POLY(PROPYLENE AMINE) DENDRIMERS DECORATED WITH DIMETHOXYBENZENE UNITS. PHOTOPHYSICAL AND ELECTROCHEMICAL PROPERTIES

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Dedicated to Professor Sergio Roffia on the occasion of his retirement.

We have investigated the absorption spectra, the fluorescence spectra and decay and the electrochemical redox processes of five dendrimers **G*n*** (n = 1 to 5) that contain $2^{n+1} - 2$ (*i.e.*, 62 for **G5**) tertiary amino groups in the interior and 2^{n+1} (*i.e.*, 64 for **G5**) 1,2-dimethoxybenzene (DMB) units in the periphery. In dichloromethane solution the absorption spectrum of the dendrimers is quite similar to that of 3,4-dimethoxy-*N*-propylbenzene-1-sulfonamide, a model compound of the peripheral DMB units. The fluorescence band of the DMB unit (λ_{max} = 319 nm, τ = 0.95 ns, Φ = 0.08 for the model compound), however, is much weaker in the dendrimers, which also display a broad emission tail above 450 nm (τ from 2 to 7 ns, depending on dendrimer generation), assigned to exciplex formation between the peripheral dimethoxybenzene groups and the inner tertiary amino groups. Upon addition of trifluoroacetic acid, which causes protonation of the inner amino groups of the dendrimers, the intensity of exciplex emission decreases and the intensity of the 319 nm band of the DMB units increases, reaches a maximum, and then decreases with increasing protonation of the dendrimer interior, presumably because of excimer formation between peripheral DMB units. Electrochemical investigations have shown that in acetonitrile the dendrimers exhibit a reversible, multielectron oxidation wave at about +1.7 V *vs* SCE, assigned to the peripheral DMB units and broad anodic peaks in the region +0.8/+1.5 V, assigned to oxidation of the inner tertiary amino groups.

Keywords: Dendrimers; Dimethoxybenzene; Electrochemistry; Photophysics; Multielectron transfer; Exciplexes; Excimers; Luminescence; Absorption spectroscopy.

Dendrimers 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[1,2]. Dendrimers are currently at-

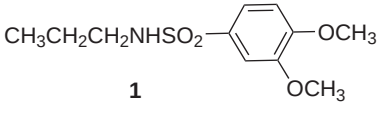
tracting the interest of a great number of scientists because of their unusual chemical and physical properties and the wide range of potential applications.

Research on dendrimers began in 1978 with a report on the synthesis of cascade molecules[3], but exploded only in the early nineties. Like trees, dendrimers usually exhibit aesthetically pleasant structures[1]. However, like in the case of a tree, the interest in a specific dendrimer does not depend on its beauty, but on the "fruit" (*i.e.*, the specific function) that it is able to produce[4].

In the last few years it has been shown that dendrimers containing luminescent components[5] are particularly interesting since luminescence signals offer a handle to better understand the dendritic structures and can be exploited for sensing purposes with signal amplification[6].

Other interesting dendrimers are those containing electroactive components[5a,5d,7]. Usually, dendrimers with peripheral electroactive units display multielectron transfer waves since each unit behaves almost independently and exhibits its characteristic property[8]. Inner electroactive units (*e.g.*, those in the core position), however, are often shielded by the dendrimer branches from interaction with the electrode so that their electron transfer processes are slowed down or completely prevented[5d,7b,7f,9].

In previous papers[6a,10a–10c] we have investigated the photophysical properties of poly(propylene amine) dendrimers (usually called POPAM) decorated at the periphery with luminescent units. Continuing our studies in this field, we have now functionalised the periphery of POPAM dendrimers (generations 1 to 5) with luminescent and redox-active 1,2-dimethoxybenzene (DMB) units and we have prepared five dendrimers **G*n*** (n = 1 to 5, Fig. 1) that contain $2^{n+1} - 2$ (*i.e.*, 62 for **G5**) tertiary amino groups in the interior and 2^{n+1} (*i.e.*, 64 for **G5**) 1,2-dimethoxybenzene units in the periphery. We have investigated the absorption spectra, the fluorescence spectra and decay, and the electrochemical behaviour of these dendrimers and of 3,4-dimethoxy-*N*-propylbenzene-1-sulfonamide (**1**), a model compound of the luminescent and redox-active DMB peripheral units of the dendrimers.



