Pergamon

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Tetrahedron 59 (2003) 9591–9598

TETRAHEDRON

Poly(amidoamine) dendrimers peripherally modified with 4-ethylamino-1,8-naphthalimide. Synthesis and photophysical properties

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Received 5 March 2003; revised 11 September 2003; accepted 2 October 2003

Abstract—New fluorescent poly(amidoamine) (PAMAM) dendrimers, comprising 4-ethylamino-1,8-naphthalmide units on the periphery have been synthesized. Their photophysical properties in organic solvents of different polarity have been determined. The photodegradation of the dendrimers in organic solvents has been investigated. The effect of the coordination of the dendrimer with transition metal cations in *N*,*N*-dimethylformamide solution has been discussed.

1. Introduction

Dendrimers are well defined macromolecules exhibiting a three-dimensional structure that is roughly spherical or globular. The chemistry of dendrimers provides a new direction of research in supramolecular architecture. Symmetrical, highly branched and comprising a good number of terminal functional groups, which can participate in different reactions,[1–3] these substances have been receiving increased attention. Dendrimers find application in different fields such as chemistry, biology, physics, and medicine.

The introduction of functional fluorescent and photoactive chromophore groups into the main dendrimer macromolecule[4] has been among the recent advancements of the dendrimer chemistry research.

The poly(amidoamine) (PAMAM) is a class of commercial dendrimers. These dendrimers are hydrophilic, highly branched macromolecules with different functional groups. PAMAM dendrimers consist of an ethylenediamine core, from which polyamidoamine repeat monomer extends in all directions.[5] This allows the modification of PAMAM dendrimers with fluorescent units. Thus novel materials with tailored properties finding a wide range of applications can be obtained.

Our first investigations on the synthesis and photophysical properties of some new PAMAM derivatives comprising 1,8-naphthalimide units in their periphery were published previously.[6] We have studied their fluorescence properties in the presence of different metal cations and we have observed enhancement of the fluorescence intensity. We found that these dendrimers could acts as sensors for metal cations.[6a,b]

1,8-Naphthalimides and their 4-substituted derivatives represent a very versatile class of compounds which have been used in a large variety of areas. It is well known, 4-ethylamino-1,8-naphthalimides are excellent yellow-green fluorophores with high quantum yields of fluorescence and very good photostability.[7] The copolymers of some traditional monomers with similar polymerizable 1,8-naphthalimide fluorophores have been recently reported.[8] We have been interested in the synthesis of dendrimer based macromolecules, comprising 4-ethylamino-1,8-naphthalimide groups on their periphery. The monomeric 4-ethylamino-1,8-naphthalimide derivatives exhibit very good photophysical and photochemical properties both in solution and as a polymer matrix.

In this paper, we report new modified PAMAM derivatives of zero and second generation bearing 4-ethylamino-1,8-naphthalimide fluorescent unit in their peripheries. Their

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Keywords: dendrimers; PAMAM; 1,8-naphthalimides; photophisics; photodegradation.

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doi:10.1016/j.tet.2003.10.006

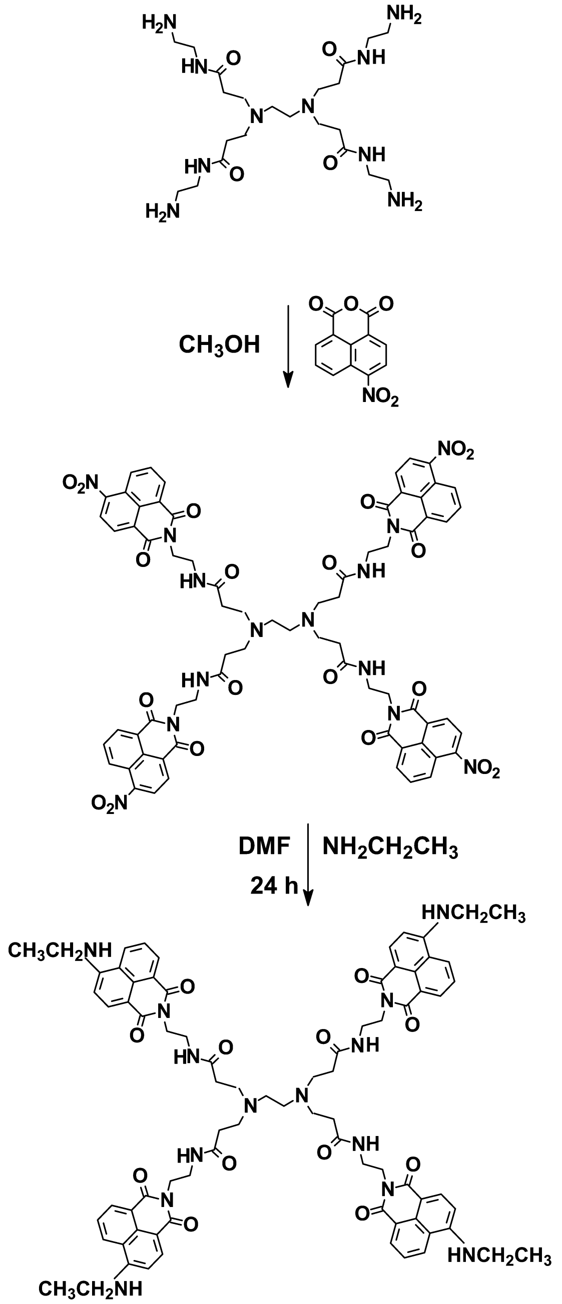
photophysical characteristics have been investigated in organic solvents of different polarity.

