It is well known that cyclam undergoes protonation in aqueous solution[15,30] as well as in other solvents.[31] In aqueous solution, the four successive pK_a values are 11.6, 10.6, 1.61, and 2.42,[15] 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. In dimethylformamide solution only two successive protonation steps have been observed with pK_a values of 9.3 and 7.5.[31]

It is well known that protonation of amines engages the lone pair of the nitrogen atoms and therefore moves the $n(\mathrm{N})\rightarrow\pi^*$ charge-transfer (CT) transitions to higher energy. The lack of any spectral change upon addition of trifluoroacetic acid 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 causes strong changes in the emission spectra of compounds **2–5**. The spectra obtained at the end of acid titration are shown in Figure 4. Comparison with the spectra of Figure 2, which have been recorded under the same experimental conditions, shows that protonation causes (i) the disappearance of the exciplex band with maximum around 480 nm in all cases, and (ii) a strong increase in the intensities of the naphthyl localized band with $\lambda_{\max}$=337 nm, particularly for compounds **2** and **3**. Moreover, the protonated species of dendrimers **4** and **5** exhibit much stronger excimer bands than the corresponding isolated dendrons,[32] suggesting that excimer formation is facilitated by the folding of the dendrimer structure.

More details on the protonation processes can be drawn from the changes in the emission intensities observed during titration (Fig. 5). In the case of model compound **2**, which contains a single naphthylamine unit, the intensity of the exciplex band decreases and the naphthyl-localized band increases linearly with increasing acid concentration and no further change is observed after addition of one proton per nitrogen atom. For compounds **3–5**, however, the intensity of the naphthyl-localized, excimer, and exciplex bands do not change linearly with increasing acid concentration. Furthermore, the spectral changes take place only during the addition of the first two equivalents of acid. These results allow us to draw the following conclusions.

(i) Under our experimental conditions (low polarity solvent), the tetraamine cyclam core apparently shows only two protonation reactions. This result is in agreement with the behaviour observed for cyclam derivatives in dimethylformamide solution.[31,33]
(ii) Addition of acid prevents, as expected, exciplex formation. There is no need to protonate each nitrogen atom to suppress exciplex formation, showing that protons are in some way shared by the nitrogen atoms.
(iii) For all the examined compounds, the increase in the naphthyl-based fluorescence intensity (337 nm) mirrors the decrease in the emission intensity at 480 nm, showing that the species emitting at 480 nm is formed in competition with the naphthyl fluorescence decay, as expected in the case of exciplex formation. The two different types of excited states responsible for the observed emission are schematically shown in Figure 3(b). However, the intensity of the naphthyl-localized emission at the end of the acid titration is much weaker for **4** and **5** than for **2** and **3** (Fig. 4). This effect can be

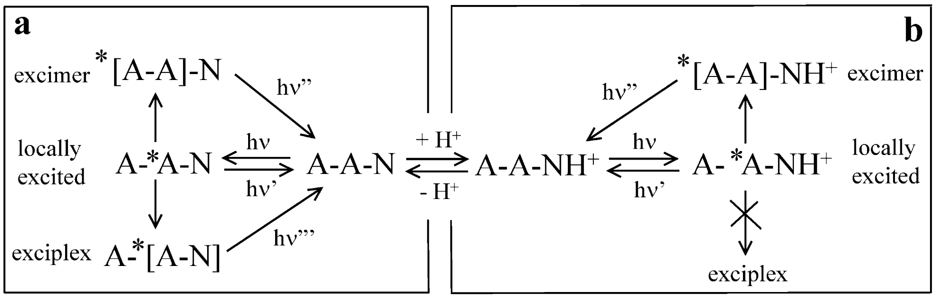

Figure 3. Schematic representation of the different types of excited states responsible for the observed emissions of the unprotonated (a) and protonated (b) forms of dendrimers **4** and **5**. A indicates a naphthalene unit and N an amine unit. A–A–N represents a dendrimer in which interaction between two A units or an A and a N unit can occur, The star indicates the localization of the electronic excitation.