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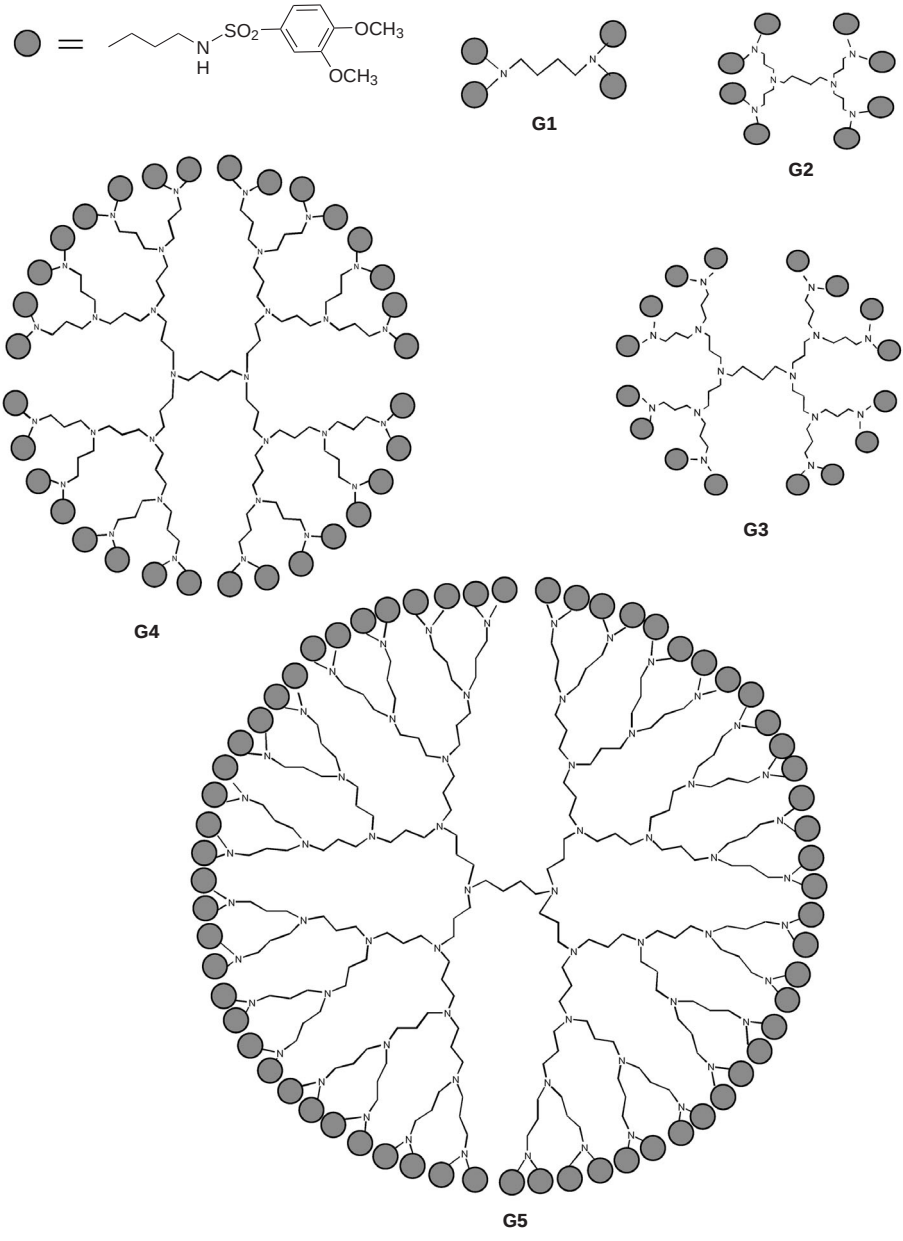

FIG. 1

Formulae of dendrimers **G*n*** (n = 1 to 5) and of model compound **1** of the peripheral dimethoxybenzene units

EXPERIMENTAL

All synthetic experiments were routinely carried out under dry argon. Starting materials (POPAM dendrimers, generations 1 to 5) were purchased from Aldrich. 3,4-Dimethoxybenzene-1-sulfonyl chloride was purchased from Lancaster. NMR-spectroscopic data were obtained at 400 MHz with a Bruker AM 400 spectrometer (for ^{1}H and ^{13}C NMR spectra, the $CDCl_3$ signals were used as an internal reference; shifts are quoted with respect to TMS). Chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz. MALDI-TOF mass spectra were obtained with a TofSpec E & SE instrument from Micromass, Manchester.