2. Results and discussion

2.1. Synthesis of fluorescent 4-ethylamino-1,8-naphthalimide-labelled PAMAM dendrimers (1) and (2)

The route to the synthesis of PAMAM dendrimer with 4-ethylamino-1,8-naphthalimide from generation zero (**1**) is shown in Scheme 1.

4-Nitro-1,8-naphthalimide-labelled PAMAM was prepared from commercial PAMAM—generation zero, which possesses four primary amine groups. 4-Ethylamino-1,8-naphthalimide fluorescent dendrimer (**1**) has been obtained in *N*,*N*-dimethylformamide solution by nucleophilic substitution of the nitro group of 4-nitro-1,8-naphthalimide-labelled PAMAM with an ethylamino group. The reaction proceeds at ambient temperature for 24 h. In this case the electron accepting carbonyl group of the naphthalimide molecule favours the nucleophilic substitution reactions.[9] The same procedure has been used for the synthesis of a PAMAM dendrimer with 4-ethylamino-1,8-naphthalimide from second generation (**2**) using the respective 4-nitro-1,8-naphthalimide-labelled PAMAM derivative (Scheme 2).



Scheme 1. Synthesis of 4-ethylamino-1,8-naphthalimide-labelled PAMAM dendrimer **1**.

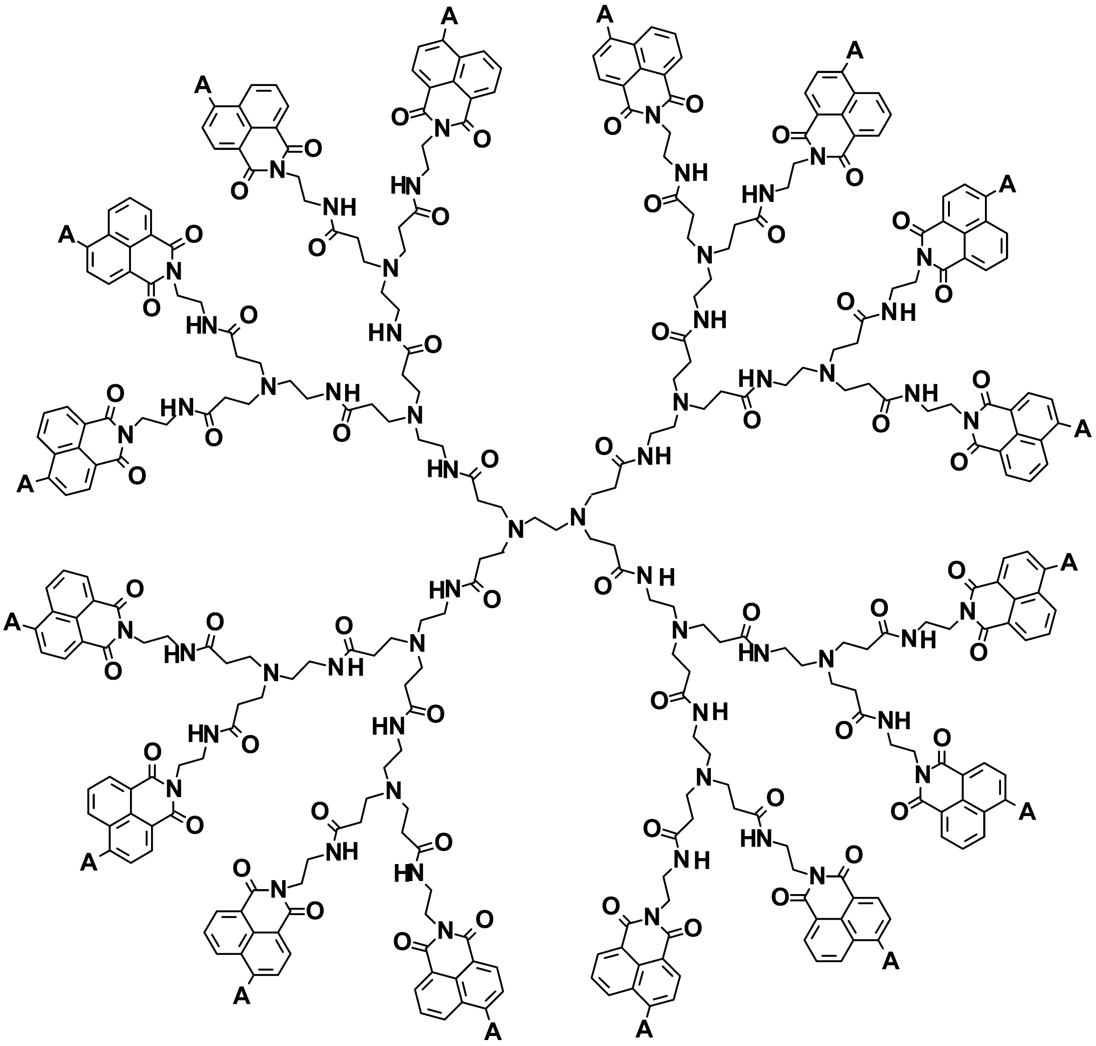
The final products for both generations were obtained after precipitation with water and filtration of the solid residue precipitate subjected to double re-crystallization from toluene. FT-IR, ^{1}H NMR, ^{13}C NMR spectroscopy studies and elemental analysis confirmed the chemical structure of the products.