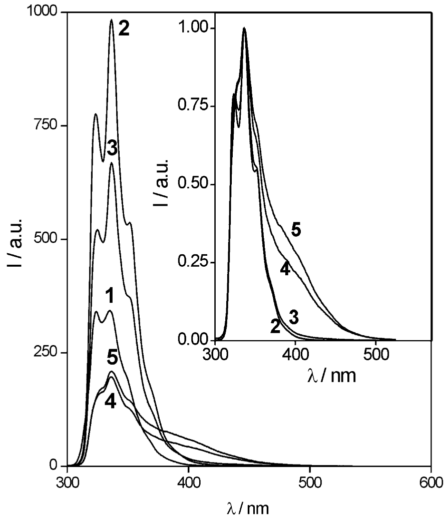

Figure 4. Emission spectra of the investigated compounds in acetonitrile–dichloromethane 1:1 v/v solution at 298 K at the end of the titration with trifluoroacetic acid. The intensities are directly comparable since in all cases the excitation wavelength was 275 nm, the solution absorbance at the excitation wavelength was 0.50, and the same experimental set up was used. Direct comparison with the spectra reported in Figure 2 can also be made. Notice, however, the different ordinate scale of the two figures. The normalized spectra shown in the inset provide evidence for the presence of the excimer emission in compounds **4** and **5**.

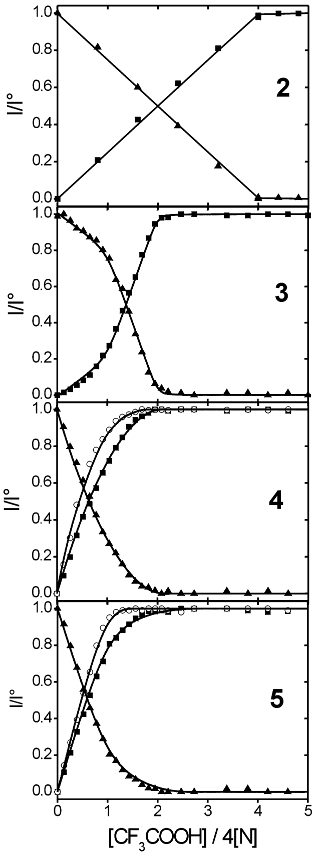

Figure 5. Normalized titration curves obtained for compounds **2**–**5** from emission measurements upon addition of trifluoroacetic acid (acetonitrile–dichloromethane 1:1 v/v solutions, 298 K). Excitation at 275 nm in all cases. Emission intensity values at 337 nm (squares), 390 nm (open circles), and 480 nm (triangles). The fitting curves and the corresponding pK_a values have been obtained by the SPECFIT software:[34] pK=7.1 for **2**, pK_1=8.0 and pK_2=6.2 for **3**, pK_1=7.4 and pK_2=7.0 for **4**, pK_1=8.0 and pK_2=6.9 for **5**.

ascribed to the formation of the excimer species in the dendritic structures, which provides a deactivation pathway in competition with the naphthyl fluorescence.

(iv) For compound **3**, the initial slope of the titration curve is very small and increases on increasing acid concentration until about one acid equivalent has been added. This result can be accounted for by assuming that protonation of a nitrogen (or sharing of a proton between two nitrogens) does not fully prevent exciplex formation between an excited naphthyl unit and a non-protonated nitrogen. The formation of different types of exciplexes upon addition of acid is indicated by the slight, progressive displacement of the maximum of the exciplex band during titration (see, e.g. inset of Fig. 6).

(v) For compounds **4** and **5**, the slope of the titration curves based on the decrease of the exciplex band and the increase of the naphthyl band is very large at the beginning and tends to decrease on increasing acid concentration. Such a behaviour is completely different from that exhibited by compound **3**. Apparently, for dendrimers **4** and **5** monoprotonation is sufficient to prevent most of the exciplex formation. This result suggests that in dendrimers **4** and **5** all the four nitrogen atoms share, in some way, the first proton, a result that requires the formation of an appropriate structure.

(vi) Particularly in the case of dendrimer **5**, the excimer band reaches its maximum intensity upon the addition of only one proton per molecule. Since excimer formation is mostly due to folding of the dendrimer structure (see above), this result suggests that in the monoprotonated species the four dendrons lie on the same side of the cyclam core, in a structure that could also be appropriate for the above mentioned sharing of the first proton among all the nitrogen atoms.