General Synthetic Procedure for the Multi-Dimethoxybenzene Dendrimers **G1**–**G5**

An amount of $1/n$ equivalents of the starting poly(propylene amine) dendrimer-$(NH_2)_n$ and *n* equivalents of triethylamine were dissolved in dry dichloromethane (200 ml) (where *n* is the number of primary amino groups on the dendrimer). The mixture was heated to reflux, whereupon a solution of *n* equivalents of 3,4-dimethoxybenzene-1-sulfonyl chloride in dichloromethane (50 ml) was added dropwise. The reaction mixture was stirred for 2–4 days under reflux. The solvent was then removed *in vacuo*, the residue was taken up in dichloromethane, and the resulting solution was thoroughly washed with water, aqueous sodium hydrogencarbonate solution, and again water (three times). After drying the organic phase with sodium sulfate and evaporation of the solvent, the multi-dimethoxybenzene dendrimers were obtained as bright-yellow solids.

4-Cascade:1,4-diaminobutane[4-N,N,N′,N′]:(1-azabutylidene)^{1}*:3,4-dimethoxybenzene-1-sulfonamide* (**G1**): Reaction procedure is described above. Amounts of reagents used to obtain the 4-cascade:1,4-diaminobutane[4-*N*,*N*,*N*′,*N*′]:(1-azabutylidene)^{1}:aminopropane (0.41 g, 1.30 mmol), triethylamine (0.52 g, 5.17 mmol), 3,4-dimethoxybenzene-1-sulfonyl chloride (1.22 g, 5.17 mmol). We obtained 1.27 g (1.14 mmol, 88%) of a bright-yellow solid; m.p. 76–77 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): 1.41–1.65 (br, 12 H, CH_2), 2.27–2.45 (br, 12 H, CH_2N), 2.82–2.94 (br, 8 H, CH_2NHSO_2), 3.75–3.82 (s, 12 H, OCH_3), 3.82–3.92 (s, 12 H, OCH_3), 6.82–6.92 (d, 4 H, CH_{ar}), 7.25–7.32 (s, 4 H, CH_{ar}), 7.35–7.45 (d, 4 H, CH_{ar}). ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): 25.12 ($CH_2CH_2NHSO_2$), 25.63 (CH_2CH_2N), 42.86 (CH_2NHSO_2), 53.16, 53.58 (CH_2N), 56.19, 56.26 (OCH_3), 109.70, 110.61, 121.07, 131.29, 149.08, 152.37 (CH_{ar}). MALDI-TOF MS (matrix: 2,5-DHB; $CHCl_3$:EtOH 3:1), *m/z* (%): 1139.4 (65) $[M + Na]^+$, 1117.5 (100) $[M]^+$, 917.7 (17) $[M - R]^+$, 586.7 (48) $[M/2 - 2CH_2]^+$ (R = dimethoxybenzenesulfonyl group). $C_{48}H_{76}N_6O_{16}S_4$: 1117.4.

8-Cascade:1,4-diaminobutane[4-N,N,N′,N′]:(1-azabutylidene)^{2}*:3,4-dimethoxybenzene-1-sulfonamide* (**G2**): Reaction procedure is described above. Amounts of reagents used to obtain the 8-cascade:1,4-diaminobutane[4-*N*,*N*,*N*′,*N*′]:(1-azabutylidene)^{2}:aminopropane (0.24 g, 0.31 mmol), triethylamine (0.25 g, 2.48 mmol), 3,4-dimethoxybenzene-1-sulfonyl chloride (0.59 g, 2.48 mmol). We obtained 0.57 g (0.24 mmol, 77%) of a bright-yellow solid; m.p. 79–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): 1.41–1.82 (br, 28 H, CH_2), 2.27–2.52 (br, 36 H, CH_2N), 2.82–2.94 (br, 16 H, CH_2NHSO_2), 3.75–3.82 (s, 24 H, OCH_3), 3.82–3.92 (s, 24 H, OCH_3), 6.82–6.92 (d, 8 H, CH_{ar}), 7.25–7.32 (s, 8 H, CH_{ar}), 7.35–7.45 (d, 8 H, CH_{ar}). ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): 25.72 ($CH_2CH_2NHSO_2$), 25.81 (CH_2CH_2N), 42.58 (CH_2NHSO_2), 51.84, 52.70 (CH_2N), 56.15–56.40 (OCH_3), 109.74, 110.47, 120.95, 131.37, 149.07, 152.33 (CH_{ar}). MALDI-TOF MS (matrix: 2,5-DHB; $CHCl_3$:EtOH 3:1), *m/z* (%): 2396.8 (55) $[M + Na]^+$, 2374.9 (70) $[M]^+$, 2173.2 (20) $[M - R]^+$, 1214.1 (100) $[M/2 + CH_2]^+$. $C_{104}H_{162}N_{14}O_{32}S_8$: 2377.0.