2.2. Photophysical properties of dendrimers 1 and 2

The bonding of fluorescent 1,8-naphthalimide units to the PAMAM structure gives new interesting photophysical and photochemical properties. The basic photophysical properties of the monomeric 1,8-naphthalimides depend mainly on the polarization of 1,8-naphthalimide molecules. This phenomenon is due to the electron donor-acceptor interaction occurring between the substituents at C-4 position and the carbonyl groups from the imidic structure of the chromophoric system. On the other hand it may be a result of the environmental effect upon the interaction. Clearly the absorption and emission bands of the 1,8-naphthalimide derivatives depend largely on the electron donating nature of the substituents at the C-4 position.[10]

Table 1 summarizes the spectral characteristics of **1** in organic solvents of different polarity: the absorption (λ_A) and fluorescence (λ_F) maxima, the extinction coefficient (ε), Stokes shift ($\nu_A - \nu_F$), quantum yield of fluorescence (Φ_F) and the energy fluorescent yield (E_F).

In all the organic solvents under study the new PAMAM dendrimers **1** and **2** are yellow-green in color and give green fluorescence. The absorption maxima of the 4-nitro-1,8-naphthalimide-labelled PAMAM **1** and **2** are in the UV region due to the electron-accepting nature of the nitro group.[6a,c] The replacement of the nitro group by an electron-donating ethylamine leads to a large bathochromic shift of the absorption maxima. The absorption maxima λ_A for **1** are in the visible region at 430–443 nm with high extinction coefficient (ε=34200–36500 mol^{-1} dm^3 cm^{-1}), corresponding to a $S_0 \rightarrow S_1$ (π,π^*), transition without a vibrational structure. The solubility of **2** in most of the organic solvents is poor. Therefore its photophysical properties (Table 2) have been studied in *N*,*N*-dimethylformamide (DMF) solution. The absorption (λ_A) maximum is at 440 nm and the respective emission spectrum has a maximum (λ_F) at 528 nm. The molar extinction coefficient (ε) is 194,600. Examples of the absorption and fluorescence spectra of the PAMAM dendrimer **1** in ethanol and *N*,*N*-dimethylformamide solutions and **2** in *N*,*N*-dimethylformamide are shown in Figs. 1–3. Each of the fluorescence spectra has a



A = $NHCH_2CH_3$

Scheme 2. 4-Ethylamino-1,8-naphthalimide-labeled PAMAM dendrimers **2**.

fluorescence band with a single maximum, without vibrational structure. The fluorescence curves are an approximate mirror image of the absorption ones. This is an indication of the prevailing fluorescence emission and of the unchanged molecular structure of the 1,8-naphthalimide fluorophore in the exited state. As seen from Tables 1 and 2 the molar extinction coefficient for dendrimers **1** and **2** is approximately 4 and 16 fold higher than that of the

Table 1. Photophysical properties of dendrimer (**1**) in organic solvents with different polarity (see text)

Solvent	λ_A (nm)	ε ($mol^{-1}\,dm^3\,cm^{-1}$)	λ_F (nm)	$\nu_A-\nu_F$ (cm^{-1})	Φ_F	E_F
Chloroform	438	36,500	517	3488	0.25	0.20
Ethylacetate	430	34,700	517	3913	0.24	0.20
Trichloroethylene	436	36,900	517	3593	0.25	0.21
Tetrahydrofurane	433	35,000	515	3677	0.24	0.20
2-Methyl-2-propanol	443	34,200	519	3305	0.21	0.18
Ethanol	443	34,100	524	3489	0.20	0.17
Methanol	443	33,500	524	3589	0.21	0.18
N,*N*-Dimethylformamide	437	34,200	521	3689	0.22	0.18

Table 2. Photophysical properties of dendrimer (**2**) in *N*,*N*-dimethylformamide (see text)

Solvent	λ_A (nm)	ε ($mol^{-1}\,dm^3\,cm^{-1}$)	λ_F (nm)	$\nu_A-\nu_F$ (cm^{-1})	Φ_F	E_F
N,*N*-Dimethylformamide	440	194,600	528	3787	0.26	0.22

