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Synthesis, photophysical and photochemical properties of fluorescent poly(amidoamine) dendrimers

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Abstract

The study reports on the synthesis of four novel PAMAM dendrimers of generation 2, modified with 1,8-napthalimide. Their photophysical characteristics have been determined in organic solvents of different polarity (chloroform and *N*,*N*-dimethylformamide). The spectral assignments of the dendrimers are dependent on the nature of the substituent at C-4 position of the 1,8-naphthalimide structure. The low quantum yield of fluorescence of the novel materials reveals that a photo-induced electron transfer is proceeding from the core of the dendrimer molecule to the naphthalimide fluorophore located in its periphery. The PAMAM dendrimers thus modified exhibit good photo stability in *N*,*N*-dimethylformamide solution.

Keywords: Fluorescent; PAMAM; Dendrimers

1. Introduction

Dendrimers are highly branched macromolecules with well controlled composition and architectures [1]. They find application in different scientific fields such as chemistry, biology, physics, and medicine. The introduction of functional fluorescent chromophore groups into the dendrimer macromolecules has been among the recent avant-gardes researches on dendrimer chemistry [2]. Novel well definite dendrimers with photoactive units in the core or at the periphery of the dendritic macromolecules have been reported and their photophysical properties investigated [3–7]. Some cationically substituted 1,4,5,8-naphthalenediimides bonded to the dendrimer macromolecules have been investigated as electro-conductive materials [5].

The poly(amidoamine)s (PAMAM) are a novel class of commercial dendrimers which possesses a definite molecular composition with different terminal functional groups. These macromolecules were first synthesized and investigated by Tomalia et al. [8]. The design and modification of the PAMAM dendrimers with fluorescent units could give them new interesting properties and expand their areas of application.

Our first investigations on the synthesis and photophysical properties of some new PAMAM derivatives from zero generation comprising 1,8-naphthalmide units in their periphery, which are able to detect some metal cations, have already been published [9]. The choice of 1,8-naphthalimide units as a fluorescent chromophore, has been determined by two factors: (i) as yellow–green chromophores the 1,8-naphthalimide derivatives [10] are able to give the dendrimers desired fluorescent properties which allow interesting and attractive applications for novel materials; (ii) they have high photo stability [11]. On the other hand, the strong fluorescence emission is the reason to investigate the 1,8-naphthalimide derivatives as co-monomers for the synthesis of linear fluorescent polymers [12].

In this paper we report on the synthesis and characterization of new modified second generation PAMAM derivatives bearing 1,8-naphthalimide fluorescent units at their peripheries. Its photophysical and photochemical characteristics have been investigated in organic solvents of different polarity.

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2. Experimental part

2.1. Materials and methods

PAMAM dendrimer of a generation 2 as a 20 wt% methanolic solution, 1,8-naphthalic anhydride and 4-nitro-1,8-naphthalic anhydride for the synthesis of the fluorescent dendrimers were used as obtained from Aldrich.

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). For all absorption and fluorescence measurements, the dendrimer concentration in the solution was 10^{-6} mol l^{-1}. Fluorescence quantum yields were determined on the basis of the absorption and fluorescence spectra. Rhodamine 6G was used as standard ($\Phi_0 = 0.88$). The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker spectrometer at 400 and 75 MHz, respectively, using $CDCl_3$ as solvent. Deuteriodimethylsulfoxide and tetramethylsilane were used as a solvent and internal standard, respectively. FT-IR spectra were measured on a Bruker IFS-113v spectrometer, using the KBr pellet technique at a 4 cm^{-1} resolution. Thin layer chromatography (TLC) analysis followed on silica gel (Fluka F_{60} 254 20 × 20; 0.2 mm) using the solvent system *n*-heptane–acetone (2:1) as eluent.

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 and values close to 1×10^{17} photons^{-1} have been found.