16-Cascade:1,4-diaminobutane[4-N,N,N′,N′]:(1-azabutylidene)^3:3,4-dimethoxybenzene-1-sulfonamide (**G3**): Reaction procedure is described above. Amounts of reagents used to obtain the 16-cascade:1,4-diaminobutane[4-*N*,*N*,*N*′,*N*′]:(1-azabutylidene)^3:aminopropane (0.45 g, 0.26 mmol), triethylamine (0.43 g, 4.27 mmol), 3,4-dimethoxybenzene-1-sulfonyl chloride (1.01 g, 4.27 mmol). We obtained 1.12 g (0.23 mmol, 85%) of a bright-yellow solid; m.p. 75–77 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): 1.41–1.85 (br, 60 H, CH_2), 2.27–2.55 (br, 84 H, CH_2N), 2.82–2.96 (br, 32 H, CH_2NHSO_2), 3.75–3.92 (br, 96 H, OCH_3), 6.82–6.92 (d, 16 H, CH_{ar}), 7.25–7.32 (s, 16 H, CH_{ar}), 7.35–7.45 (d, 16 H, CH_{ar}). ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): 23.90 ($CH_2CH_2NHSO_2$), 25.91 (CH_2CH_2N), 42.51 (CH_2NHSO_2), 51.19–53.00 (CH_2N), 56.19, 56.29 (OCH_3), 109.70, 110.67, 120.94, 131.57, 149.06, 152.31 (CH_{ar}). MALDI-TOF MS (matrix: 2,5-DHB; $CHCl_3$:EtOH 3:1), *m/z* (%): 4891.5 (25) $[M]^+$, 2473.0 (10) $[M/2 + 2CH_2]^+$. $C_{216}H_{336}N_{30}O_{64}S_{16}$: 4890.2.

32-Cascade:1,4-diaminobutane[4-N,N,N′,N′]:(1-azabutylidene)^4:3,4-dimethoxybenzene-1-sulfonamide (**G4**): Reaction procedure is described above. Amounts of reagents used to obtain the 32-cascade:1,4-diaminobutane[4-*N*,*N*,*N*′,*N*′]:(1-azabutylidene)^4:aminopropane (0.46 g, 0.13 mmol), triethylamine (0.42 g, 4.16 mmol), 3,4-dimethoxybenzene-1-sulfonyl chloride (0.98 g, 4.16 mmol). We obtained 1.08 g (0.11 mmol, 84%) of a bright-yellow solid; m.p. 75–77 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): 1.45–1.72 (br, 124 H, CH_2), 2.27–2.62 (br, 180 H, CH_2N), 2.82–2.99 (br, 64 H, CH_2NHSO_2), 3.75–3.96 (br, 192 H, OCH_3), 6.85–6.92 (d, 32 H, CH_{ar}), 7.27–7.35 (s, 32 H, CH_{ar}), 7.35–7.48 (d, 32 H, CH_{ar}). ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): 25.98 ($CH_2CH_2NHSO_2$), 25.98 (CH_2CH_2N), 42.31 (CH_2NHSO_2), 51.51–52.19 (CH_2N), 56.17, 56.28 (OCH_3), 109.70, 110.66, 120.91, 131.57, 149.04, 152.28 (CH_{ar}). MALDI-TOF-MS (matrix: 2,5-DHB; $CHCl_3$:EtOH 3:1), *m/z* (%): 9935.7 (25) $[M + Na]^+$, 9912.7 (35) $[M]^+$, 4984.1 (8) $[M/2 + CH_2]^+$. $C_{440}H_{688}N_{62}O_{128}S_{32}$: 9920.6.