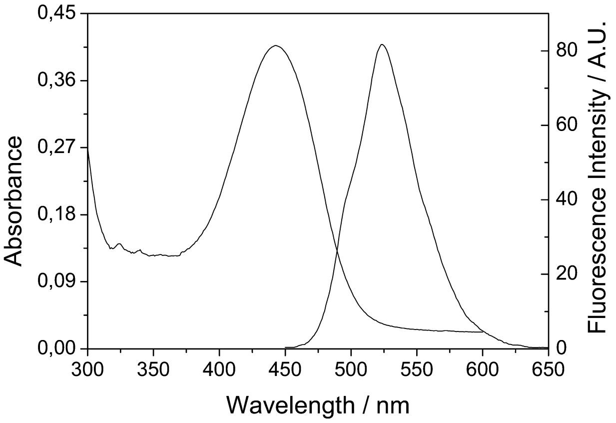


Figure 1. Absorption and fluorescence spectra of 4-ethylamino-1,8-naphthalimide-labelled PAMAM **1** in ethanol

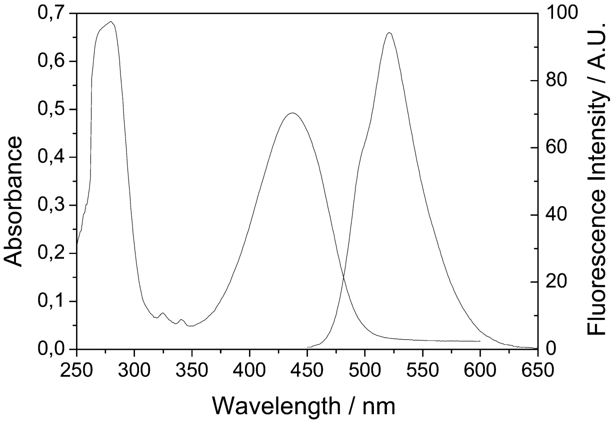


Figure 2. Absorption and fluorescence spectra of 4-ethylamino-1,8-naphthalimide-labelled PAMAM **1** in *N*,*N*-dimethylformamide.

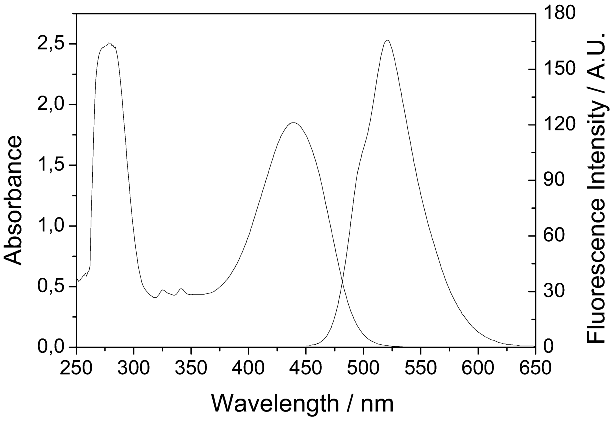


Figure 3. Absorption and fluorescence spectra of 4-ethylamino-1,8-naphthalimide-labelled PAMAM **2** in *N*,*N*-dimethylformamide.

monomeric 1,8-naphthalimide derivatives with the same substituents at C-4 position.[10] This allows the suggestion that no ground state interaction occurs between the 1,8-naphthalimide chromophoric units.[11]

The effect that different media have upon the absorption and fluorescent maxima of 4-ethylamino-1,8-naphthalimide-labelled PAMAM **1** is illustrated in Figure 4 which plots the absorption maxima of the dendrimer in media of increasing polarity. The polarity is characterized by the empirical parameter of solvent polarity E_T(30 kcal mol^{-1}).[12] As seen from Figure 4, the nature of the solvent influences the spectral properties of PAMAM dendrimer **1**. The position of the maxima of the chromophore change as a result from the solvatochromic effect. The absorption and fluorescent maxima of the dendrimer in apolar solvents are hypsochromically shifted ($\Delta\lambda_A$=13 nm and $\Delta\lambda_F$=7 nm) in comparison with the spectra taken in polar solvents. As seen, the PAMAM dendrimer under study has a positive solvatochromism.

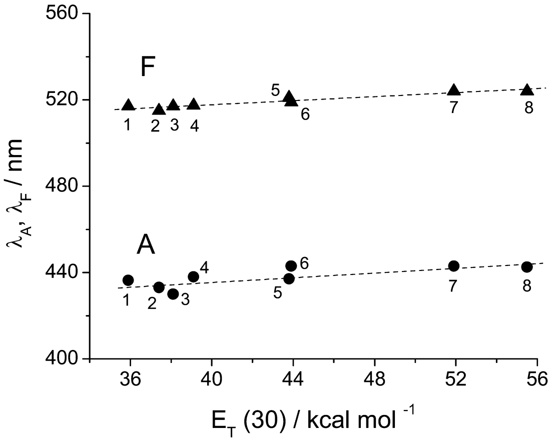


Figure 4. Dependence of absorption (A) and fluorescence (F) maxima of 4-ethylamino-1,8-naphthalimide-labelled PAMAM (**1**) on the empirical parameters of solvent polarity E_T(30). Solvent used: 1, trichloroethylene; 2, tetrahydrofuran; 3, ethyl acetate; 4, chloroform; 5, *N*,*N*-dimethylformamide; 6, 2-methyl-2-propanol; 7, ethanol; 8, methanol.