In an attempt to obtain further information on the protonation processes, the spectra were investigated using the SPECFIT software.[34] The resulting values for the two

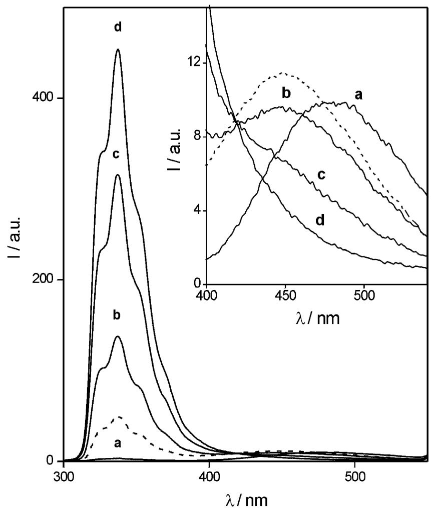

Figure 6. Emission spectra of **3** (2.93×10^{-5} M) in acetonitrile–dichloromethane 1:1 v/v solution at 298 K upon addition of increasing amounts of trifluoroacetic acid from 0 (line a) to 2.1 (line d) equivalents. The dashed line represents the spectrum of the monoprotonated form, as obtained from SPECFIT. The inset shows the progressive displacement of the exciplex band towards higher energies as the concentration of trifluoroacetic acid increases.

association constants are very large (for example, pK_a=7.4 and pK_2=7.0 for compound **4**) and do not appreciably differ for compounds **3**–**5**. The fitting procedure also allows the spectrum of the monoprotonated form to be obtained. The calculated spectra of the monoprotonated forms of compounds **4** and **5** are very close to that of the diprotonated one, contrary to what happens for compound **3** (Fig. 6). This different behaviour is also apparent from the plots of Figure 5: the initial slope for compound **3** is very small, indicating that the emission spectrum of the monoprotonated form has to be close to that of the unprotonated one, whereas for compounds **4** and **5** the steep slopes suggest that the spectrum of the monoprotonated form is similar to that of the diprotonated species.

3. Conclusions

Cyclam (1,4,8,11-tetraazacyclotetradecane) is a very interesting core for constructing dendrimers for the following reasons: (i) it can be easily functionalised with dendrons at each one of its four nitrogen atoms; (ii) it is 'silent' from the viewpoint of absorption and emission spectra, but it can interact with photoactive groups contained in the dendrimer branches; such interactions can modify the emission properties of the dendron chromophoric units and can cause the appearance of new emission bands; (iii) it can undergo protonation reactions which induce electronic as well as structural rearrangements, with dramatic effects on the emission spectra of the whole dendrimer; (iv) it is an excellent ligand for a variety of transition metal ions. This last property will be exploited in our future work with the aims of designing novel luminescent species and switching processes.

4. Experimental

4.1. Synthesis

4.1.1. *N*-Methyl(2-methylnaphthalene)ethylamine (2). *N*-Ethylmethylamine (1.00 g, 16.92 mmol) and a 5-fold excess of potassium carbonate were dissolved in dry dichloromethane (100 ml). To this suspension a solution of 2-bromomethyl-naphthalene (3.74 g, 16.92 mmol) in dichloromethane (40 ml) was added dropwise. The mixture was stirred at 25°C for 5 h. After filtering the undissolved K_2CO_3, the solvent was removed in vacuo and the residue was collected in dichloromethane. After washing with water, aq. Na_2CO_3 and again with water, the organic phase was dried with Na_2SO_4. Further purification was achieved by column chromatography (SiO_2, 40–63 μm, ethylacetate/petroleum ether 44:56) yielding 1.04 g (31%) of a bright yellow oil; TLC (SiO_2): R_f=0.21 ethylacetate–cyclohexane 44:56 v/v); ^1H NMR: (400 MHz, $CHCl_3$, 25°C) δ=1.05 (t, $^3J_{HH}$=7.2 Hz, 3H, CH_3), 2.17 (s, 3H, NCH_3), 2.41 (q, $^3J_{HH}$=7.2 Hz, 2H, CH_2N), 3.53 (s, 2H, CH_2–Ar), 7.36 (m, 2H, CH_{Naph}), 7.65 (s, 1H, CH_{Naph}), 7.72 (m, 4H, CH_{Naph}); ^{13}C NMR: (100.6 MHz, $CHCl_3$, 25°C) δ=12.5 (CH_3), 41.8 (NCH_3), 51.3 (CH_2N), 62.2 (CH_2–Ar) 125.5, 125.8, 127.4, 127.5, 127.6, 127.7, 127.8 (CH_{Naph}), 132.7, 133.4, 136.9 (C_{Naph}); FAB-MS: *m*/*z* (%): 200.1 (M+H$^+$, 100); $C_{14}H_{17}N$: 199.29.