64-Cascade:1,4-diaminobutane[4-N,N,N′,N′]:(1-azabutylidene)^5:3,4-dimethoxybenzene-1-sulfonamide (**G5**): Reaction procedure is described above. Amounts of reagents used to obtain the 64-cascade:1,4-diaminobutane[4-*N*,*N*,*N*′,*N*′]:(1-azabutylidene)^5:aminopropane (0.71 g, 0.10 mmol), triethylamine (0.65 g, 6.40 mmol) 3,4-dimethoxybenzene-1-sulfonyl chloride (1.51 g, 6.40 mmol). We obtained 1.57 g (0.08 mmol, 79%) of a bright-yellow solid; m.p. 78–79 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): 1.42–1.75 (br, 252 H, CH_2), 2.24–2.69 (br, 372 H, CH_2N), 2.98–2.98 (br, 128 H, CH_2NHSO_2), 3.78–3.96 (br, 384 H, OCH_3), 6.83–6.95 (d, 64 H, CH_{ar}), 7.25–7.34 (s, 64 H, CH_{ar}), 7.35–7.49 (d, 64 H, CH_{ar}). ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): 26.13 ($CH_2CH_2NHSO_2$), 26.15 (CH_2CH_2N), 42.34 (CH_2NHSO_2), 51.70–52.19 (CH_2N), 56.17, 56.24 (OCH_3), 109.66, 110.55, 120.91, 131.57, 149.06, 152.29 (CH_{ar}). $C_{888}H_{1392}N_{126}O_{256}S_{64}$: 19 981.5.

We have tried to obtain mass-spectra without success. Such a negative result is very common with high generation dendrimers[11a]. We have experience with dendrimers of high generation[11b,11c] and we are confident that we obtained dendrimer **G5**. As discussed below (see, section on Absorption Spectra), we cannot exclude that the higher generation dendrimers have a few defects, which, however, do not affect the general properties of these compounds.

Photophysical and Electrochemical Measurements

The absorption spectra and the photophysical properties (emission spectra, emission quantum yields, and excited state lifetimes) have been studied in dichloromethane solution where both the model compound and the dendrimers are soluble enough to be studied. The

equipment used has been described elsewhere[6a]. Luminescence quantum yields were measured following the method described by Demas and Crosby[12] (standard used: naphthalene in cyclohexane, $\Phi = 0.23$ [13]). The estimated experimental error is 2 nm on the band maximum, 5% on the molar extinction coefficient, 10% on the fluorescence quantum yield, and 5% on the fluorescence lifetime.

The electrochemical experiments were carried out in argon-purged acetonitrile (Romil Hi-Dry(tm)) solutions with tetraethylammonium hexafluorophosphate ($TEAPF_6$) as supporting electrolyte by an EcoChemie Autolab 30 multipurpose instrument interfaced to a personal computer. In the cyclic voltammetry (CV) the working electrode was a glassy carbon electrode (0.09 cm^2, Amel), the counter electrode was a Pt spiral, separated from the bulk solution with a fine glass frit, and a silver wire was employed as a quasi-reference electrode (AgQRE). All the potentials reported are referred to SCE by measuring the AgQRE potential with respect to $[Ru(bpy)_3](ClO_4)_2$. The concentration of the compounds was chosen so that in each case the DMB unit concentration was 1.0×10^{-3} mol l^{-1}. Cyclic voltammograms were obtained with scan rates in the range 0.05–10 V s^{-1}. For the chronoamperometric experiments a Pt-disk ultramicroelectrode with 25 μm radius was used as working electrode.

RESULTS AND DISCUSSION

Absorption Spectra

The absorption spectrum of model compound **1** in dichloromethane (Fig. 2) shows two intense bands in the UV spectral region with λ_{max} = 247 and 281 nm, typical of dimethoxybenzene-type chromophoric units.

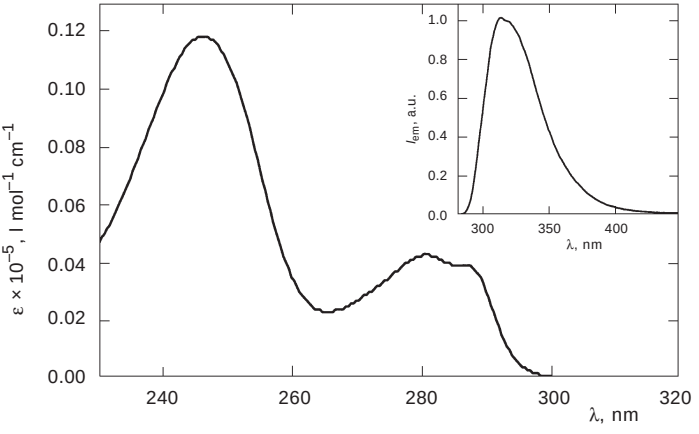

FIG. 2
Absorption and emission (inset) spectra (λ_{exc} = 250 nm) of reference compound **1** in dichloromethane solution