Figure 4 also shows that the polarization of the 1,8-naphthalimide chromophoric system is affected by the solvent polarity less than the analogous monomeric 1,8-naphthalimide.[13] The similar weak effect of the solvents upon the spectral properties of 1,8-naphthalimide PAMAM labelled dendrimers has been described recently.[6a]

The Stokes shift is an important parameter for the fluorescence compounds. This parameter indicates the difference in the properties and structures of the compounds between the ground state S_0 and the first exited state S_1. The Stokes shift has been estimated according to Eq. (1):

$$(\nu_A - \nu_F) = (1/\lambda_A - 1/\lambda_F) \times 10^{-7} \quad (1)$$

The Stokes shift calculated is in the region 3305–3913 cm^{-1}, which is common for the 1,8-naphthalimide derivatives.[14,15] The overlap between absorption and fluorescence spectra is low and an aggregation effect in the concentration at about 10^{-6} mol dm^{-3} has not been observed.

The ability of the PAMAM dendrimers being studied to emit absorbed light energy has been characterized quantitatively by the quantum yield of fluorescence (Φ_F). This has been calculated on the basis of the absorption and fluorescence spectra in organic solvents of different polarity. Fluorescence quantum yields have been determined relative to Rhodamine 6G. The data presented in Table 1 show that the fluorescence quantum yield (Φ_F) is low and is in the 0.20–0.25 region for dendrimer **1**. A lower Φ_F has been

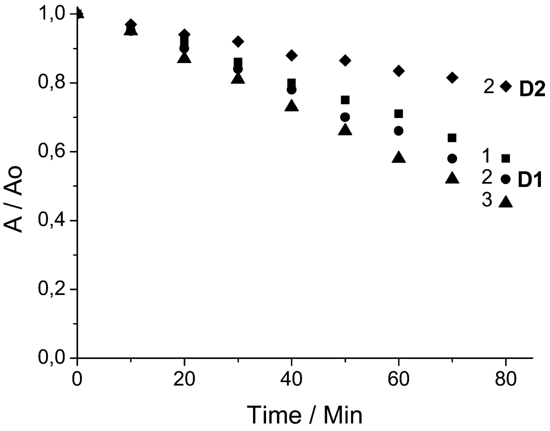


Figure 5. Photodegradation of 4-ethylamino-1,8-naphthalimide-labelled PAMAM (**1**) and 4-ethylamino-1,8-naphthalimide-labelled PAMAM (**2**) in different organic solvents: 1, ethanol; 2, *N*,*N*-dimethylformamide; 3, trichloroethylene. The concentration of the dendrimers is 1×10^{-6} mol.

observed in the alcohols. Compared with those for similar monomeric 4-alkylamino-1,8-naphthalimides[10,15] the present values obtained for Φ_F are very low. This might be due to the possible photoinduced electron transfer from the central part of PAMAM to the peripheral naphthalimide units.[16]

Besides Φ_F, the energy yield of fluorescence, E_F, can also be used (Eq. (2)):[17]

$$E_F = \Phi_F\lambda_A/\lambda_F \qquad (2)$$

The respective results for E_F are 0.17–0.21 for **1** in different organic solvents and 0.22 for **2** in DMF. Their dependence is like the one of Φ_F.

2.3. Photostability of dendrimer in organic solvents

Photodegradation of the 4-ethylamino-1,8-naphthalimide-labelled PAMAM **1** and **2** has been measured comparing the absorption maxima of the solutions before and after irradiation. Figure 5 presents the kinetics of photodegradation of the dendrimers in different organic solvents. It has been found that the photodegradation of the dendrimers follows a pseudo first order reaction. The calculated rate constants *Kp* for dendrimer photodegradation are listed in Table 3. As seen the photodegradation of **1** is higher in trichloroethylene solution ($Kp=5.20\times10^{-8}\ \mathrm{s}^{-1}$). When ethanol is used as solvent the dendrimer degradation is less pronounced. This may be due to the stabilizing effect of H-bonds occurring between the dendrimer molecules and the solvent ($Kp=3.16\times10^{-8}\ \mathrm{s}^{-1}$). In the case of dendrimer **2** the photodegradation is less pronounced than in the case of dendrimer **1**. Probably it is due to the greater number of chromophore units that **2** dendrimer molecule comprises. The energy needed for the photodestruction of dendrimer **2** is greater than that in the case of dendrimer **1**, due to the higher molar extinction coefficient of dendrimer **2**. No new absorption or emission maxima appear in any organic solvent used. Also there is not any change in the fluorescence maxima before and after the irradiation. This fact demonstrates that the products of photo-destruction neither absorb nor fluoresce in the spectral region where the 4-ethylamino-1,8-naphthalimide-labelled PAMAM is photoactive, which is in agreement with the observations on the good photostability of some other similar monomeric 1,8-naphthalimide derivatives.[15a,18]