2.2. Synthesis

2.2.1. Synthesis of 1,8-naphthalimide-labelled PAMAM (D1)

16.2 ml of 20% PAMAM methanolic solution and 3.17 g of 1,8-naphthalic anhydride were dissolved in 50 ml methanol. The solution was refluxed and the reaction was monitored using TLC. After 6 h the liquid was poured into 200 ml water and the resulting precipitate was filtered and dried in vacuum. Yield. 95 %. FT-IR (KBr) cm^{-1}: 3372, 3281, 3073, 2932, 2827, 1699, 1958, 1549, 1345, 779; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 8.28 (m, 32H, ArH-2 and ArH-7); 7.93 (m, 32H, ArH-4 and ArH-5); 7.59 (m, 32H, ArH-3 and ArH-6); 4.15 (br s, 32H, $(CO)_2NCH_2$); 3.54 (br s, 56H, CONH$CH_2$$CH_2$N); 3.16 (br s, 28H, NH); 2.61 (br s, 56H, N$CH_2$$CH_2$CONH); 2.44 (br s, 28H, CONH$CH_2$$CH_2$-N); 2.25 (br s, 56H, N$CH_2$$CH_2$CONH); ^{13}C NMR ($CDCl_3$) δ (ppm): 173.21, 164.96, 164.12, 132.32, 131.14, 130.54, 129.54, 126.22, 125.36, 122.59, 115.60, 114.56, 54.76, 52.69, 50.39, 39.86, 38.50, 38.21, 34.41. $C_{334}H_{352}O_{60}N_{58}$ (6132): calcd C 65.36, H 5.74, N 13.28; found: C 65.42, H 5.61, N 13.19.

2.2.2. Synthesis of 4-nitro-1,8-naphthalimide-labelled PAMAM (D2)

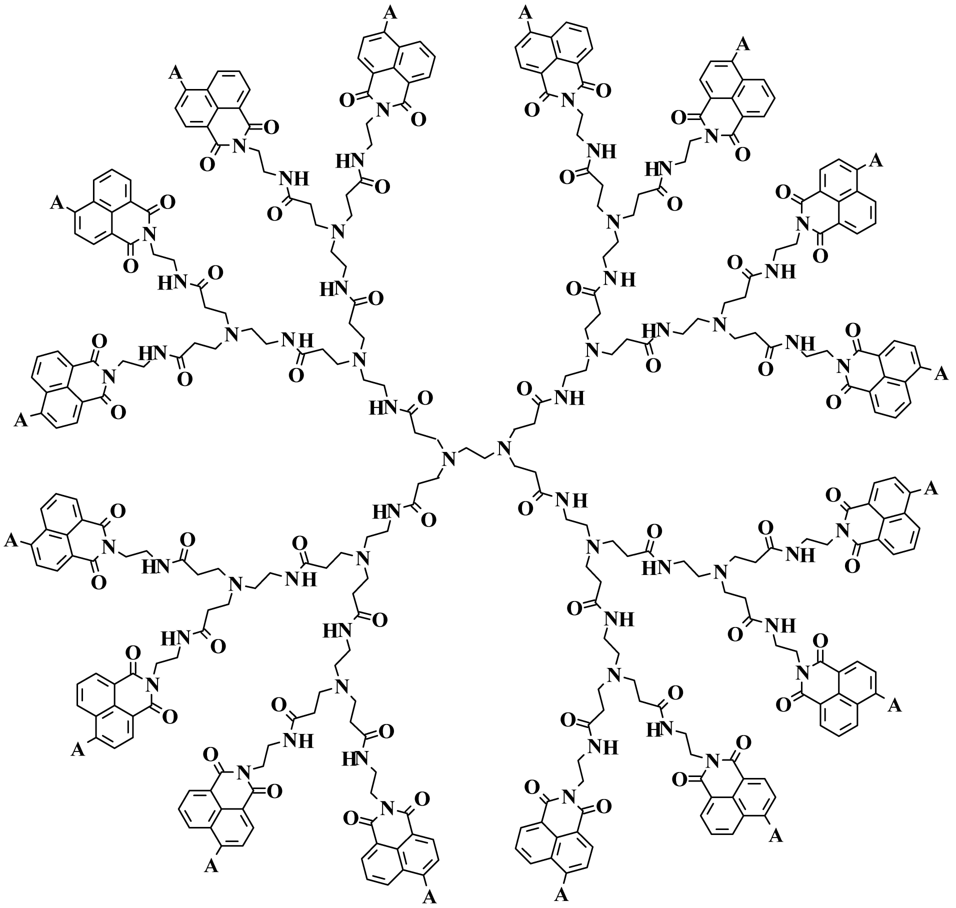
16.2 ml of 20% PAMAM methanolic solution and 3.90 g of 4-nitro-1,8-naphthalic anhydride were dissolved in 50 ml of methanol. The solution was refluxed and the reaction was monitored by TLC. After 6 h the liquor was poured into 200 ml of water and the resulting precipitate was filtered. Yield: 91 %. FT-IR (KBr) cm^{-1}: 3376, 3280, 3076, 1702, 1664, 1583, 1528, 1342, 1223, 786; $C_{334}H_{336}O_{92}N_{74}$ (6852): calcd C 58.49, H 4.90, N 15.12; found: C 58.56, H 4.81, N 15.14.