The absorption spectra of the dendrimers (Fig. 3) display only the absorption bands of the peripheral DMB groups since the inner POPAM structures do not exhibit any absorption above 230 nm. The molar absorption coefficients increase strongly with increasing number of generations because of the increasing number of DMB units contained in the dendrimer. The inset of Fig. 3 shows that the molar absorption coefficient at 247 nm (as well as at 280 nm) increases linearly with increasing number of peripheral DMB units up to generation 3, whereas for **G4** and **G5** the large ε values (296 000 and 548 000 l mol^{-1} cm^{-1} at 247 nm, respectively) are smaller than expected from 2^{n+1} DMB units. This commonly observed effect[10a,10c] for high generation dendrimers can be due to a few defects in the structure of the commercial poly(propylene amine) dendrimer and/or to interactions between chromophoric units in the crowded periphery of the largest dendrimers.

Luminescence

The emission spectrum of model compound **1** in dichloromethane (Fig. 2, inset) shows a band in the UV region (λ_{max} = 319 nm), with relatively low quantum yield (Φ = 0.08) and very short lifetime (τ = 0.95 ns), typical of dimethoxybenzene chromophoric groups.

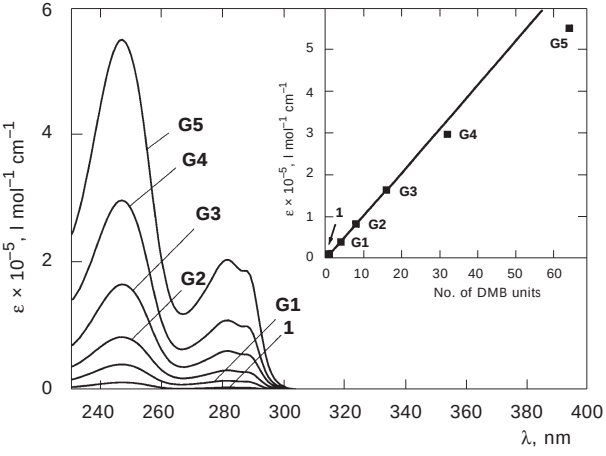

FIG. 3
Absorption spectra of the **G1**–**G5** dendrimers in dichloromethane solution. The inset shows the increase in the molar absorption coefficient at 247 nm on increasing number of dendrimer generations

The band at 319 nm is present also in the emission spectra of the dendrimers (Fig. 4), but its intensity is much lower than that of the model compound **1** and it decreases slightly with increasing number of dendrimer generations (the emission quantum yields are displayed in the inset of Fig. 4). Furthermore, as shown in the right-hand part of Fig. 4, the emission bands of dendrimers show a broad tail above 450 nm, which is not present in the band of model compound **1**. The presence of at least two distinct emitting species is also demonstrated by the double exponential decay of the emission intensity, with a short lifetime of about 1 ns in all cases and a longer lifetime increasing from *ca* 2 to *ca* 7 ns with increasing number of dendrimer generations. Lifetime measurements performed with filters isolating the emission below and above 450 nm showed that the shorter lifetime is related to the 319 nm band and the longer one to the emission tail in the visible region.

The broad tail above 450 nm is typical of excimer or exciplex formation, a phenomenon frequently observed in dendrimers because each excited component is closely surrounded by other units and can interact with them[10d]. In the present case, there are only two possibilities since an excited DMB unit can interact either with another, unexcited, DMB unit to give an excimer, or with an amino group to give an exciplex. Since the structure of these dendrimers is very flexible, both types of interactions are

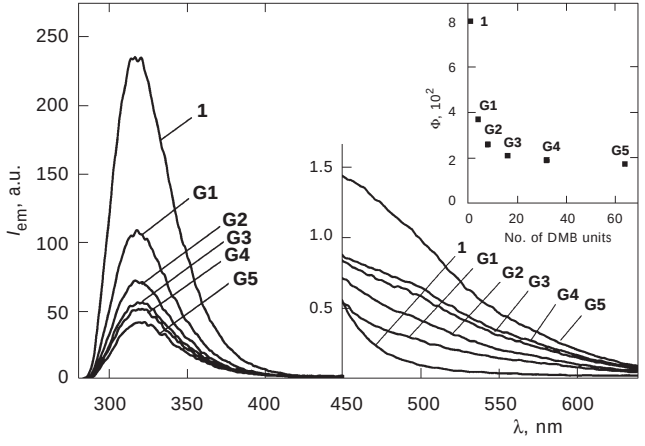

FIG. 4

Emission spectra of the **G1**–**G5** dendrimers and of model compound **1** in dichloromethane solution (λ_{exc} = 261 nm, isoabsorbing solutions). The inset shows the decrease in the emission quantum yield on passing from **1** to **G1** and on increasing number of dendrimer generations

likely to occur. Note that formation of both excimers and exciplexes is expected to cause the observed decrease in the emission of unperturbed DMB units.