4.1.2. 1,4,8,11-Tetrakis(2-naphthylmethyl)-1,4,8,11-tetraazacyclotetradecane (3). A solution of 1,4,8,11-tetraazacyclotetradecane (cyclam) (0.10 g, 0.50 mmol), 2-bromomethylnaphthalene (1.93 g, 8.70 mmol) and triethylamine (1.53 g, 15.10 mmol) in dry THF (10 ml) was refluxed for 6 h. The deposited solid was recovered by filtration and washed with 1 M NH_3 (10 ml) und MeOH (30 ml). The residue was suspended in chloroform and after addition of NaOH solution the separated organic phase was evaporated to dryness. The compound was then recrystallised from hot THF yielding 100 mg (26%) of white solid; mp 204°C; TLC (SiO_2): R_f=0.36 (dichloromethane–methanol 20:1); ^1H NMR: (400 MHz, $CDCl_3$, 25°C) δ=1.85 (t, $^3J_{HH}$=6.8 Hz, 4H, CH_2), 2.62 (t, $^3J_{HH}$=6.8 Hz, 8H, CH_2N), 2.71 (s, 8H, CH_2N), 3.57 (s, 8H, Ar–CH_2), 7.41 (m, 18H, C_{ar}), 7.51 (d, 4H, C_{ar}), 7.65 (m, 12H, C_{ar}), 7.78 (d, 4H, C_{ar}); ^{13}C NMR: (100.6 MHz, $CDCl_3$, 25°C) δ=24.2 (CH_2), 50.4 (CH_2N), 51.6 (CH_2N), 59.4 (Ar–H_2), 125.3, 125.7, 127.2, 127.5, 127.6, 132.7, 133.3, 137.8; FAB-MS: *m*/*z* (%): 761.41 (100, M$^+$); $C_{54}H_{56}N_4$: (761.05).

4.2. General synthetic procedure for dendrimers 4 and 5

To the mixture of 1 equiv. of the starting 1,4,8,11-tetraazacyclotetradecane (cyclam) and a 40–50-fold excess of potasium carbonate in dry chloroform (100 ml) a solution of 4.4–5 equiv. of the corresponding benzyl bromide in 30 ml dry chloroform was added dropwise. The mixture was stirred for 2–3 days under reflux and after filtering off the undissolved K_2CO_3, the solvent was removed in vacuo. After collecting the residue in dichloromethane and washing with water, aq. Na_2CO_3 and again with water, the organic phase was dried with Na_2SO_4. Further purification was achieved by column chromatography yielding a bright yellow solid.

4.2.1. 1,4,8,11-Tetra(3,5-bis-2′-oxymethylnaphthylbenzyl)-1,4,8,11-tetraazacyclotetradecane (4). Reaction procedure as described above. Amounts: 1,4,8,11-tetraazacyclotetradecan (0.1 g, 0.49 mmol), 3,5-bis-2′-oxymethylnaphthyl-benzylbromide (1.04 g, 2.15 mmol) and potassium carbonate (2.63 g, 19.06 mmol). Column chromatography (SiO_2, 40–63 μm, 1. CH_2Cl_2, 2. CH_2Cl_2–MeOH 50/1–30/1) yielding 0.32 g (36%) of a bright yellow solid; mp 75–77°C; TLC (SiO_2): R_f=0.41 (dichloromethane–methanol 20:1); ^1H NMR: (400 MHz, $CDCl_3$, 25°C) δ=1.75 (t, br, $^3J_{HH}$=6.5 Hz 4H, CH_2), 2.35 (m, br, 16H, CH_2N), 3.28 (s, br, 8H, Ar–CH_2), 4.88 (s, 16H, 8 Naph-C_2O–Ar), 6.40 (t, $^4J_{HH}$=2.2 Hz, 4H, C_{ar}), 6.65 (d, $^4J_{HH}$=2.2 Hz, 8H, C_{ar}), 7.28–7.47 (m, 24H, C_{Naph}), 7.61–7.80 (m, 32H, C_{Naph}); ^{13}C NMR: (100.6 MHz, $CDCl_3$, 25°C) δ=24.9 (CH_2), 50.2 (CH_2N), 51.7 (CH_2N), 59.0 (Ar–H_2), 69.9 (Naph-H_2O–Ar), 100.8, 107.7, 125.3, 125.4, 126.0, 126.1, 126.2, 126.3, 126.4, 127.7, 127.9, 128.2, 133.0, 133.3, 134.5, 143.4, 159.9; MALDI-TOF-MS: *m*/*z* (%): 1810.8 (20, M$^+$), 1407.5 (8, M$^+$–Dendron); Anal. calcd for $C_{126}H_{112}N_4O_8$: (1810.2): C, 83.60; H, 6.24; N, 3.09. Found: C, 83.24; H, 6.18; N, 2.99.