2.2.3. Synthesis of 4-piperidino-1,8-naphthalimide-labelled PAMAM (D3)

0.683 g of 4-nitro-1,8-naphthalimide-labeled PAMAM D2 was reacted with 0.2 ml of piperidine in 50 ml of *N*,*N*-dimethylformamide for 24 h at room temperature. After that 500 ml of water were added to the solution, the precipitate was filtered off, washed with water, then dried in vacuum at 40 °C. Yield: 91 %. FT-IR (KBr) cm^{-1}: 3554, 3285, 3075, 2833, 2847, 2822, 1693, 1650, 1586, 1349, 783; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 8.11 (m, 32H, ArH-5 and ArH-7); 7.52 (br s, 16H, ArH-2); 7.39 (br s, 16H, ArH-6); 6.91 (d, 16H, $J = 7$ Hz, ArH-3); 4.12 (br s, 32H, $(CO)_2NCH_2$); 3.54 (br s, 56H, CONH$CH_2$$CH_2$N); 3.20 (br s, 28H, NH); 3.06 (br s, 64H, ArNCH_2); 2.64 (br s, 28H, CONH$CH_2$$CH_2$N); 2.42 (br s, 56H, N$CH_2$$CH_2$CONH); 2.28 (br s, 56H, N$CH_2$$CH_2$-CONH); 1.82 (br s, 64H, CH_2–piperidine); 1.69 (br s, 32H, CH_2–piperidine); ^{13}C NMR ($CDCl_3$) δ (ppm): 173.3, 164.82, 164.37, 157.42, 132.82, 131.08, 130.67, 129.85, 126.12, 125.42, 122.85, 115.58, 114.87, 54.78, 52.77, 50.43, 39.97, 38.45, 38.20, 34.35, 26.61, 24.71; $C_{414}H_{496}O_{60}N_{74}$ (7460): calcd C 66.59, H 6.65, N 13.88; found: C 66.67, H 6.59, N 13.83.