In an attempt to elucidate the nature of the species responsible for the broad emission, we have added trifluoroacetic acid to dichloromethane solutions of compound **1** and of the dendrimers. In the case of compound **1**, addition of acid (up to 100 equivalents) did not cause any change in the absorption and emission spectra. This was an expected result since **1** has no basic function.

In the case of the dendrimers, addition of acid is expected to cause protonation of the interior tertiary amino groups. It should be noted, however, that trifluoroacetic acid is relatively weak. Therefore, it cannot be expected that protonation of the dendrimer amino groups takes place on a stoichiometric basis.

Addition of acid did not cause appreciable changes in the absorption spectra, but, as shown in Fig. 5 for **G1**, it caused an increase in the intensity of the DMB band at 319 nm, accompanied by a decrease in the broad emission tail at longer wavelength. Qualitatively similar results have been obtained for the other dendrimers. The spectral changes caused by addition of acid are fully reverted upon addition of stoichiometric amounts of base (tributylamine) and therefore can be assigned to the occurrence of protonation reactions, *i.e.* to the conversion of the amino groups of the dendrimer into ammonium moieties.

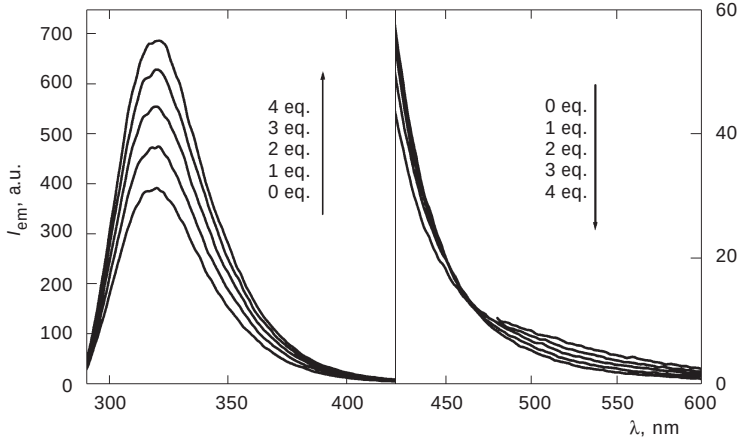

FIG. 5

Changes in the emission spectrum of **G1** caused by addition of trifluoroacetic acid in dichloromethane solution (λ_{exc} = 250 nm)

The first conclusion that can be drawn from the effect of acid addition is that in the non-protonated dendrimers exciplexes are formed which are responsible for the quenching of the non-interacting DMB emission at 319 nm and the presence of the broad emission tail at longer wavelength. In fact, a much more complex behaviour is observed on continuing acid addition: (i) the intensity of 319 nm band reaches a maximum and then begins to decrease; (ii) the maximum increase reached in the intensity of the 319 nm band does not lead to the value exhibited by the model compound **1**, where neither exciplexes nor excimers can be present; (iii) the emission tail at longer wavelengths does not disappear even at high acid concentrations. These results can be accounted for by assuming that with increasing protonation of the interior of the dendrimer the possibility of forming exciplexes decreases, while excimer formation (in unfolded structures) is likely favoured. Indeed the protonation of the interior presumably enhances the rigidity of the dendrimer, thus forcing the peripheral DMB units to stay close to each other.

Electrochemical Behaviour

It is well known that in acetonitrile solutions aliphatic tertiary amines undergo irreversible oxidation around +1 V *vs* SCE (*e.g.*, for tributylamine E_{pa} = +0.95 V at 0.2 V s^{-1}) and that 1,2-dimethoxybenzene is reversibly oxidised at +1.45 V [14].