4.2.2. 1,4,8,11-Tetra-3,5-bis[3′,5′-bis(2″-oxymethylnaphthyl)benzyloxy]benzyl-1,4,8,11-tetraazacyclotetradecane (5). Reaction procedure as described above. Amounts: 1,4,8,11-Tetraazacyclotetradecane (0.05 g, 0.25 mmol), 3,5-bis[3′,5′-bis-(2″-oxymethylnaphthyl) benzyloxy]benzylbromide (1.21 g, 1.20 mmol) and potassium carbonate (1.38 g, 10.00 mmol). Column chromatography (SiO_2, 40–63 μm, CH_2Cl_2–MeOH: 30/1) yielding 0.70 g (72%) of bright yellow solid; mp 80–82°C; TLC (SiO_2): R_f=0.25 (dichloromethane–methanol 30:1); ^{1}H NMR: (400 MHz, $CDCl_3$, 25°C) δ=1.68 (t, br, 4H, CH_2), 2.38 (m, br, 16H, CH_2N), 3.13 (s, br, 8H, Ar–CH_2), 4.62 (s, 16H, 2Ar–C_2O–Ar), 4.95 (s, 32H, 16 Naph-C_2O–Ar), 6.31 (t, $^4J_{HH}$=2.2 Hz, 4H, C_{ar}), 6.45 (t, $^4J_{HH}$=2.2 Hz, 8H, C_{ar}), 6.57 (m, 24H, C_{ar}), 7.25–7.39 (m, 48H, C_{Naph}), 7.59–7.72 (m, 64H, C_{Naph}); ^{13}C NMR: (100.6 MHz, $CDCl_3$, 25°C) δ=24.2 (CH_2), 50.4 (CH_2N), 51.6 (CH_2N), 59.4 (Ar–H_2), 69.7 (Naph-H_2O–Ar), 70.2 (Naph-H_2O–Ar), 101.6, 106.5, 107.6, 125.3, 125.9, 126.1, 126.4, 127.7, 127.9, 128.3, 133.0, 133.3, 134.3, 139.6, 143.4, 159.7, 160.1; MALDI-TOF-MS: DHB, *m*/*z* (%): 3910.1 ($M-H^+$, 100), 2982.6 ($M+H^+-$Dendron, 31); Anal. calcd for $C_{270}H_{174}N_4O_{24}$: (3908.7): C, 82.97; H, 5.78; N, 1.43. Found: C, 82.07; H, 5.80; N, 1.11.

4.2.3. 3,5-Bis[3′,5′-bis-(2″-oxymethylbenzyl) benzyloxy]-benzylbromide (6) and 3,5-bis[3′,5′-bis-(2″-oxymethyl-naphthyl) benzyloxy]benzylbromide (7). The synthesis of dendrons **6** and **7** was performed according to literature procedures.[35,36]

4.3. Photophysical experiments

Most of the experiments were carried out in air-equilibrated acetonitrile–dichloromethane 1:1 v/v solution at 298 K. When necessary, the behaviour in rigid butyronitrile matrix at 77 K was also investigated. The equipment used for measuring the absorption spectra and the photophysical properties has been described elsewhere.[8b] The estimated experimental errors are: ±2 nm on the band maximum, ±5% on the molar absorption coefficient, and ±5% on the p*K* values.