Table 3. Rate constant *Kp* of photodegradation of 4-ethylamino-1,8-naphthalimide-labelled PAMAM **1** and **2**

Solvents	*Kp*	
	1 ($10^{-8}\ \mathrm{s}^{-1}$)	**2** ($10^{-5}\ \mathrm{s}^{-1}$)
Trichloroethylene	5.20	–
Ethanol	3.16	–
N,*N*-Dimethylformamide	3.32	3.52

2.4. Fluorescence quenching measurements

This study also covers the fluorescence properties that dendrimer **2** in DMF solution acquires upon the addition of transition metal cations.

The fluorescence intensity of dendrimer **2** is studied at increasing concentrations of metal cations. Its fluorescence responses to the presence Co^{2+} cations as a ‘guest’ are presented in Figure 6 as a typical example. As shown in Figure 6 fluorescence quenching of the dendrimer solution is observed upon the addition of cobalt cations. This dependence has been studied in the Co^{2+} cation concentration range of $0-8\times10^{-5}$ mol dm^{-3}. At low cobalt cations concentration (1.8×10^{-6} mol dm^{-3}) the quenching effect is 23.5 %, which demonstrates good fluorescence sensitivity. Further addition of Co^{2+} cations (7.6×10^{-5} mol dm^{-3}) to the dendrimer solution, also decreases—up to 56%—the intensity of fluorescence. At a certain concentration of 4×10^{-5} mol dm^{-3} the effect of additional metal ions lowers.

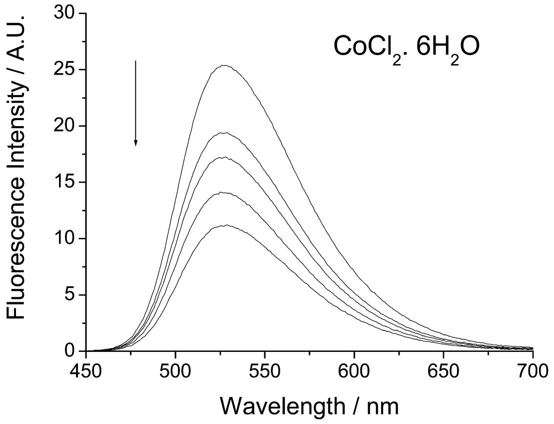


Figure 6. Fluorescence spectra of dendrimer **2** in *N*,*N*-dimethylformamide at various concentrations of Co^{2+} cations. The dendrimer concentration in solution is 1×10^{-6} mol.

Figure 7 shows the dependence of fluorescence quenching (FQ) of the dendrimer **2** in DMF solution on the nature of metal cations. The FQ is determined from the ratio between the maximum fluorescence intensity (before the addition of metal cations) and minimum fluorescence intensity (after the addition of metal cations). It is seen that fluorescence quenching depends on the kind of metal cations. The highest effect is observed in the presence of Co^{2+} cations yielding fluorescent quenching (FQ) of 2.26. The similar effect has

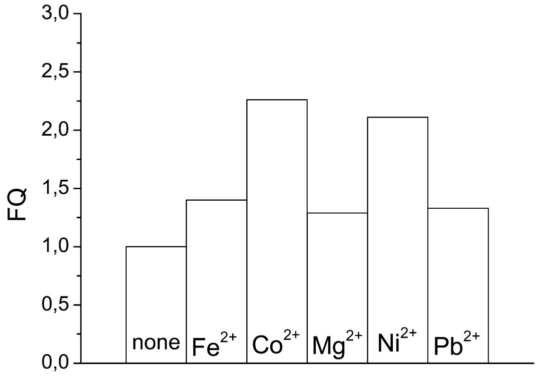


Figure 7. Fluorescence quenching (FQ) of dendrimer **2** in the presence of different metal cations in, *N*,*N*-dimethylformamide solution. The dendrimer concentration in solution is 1×10^{-6} mol.

been observed using Ni^{2+} (FQ=2.11). In the cases of Fe^{2+}, Pb^{2+} and Mg^{2+} cations the decrease of the fluorescence intensity is lower (FQ=1.29–40). The FQ effect produced by the different metal cations can be ranked as follows: $Co^{2+}>Ni^{2+}>Fe^{2+}>Pb^{2+}>Mg^{2+}$.