2.2.4. Synthesis of 4-hexylamino-1,8-naphthalimide-labelled PAMAM (D4)

The synthesis was run according to the same procedure as D3 using *n*-hexylamine. Yield: 84 %. FT-IR (KBr) cm^{-1}: 3348, 3085, 2954, 2958, 2855, 1681, 1638, 1580, 1548, 1364, 1247, 774; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 8.60 (d, 16H, $J = 7.3$ Hz, ArH-7); 8.48 (d, 16H, $J = 8.3$ Hz, ArH-5); 8.08 (d, 16H, $J = 8.4$ Hz, ArH-2); 7.64 (t, 16H, $J = 7.5$ Hz, ArH-6); 6.74 (d, 16H, $J = 8.5$ Hz, ArH-3); 4.16 (t, 32H, $J = 7.5$ Hz, $(CO)_2N$ $CH_2$$CH_2$); 3.57 (br s, 16H, ArNH); 3.48 (q, 32H, $J = 6.5$ Hz, ArNH $CH_2$$CH_2$); 3.30 (q, 56H, $J = 6.5$ Hz, CONH$CH_2$$CH_2$N); 2.61 (br s, 28H, CONH); 2.30 (m, 56H, N$CH_2$$CH_2$CONH); 1.72 (m, 116H, N$CH_2$$CH_2$CONH and ArNH $CH_2$$CH_2$$CH_2$); 1.37 (m, 96H, $CH_2$$CH_2$$CH_2$$CH_2$$CH_3$); 0.90 (t, 48H, $J = 6.5$ Hz, $CH_2$$CH_3$); ^{13}C NMR ($CDCl_3$) δ (ppm): 172.9, 164.22, 164.01, 157.53, 132.48, 131.13, 130.59, 129.78, 126.24, 125.39, 122.75, 115.63, 114.77, 54.69, 52.75, 50.35, 39.89, 38.50, 38.19, 34.19, 31.50, 28.40, 26.42, 22.69, 14.8; $C_{430}H_{560}O_{60}N_{74}$ (7716): calcd C 66.87, H 7.65, N 13.42; found: C 66.94, H 7.59, N 13.39.



Scheme 1. 1,8-naphthalimide-labeled PAMAM dendrimers D1–D4.

3. Results and discussion

The general formula of 1,8-naphthalimide-labelled PAMAM dendrimers (D1–D4) are presented in Scheme 1. As seen the fluorescent 1,8-naphthalimide units are bonded to the periphery of the dendrimer macromolecules.

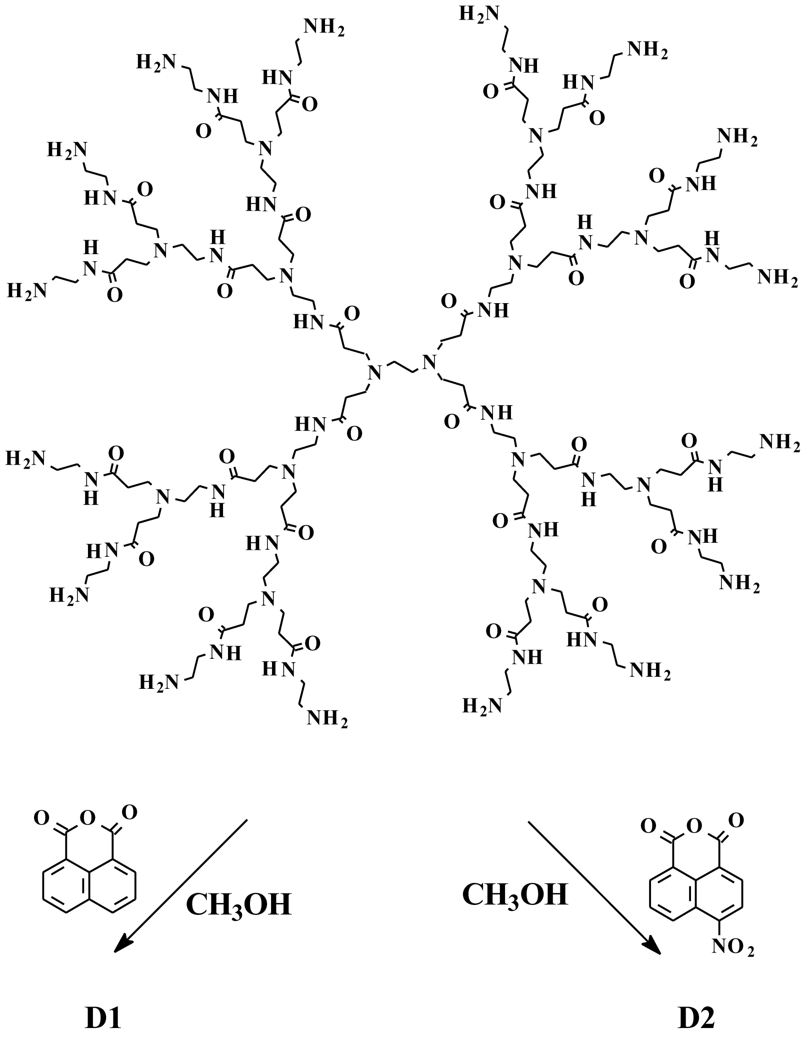
3.1. Synthesis of modified PAMAM dendrimers D1–D4