The cyclic voltammetry pattern of model compound **1** in acetonitrile solution (Fig. 6) shows a reversible one-electron transfer process with $E_{1/2}$ = +1.66 V, positively shifted in comparison with 1,2-dimethoxybenzene because of the presence of the electron withdrawing sulfonamide substituent. The CV patterns obtained on oxidation of dendrimers **G1**, **G4** and **G5** are also displayed in Fig. 6. As one can see, **G1** exhibits broad and ill-defined peaks in the potential range from +0.8 to +1.5 V, that correspond to chemically irreversible electron transfers, and a reversible, multielectron transfer process at +1.71 V. **G4** and **G5** show a peak at *ca* +1.5 V, corresponding to chemically irreversible electron transfer processes (no reversibility is observed at scan rates up to 10 V s^{-1}) and a multielectron oxidation process with $E_{1/2}$ values of +1.71 and +1.74 V for **G4** and **G5**, respectively. A closer look at the anodic scan in the case of the two largest dendrimers reveals a small contribution to the Faradaic current, not present in the baseline curve, in the potential range from +0.8 to +1.4 V, due to the presence of very broad overlapping peaks at different potential values. These chemically irreversible electron-transfer processes observed for **G1**, **G4** and **G5** in

the potential range from +0.8 to +1.5 V are not present in the model compound **1** and they can be assigned to the oxidation of the amino groups lying in the interior of the dendrimers. The broadness of the corresponding peaks increases upon increasing number of dendrimer generations and suggests a slow kinetics of electron transfer due to the increasing shielding of the amine functions by the peripheral DMB units. Furthermore, the interior amino groups are not oxidised at the same potential value, demonstrating that they do not behave independently because of electrostatic reasons.

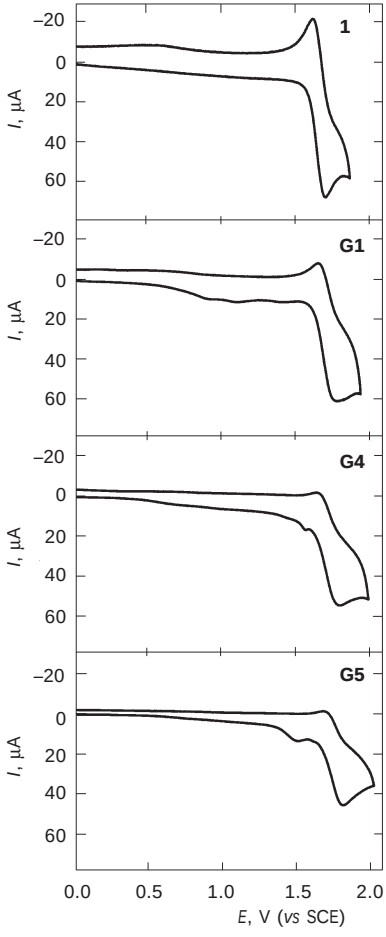

FIG. 6

Cyclic voltammetry oxidation pattern in acetonitrile/$TEAPF_6$ solution of model compound **1**, dendrimers **G1**, **G4** and **G5**. The concentration of the DMB units was 1.0×10^{-3} mol l^{-1} in all cases. Scan rate $v = 0.2$ V s^{-1}

The multielectron transfer process at *ca* +1.7 V can be assigned to the oxidation of the peripheral DMB units. The slight positive shift of the $E_{1/2}$ value, compared to that of the model compound **1**, is likely related to the electrostatic interaction with the already oxidised amino groups, while the increasing separation between the anodic and cathodic peaks upon increasing number of dendrimer generations is due to the concomitant oxidation of a large number of electrochemically equivalent DMB units[15]. A precise determination of the number of exchanged electrons in this process is prevented by the irreversible oxidation of the amino groups in the dendrimers at less positive potential[16]. However, a rough estimation can be made by the analysis of CV peak currents, assuming that the diffusion coefficient D decreases upon increasing number of dendrimer generations according to the following equation[15]:

$$D_2/D_1 = (M_1/M_2)^{0.55} ,$$

where M is the molecular weight. Within this hypothesis, the number of exchanged electrons is consistent with the oxidation of all the DMB units present at the periphery of the dendritic structures. Indeed, the comparison of the CV curves of **1**, **G1**, **G4** and **G5** with the same concentration of DMB units (Fig. 6) shows only a slight decrease in the peak currents at *ca* +1.7 V due to the decrease in the diffusion coefficient upon increasing molecular size.

CONCLUSIONS

The results obtained from the examination of the photophysical and electrochemical behaviour of dendrimers **G1**–**G5** have proved that, as expected, the 1,2-dimethoxybenzene peripheral units exhibit luminescence and undergo oxidation processes. However, the luminescence data indicate that some of the excited DMB units interact with the inner amino groups to give exciplexes. When exciplex formation is precluded by protonation of the amino groups, evidence for excimer formation has been obtained. These results show that in dendrimers excited states can be easily involved in interactions with other groups because of steric crowding. Shielding of inner redox-active units (in this case, amines) by peripheral units has also been observed.

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