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References

1. (a) Tomalia, D. A.; Durst, H. D. *Top. Curr. Chem.* **1993**, *165*, 193. (b) Ardoin, N.; Astruc, D. *Bull. Soc. Chim. Fr.* **1995**, *132*, 875. (c) Newkome, G. R.; Moorefield, C.; Vögtle, F. *Dendrimers and Dendrons: Concepts, Syntheses, Perspectives*; VCH: Weinheim, 2001.
2. For some recent reviews, see: (a) Adronov, A.; Fréchet, J. M. J. *Chem. Commun.* **2000**, 1701. (b) Juris, A. *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley VCH: Weinheim, 2001; Vol. 3, p 655. (c) Hecht, S.; Fréchet, J. M. J. *Angew. Chem. Int. Ed.* **2001**, *40*, 75. (d) Gorman, C. B.; Smith, J. C. *Acc. Chem. Res.* **2001**, *34*, 60. (e) Balzani, V.; Ceroni, P.; Juris, A.; Venturi, M.; Campagna, S.; Puntoriero, F.; Serroni, S. *Coord. Chem. Rev.* **2001**, *219–221*, 545. (f) Grayson, S. M.; Fréchet, J. M. J. *Chem. Rev.* **2001**, *101*, 3819. (g) Oosterom, G. E.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Angew. Chem. Int. Ed.* **2001**, *40*, 1828.
3. Baars, M. W. P. L.; Meijer, E. W. *Top. Curr. Chem.* **2001**, *210*, 131.
4. (a) Ottaviani, M. F.; Bossamann, S.; Turro, N. J.; Tomalia, D. A. *J. Am. Chem Soc.* **1994**, *116*, 661. (b) Epperson, J. D.; Ming, L.-J.; Woosley, B. D.; Baker, G. R.; Newkome, G. R. *Inorg. Chem.* **1999**, *38*, 4498.
5. (a) Balogh, L.; Tomalia, D. A. *J. Am. Chem. Soc.* **1998**, *120*, 7355. (b) Zhao, M.; Sun, L.; Crooks, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 4877. (c) Zhao, M.; Crooks, R. M. *Adv. Mater.* **1999**, *11*, 217. (d) Zhao, M.; Crooks, R. M. *Angew. Chem. Int. Ed.* **1999**, *38*, 364. (e) Chechik, V.; Zhao, M.; Crooks, R. M. *J. Am. Chem. Soc.* **1999**, *121*, 4910. (f) Chechik, V.; Crooks, R. M. *J. Am. Chem. Soc.* **2000**, *122*, 1243. (g) Zhou, L.; Russell, D. H.; Zhao, M.; Crooks, R. M. *Macromol.* **2001**, *34*, 3567. (h) Crooks, R. M.; Zhao, M.; Sun, L.; Chechik, V.; Yeung, L. K. *Acc. Chem. Res.* **2001**, *34*, 181.
6. Gebbink, R. J. M. K.; Bosman, A. W.; Feiters, M. C.; Meijer, E. W.; Nolte, R. J. M. *Chem. Eur. J.* **1999**, *5*, 65.
7. Stephan, H.; Spies, H.; Johannsen, B.; Klein, L.; Vögtle, F. *Chem. Commun.* **1999**, 1875.
8. (a) Balzani, V.; Ceroni, P.; Gestermann, S.; Kauffmann, C.; Gorka, M.; Vögtle, F. *Chem. Commun.* **2000**, 853. (b) Vögtle, F.; Gestermann, S.; Kauffmann, C.; Ceroni, P.; Vicinelli, V.; Balzani, V. *J. Am. Chem. Soc.* **2000**, *122*, 10398. (c) Balzani, V.; Ceroni, P.; Gestermann, S.; Gorka, M.; Kauffmann, C.; Vögtle, F. *J. Chem. Soc., Dalton Trans.* **2000**, 3765.
9. (a) Vögtle, F.; Gorka, M.; Vicinelli, V.; Ceroni, P.; Maestri, M.; Balzani, V. *Chem Phys Chem.* **2001**, *12*, 769. (b) Vicinelli, V.; Ceroni, P.; Maestri, M.; Balzani, V.; Gorka, M.; Vögtle, F. *J. Am. Chem. Soc.* **2002**, *124*, 6461.
10. Gorman, C. *Nature* **2002**, *415*, 487.
11. van de Coevering, R.; Kuil, M.; Gebbink, J. M. K.; van Koten, G. *Chem. Commun.* **2002**, 1636.
12. Kawa, M.; Fréchet, J. M. *J. Chem. Mater.* **1998**, *10*, 286.
13. See for example, (a) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26. (b) Huisman, B.-H.; Schönherr, H.; Huck, W. T. S.; Friggeri, A.; van Manenm, H.-J.; Menozzi, E.; Vancso, G. J.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *Angew. Chem. Int. Ed.* **1999**, *38*, 2248. (c) McClenaghan, N. D.; Loiseau, F.; Puntoriero, F.; Serroni, S.; Campagna, S. *Chem. Commun.* **2001**, 2634.
14. (a) Enomoto, M.; Aida, T. *J. Am. Chem. Soc.* **1999**, *121*, 874. (b) Enomoto, M.; Aida, T. *J. Am. Chem. Soc.* **2002**, *124*, 6099.
15. Hancock, R. D.; Motekaitis, R. J.; Mashishi, J.; Cukrowsky, I.; Reibenspies, J. H.; Martell, A. E. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1925.
16. (a) Bianchi, A.; Micheloni, M.; Paoletti, P. *Coord. Chem. Rev.* **1991**, *110*, 17. (b) Kimura, E. *Prog. Inorg. Chem.* **1994**, *41*, 443. (c) Fabbrizzi, L.; Licchelli, M.; Pallavicini, P.; Sacchi, D. *Supramol. Chem.* **2001**, *13*, 569.
17. Meyer, M.; Dahaoui-Gindrey, V.; Lecomte, C.; Guilard, R. *Coord. Chem. Rev.* **1998**, *178*, 1313.
18. Sibert, J. W.; Cory, A. H.; Cory, J. G. *Chem. Commun.* **2002**, 154.
19. (a) Brucher, E.; Sherry, A. D. In *The Chemistry of Contrast Agents in Medical Magnetic Resonance Imaging*; Merbach,