Scheme 2 presents the route to the synthesis of the new 1,8-naphthalimide-labelled PAMAMs.

The new 1,8-naphthalimide-labelled PAMAM dendrimers are prepared from second generation PAMAM, which possesses 16 primary amine groups. 1,8-naphthalic anhydride reacts with PAMAM in methanol solution, yielding a new compound comprising 1,8-naphthalimide units in its dendrimer structure (D1). The same procedure was used to obtain a 4-nitro-1,8-naphthalimide-labeled dendrimer (D2). The D1 and D2 are obtained as a solid by filtration. The consummation reaction of the initial 1,8 naphthalimide and the purity of the final products were monitored by TLC. Unfortunately, D1 and D2 being of high molecular weight remain at the start of the chromatogram. Running the reaction at ambient temperature for 24 h green fluorescent 4-piperidino- (D3) and 4-hexylamino-1,8-naphthalimide (D4) PAMAM dendrimers are obtained. The nitro group of 4-nitro-1,8-naphthalimide-labelled PAMAM dendrimer in *N*,*N*-dimethylformamide solution undergoes nucleophilic substitution with the respective amino groups (Scheme 3). In this case the electron accepting carbonyl group of the naphthalimide molecule favors the nucleophilic substitution reactions of the nitro group with the amines [13]. The final products are obtained after precipitation with water and filtration of the solid precipitate, which is then subjected to double re-crystallization from toluene. The D3 and D4 dendrimers obtained in a high yield are dark yellow solids with a fairly good purity.

3.2. FT-IR and characteristics

Fig. 1 shows as an example the 1450–1750 cm^{-1} region IR spectra of the D1–D4 PAMAM dendrimers. The naphthalimides give rise to two frequency bands of the C=O absorption. The IR spectrum of 4-nitro-1,8-naphthalimide-PAMAM dendrimer (D2) has intense absorption bands at 1702 and 1664 cm^{-1}, respectively. The absorption bands for 4-aminosubstituted-1,8-naphthalimide-PAMAM dendrimers (D3 and D4) are hypsochromically shifted and the absorbances are at 1693–1669 cm^{-1} and 1650–1628 cm^{-1}, respectively. In the case of dendrimer D1 these values are at 1699 and



Scheme 2. Synthesis of PAMAM dendrimer D1and D2.

1658 cm^{-1}. These bands are characteristic of the vibrations caused by symmetric and asymmetric carbonyl groups [14]. A comparison of the four spectra mentioned reveals that the polarization of the 1,8-naphthalimide molecules has a strong effect upon the absorption properties of the chromophores. As seen the bands for 4-hexylamino-1,8-naphthalimide dendrimer are the most hypsochromically shifted. The carbonyl groups from the dendrimer amidic groups (HNC=O) for all dendrimer D1–D4 have absorption bands at 1627 cm^{-1} (Amide I) and 1580 cm^{-1} (Amide II). The band at 774–786 cm^{-1} are characteristic for the aromatic ring deformation vibrations. The 4-nitro-1,8-naphthalimide-PAMAM dendrimer (D2) containing a nitro group ($-NO_2$) gives absorption band at 1528 cm^{-1} for the asymmetric vibrations of the nitro group.

$$\mathbf{D2{-}NO_2} \xrightarrow[\mathbf{DMF,\ 24h}]{\mathbf{AH}} \mathbf{D3\ or\ D4}$$

Scheme 3. Synthesis of PAMAM dendrimer D3 and D4.