Figure 8 plots the effect of addition of the metal cations upon the fluorescence intensity of dendrimer **2**. It can be expected that each dendrimer molecule coordinates several metal cations giving rise to a complex curve. As seen from Figure 8 at a low metal cations concentration the fluorescence intensity decreases linearly with the increasing metal concentration. Higher concentrations change the pattern of the curve and the dependence is no more linear. This fact indicates the formation of species containing more than one metal cation per dendrimer molecule. Similar results have been recently observed by Balzani and Vögtle in the case of poly(propylene amine) dendrimer treated with Co^{2+} cations.[4c,19] Figure 8 also shows differences in the curve pattern when using various metal cations. This fact is due to the different coordination potencies of the cations of each metal studied.

The position of the absorption maximum of dendrimer **2** appears at the same position regardless of the presence of metal cations. This fact indicates that the ligand sites responsible for metal–ion coordination have to be bonded to the aliphatic amine groups from the interior part of the PAMAM dendrimer molecule.[20] Once the coordination has occurred, the fluorescence quenching is caused by an electron or energy transfer reaction proceeding between the metal complexes and chromophore 1,8-naphthalimide units in the dendrimer molecules.

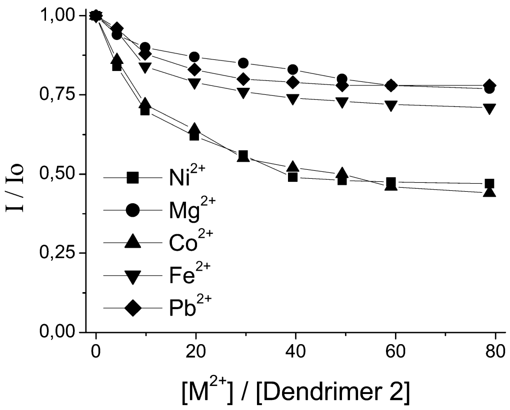


Figure 8. Effect of addition of metal cations on the fluorescence intensity of the dendrimer **2**. The dendrimer concentration in solution is 1×10^{-6} mol.

3. Conclusion

Two new fluorescent 4-ethylamino-1,8-naphthalimide-labelled PAMAM of zero and second generation with high yield and purity have been synthesized. The influence of the solvent polarity upon the photophysical characteristics has been investigated. In organic solvents the photostability of the dendrimers **1** and **2** is good.

The relatively low quantum yield of fluorescence is due to a photoinduced electron transfer that might occur from the amino groups of the central part of PAMAM to the peripheral naphthalmide units. Quenching of the fluorescence intensity of dendrimer **2** indicates the presence of ‘guest’ metal cations. It has been shown that the fluorescence quenching of the dendrimer depends on the nature of metal cations added to the solutions.

4. Experimental

4.1. Materials and methods

4-Nitro-1,8-naphthalimide-labelled PAMAM from zero and second generation have been synthesized according to the method described recently.[6a,c] $CoCl_2\cdot6H_2O$, $FeSO_4\cdot7H_2O$, $MgCl\cdot6H_2O$, $NiSO_4\cdot6H_2O$ and $PbCl_2$ have been investigated as metal cations. The effect of the metal cations on the fluorescence intensity was examined by adding a few μl of stock solution of the metal cations to a known volume of a solution of dendrimer **2** (3 ml). The addition was limited to 0.08 ml such that the volume change was insignificant.[20]

UV–Vis spectrophotometric investigations were performed on a UVIKON 930 spectrophotometer (KONTRON instruments). The fluorescence spectra were taken on a SFM 25 spectrophotometer (KONTRON instruments). Fluorescence quantum yield were determined on the basis of the absorption and fluorescence spectra. Rhodamine 6G was used as reference ($\Phi_0=0.88$). All organic solvents used in this study were of spectroscopic grade. The NMR spectra were obtained on a Bruker DRX-250 spectrometer, operating at 250.13 and 62.90 MHz for ^1H and ^{13}C, respectively using a dual 5 mm probe head. The measurements were carried out in DMSO-d_6 solution at ambient temperature. The chemical shift were referenced to tetramethylsilane (TMS), standard experiments with 30° pulses, 1 s relaxation delays, 16 K time domain points, zero-filled to 64 K for protons and 32 K for carbons were performed. The distortionless enhancement by polarisation transfer (DEPT) spectra were recorded under the same conditions as the ^{13}C NMR spectra and $\tau=(2^1J_{CH})^{-1}=3.45$ μs was used. The 2D $^1H/^1H$ correlated spectra (COSY) were performed with spectral width 2200 Hz, relaxation delay 2 s, number of increments 512, size 1 K×1 K. The 2D

$^{1}H/^{13}C$ heteronuclear multiple quantum coherence (HMQC) experiments were carried out with a spectral width of 2200 Hz for ^{1}H and 9000 Hz for ^{13}C, relaxation delay 1.5 s, FT size 1 K×256 W.

The photodegradation was carried out using a solar light simulator (Suntest CPS+, heraus) equipped with a 1.5 kW xenon arc lamp. Incident photonic flux was measured by chemical actinomery using uranyl oxalate from Fluka–Riedel. Values close to 1×10^{17} photons^{-1} have been found.