A. E., Toth, E., Eds.; Wiley: New York, 2001; Chapter 6. (b) Caravan, P.; Ellison, J. J.; McMurry, T. J.; Lauffer, W. H. *Chem. Rev.* **1999**, *99*, 2293.

20. (a) Kimura, E.; Koike, T.; Inouye, Y. *Perspective on Bioinorganic Chemistry*; Hay, R. W., Dilworth, J. R., Nolan, K. B., Eds.; JAI: Stamford, CT, 1999; Vol. 14, p 145. (b) Liang, X.; Parkinson, J.; Weishäupl, M.; Gould, R. O.; Paisey, S. J.; Park, H.-S.; Hunter, T. M.; Blindauer, C. A.; Parson, S. A.; Sadler, P. J. *J. Am. Chem. Soc.* **2002**, *124*, 9105.
21. Simpson, N. R. M.; Ward, M. D.; Farran Morales, A.; Ventura, B.; Barigelletti, F. *J. Chem. Soc., Dalton Trans.* **2002**, 2455.
22. Jaffé, H. H.; Orchin, M. *Theory and Application of Ultraviolet Spectroscopy*; Wiley: New York, 1964.
23. 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.
24. Kubo, K.; Yamamoto, E.; Sakurai, T. *Heterocycles* **1998**, *4*, 1477.
25. Collins, G. E.; Choi, L.-S.; Callahan, J. H. *J. Am. Chem. Soc.* **1998**, *120*, 1474.
26. Quici, S.; Manfredi, A.; Maestri, M.; Manet, I.; Passaniti, P.; Balzani, V. *Eur. J. Org. Chem.* **2000**, 2041.
27. Bernhard, P. V.; Moore, E. G.; Riley, M. *J. Inorg. Chem.* **2001**, *40*, 5799.
28. Parker, D.; Williams, J. A. G. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1305.
29. Beeby, A.; Parker, D.; Williams, J. A. G. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1565.
30. (a) Micheloni, M.; Sabbatini, A.; Paoletti, P. *J. Chem. Soc., Perkin Trans. 2* **1978**, 828. (b) Thöm, V. J.; Hosken, G. D.; Hancock, R. D. *Inorg. Chem.* **1985**, *24*, 3378.
31. Röper, J. R.; Elias, H. *Inorg. Chem.* **1992**, *31*, 1202.
32. For the emission spectrum of dendron **7** see: Hahn, U.; Gorka, M.; Vögtle, F.; Vicinelli, V.; Ceroni, P.; Maestri, M.; Balzani, V. *Angew. Chem. Int. Ed.* **2002**, *41*, 3595.
33. Röper, J. R.; Elias, H. *Inorg. Chem.* **1992**, *31*, 1210.
34. (a) Binstead, R. A. *SPECFIT; Spectrum Software Associates: Chapel Hill*; Spectrum Software Associates: Chapel Hill, NC, 1996. (b) Gampp, H.; Maeder, M.; Meyer, C. J.; Zuberbulher, A. *Talanta* **1985**, *32*, 257.
35. Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638.
36. Stewart, G. M.; Fox, M. A. *J. Am. Chem. Soc.* **1996**, *118*, 4354.