4.1.1. Synthesis of 4-ethylamino-1,8-naphthalimide-labelled PAMAM (1). 4-Nitro-1,8-naphthalimide-labeled PAMAM (0.0005 mol, 0.680 g) from zero generation was reacted with ethylamine (0.004 mol, 0.32 ml) in 50 ml of *N*,*N*-dimethylformamide for 24 h at room temperature. After that, water (500 ml) was added to the solution. The precipitate was filtered off, washed with water and then dried under vacuum at 40°C. Yield: 90%. FT-IR (KBr) cm^{-1}: 3455, 3362, 2953, 2925, 2856, 1661,1632, 1578, 1552, 1459, 1365, 1186, 1033, 771; ^{1}H NMR (250.13 MHz, DMSO-d$_6$): δ 1.25 (t, 12H, CH_3), 2.50 (m, 8H, $OCCH_2CH_2N$), 3.00 (m, 8H, NCH_2CH_2CO), 3.00 (m, 4H, NCH_2CH_2N), 3.25 (m, 8H, Ar-$NHCH_2CH_3$), 3.30 (m, 8H, $(OC)_2N{-}CH_2CH_2NHCO$), 4.00 (br s, 8H, $(OC)_2NCH_2CH_2NHCO$), 6.60 (m, 4H, Ar-H), 7.50 (t, 4H, J=6.1 Hz, Ar-*NH*–CH_2CH_3), 7.60 (m, 4H, Ar-H), 8.15 (m, 4H, Ar-H), 8.25 (br s, 4H, $(OC)_2NCH_2CH_2NHCO$), 8.35 (m, 4H, Ar-H), 8.60 (m, 4H, Ar-H); ^{13}C NMR (62.9 MHz, DMSO-d$_6$): δ 14.8 (CH_3), 31.2 (NCH2CH_2–CO), 37.0 (Ar-$NHCH_2CH_3$), 37.7 ($(OC)_2NCH_2CH_2NHCO$), 38.6 ($(OC)_2NCH_2CH_2NHCO$), 47.5 (NCH_2CH_2CO), 103.5–134.0 (Ar-C), 163.0 (*CO*NH*CO*), 171.3 and 171.7 (*CO*NH); Elemental analysis: $C_{78}H_{84}O_{12}N_{14}$ (1408.2): calcd C 66.46 H 5.96 N 13.92. Found C 66.35 H 5.89 N 13.84.

4.1.2. Synthesis of 4-ethylamino-1,8-naphthalimide-labelled PAMAM (2). 4-Nitro-1,8-naphthalimide-labeled (0.0001 mol, 0.68 g) PAMAM from second generation was reacted with ethylamine (0.005 mol, 0.40 ml) in 50 ml of *N*,*N*-dimethylformamide for 24 h at room temperature. After that, water (500 ml) was added to the solution The precipitate was filtered off, washed with water and then dried under vacuum at 40°C. Yield: 92%. FT-IR (KBr) cm^{-1}: 3326, 2927, 2853, 1676, 1641, 1578, 1546, 1357, 1242, 773; ^{1}H NMR (250.13 MHz, DMSO-d$_6$): δ 1.03 (t, 48H, J=6.1 Hz, $HNCH_2CH_3$), 2.10 (m, 32H, $HNCH_2CH_3$), 2.35 (br s, 56H, $OCCH_2CH_2N$), 3.00 (m, 56H, NCH_2CH_2CO), 3.00 (m, 4H, NCH_2CH_2N), 3.20 (m, 24H, $CONHCH_2CH_2N$), 3.30 (m, 32H, $(OC)_2N{-}CH_2CH_2NHCO$), 4.02 (br s, 32H, $(OC)_2NCH_2CH_2NHCO$), 6.30 (br s, 16H, Ar-H), 7.46 (m, 16H, Ar-H), 7.66 (br s, 12H, $CONHCH_2CH_2N$), 7.92 (br s, 16H, $(OC)_2NCH_2CH_2NHCO$), 7.97 (m, 16H, Ar-H), 8.22 (m, 16H, Ar-H), 8.43 (m, 16H, Ar-H); ^{13}C NMR (62.9 MHz, DMSO-d$_6$): δ 14.0 ($NHCH_2CH_3$), 33.6 (NCH_2CH_2CO), 34.6 (Ar-$NHCH_2CH_3$), 37.1 ($CONHCH_2CH_2N$), 37.9 ($(OC)_2NCH_2CH_2{-}NHCO$), 39.2 ($NHCH_2CH_2N(CH_3)_2$), 49.8 (NCH_2CH_2CO), 52.4 ($CONHCH_2CH_2N$), 103.7–134.6 (Ar-C), 162.8 and 164.2 (*CO*NH*CO*), 171.7 and 171.9 (*CO*NH); Elemental analysis: $C_{366}H_{432}O_{60}N_{74}$ (6820.3): calcd C 64.39 H 6.33 N 15.19. Found C 64.25 H 6.28 N 15.09.

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