3.3. Photophysical characteristics of dendrimers D1–D4

1,8-Naphthalimide derivatives are fluorescent compounds that present very interesting photophysical properties. These properties are often very sensitive to the nature

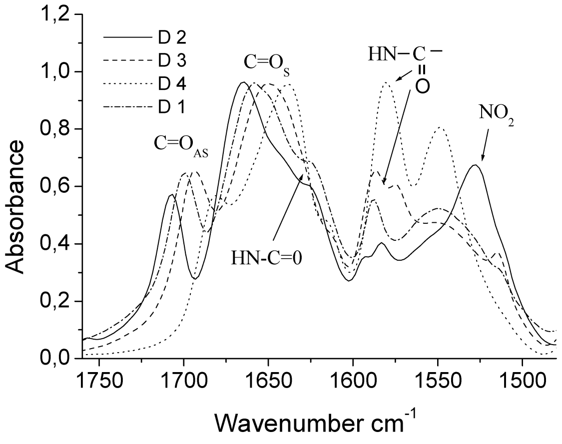


Fig. 1. FT-IR spectra of dendrimers D1–D4 in KBr.

Table 1
Photophysical characteristics of dendrimers D1–D4 in chloroform

	D1	D2	D3	D4
λ_A (nm)	334	339	414	437
ε (l mol^{-1} cm^{-1}	185800	89100	192900	181600
λ_F (nm)	459	–	520	520
$\nu_A - \nu_F$ (cm^{-1})	8153	–	4923	3652
Φ_F	0.002	–	0.20	0.24
f	3.69		3.92	3.75

of the organic solvents in which they are dissolved. The photophysical characteristics of dendrimers D1–D4 were recorded in two organic solvents with different polarity: chloroform (E_T (30) [kcal mol^{-1}] = 39.1) and *N*,*N*-dimethylformamide (E_T (30) [kcal mol^{-1}] = 43.8): 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 oscillator strength (f) are presented in Tables 1 and 2.

Fig. 2 shows as an example the absorption spectra of PAMAM dendrimer D1–D4 in *N*,*N*-dimethylformamide solution. It has been observed that the dendrimers have different absorption maxima. The position of the maxima depends on the polarization of the chromophoric 1,8-naphthalimide system. In both organic solvents dendrimer D1 has an absorption maximum in the near UV-region at $\lambda_A = 333$–334 nm (Tables 1 and 2). In the case of dendrimer D2 with an electron accepting nitro group as a substituent at C-4 position in the 1,8-naphthalimide structure the absorption maxima are bathochromically shifted by 4–5 nm. After the change of the nitro groups with the electron donating amino groups (D3 and D4) the absorption maxima are much more bathochromically shifted (up to 103 nm). The respective maxima are in the visible region at $\lambda_A = 414$–437 nm (chloroform) and at $\lambda_A = 408$–439 nm (*N*,*N*-dimethylformamide). In this case the dendrimer D3 and D4 are yellow–green in colour. The absorption maxima assigned to dendrimer D3, which has a tertiary cycloamino group as a substituent at C-4 in the 1,8-naphthalimide structure are hypsochromically shifted if compared with the absorption maxima of D4. The latter dendrimer comprises a secondary hexylamino substituent at position C-4 in its 1,8-naphthalimide structure. The molar extinction coefficients (ε) in the long-wavelength band of the absorption spectra are higher than 10000 mol l^{-1} cm^{-1}, indicating that this is a charge transfer (CT) band, due to (π,π^*) character of the $S_0 \rightarrow S_1$ transition. On the other hand the molar extinction coefficient for dendrimers is approximately 16 fold larger than that of the monomeric 1,8-naphthalimide derivatives with the same substituents at C-4 position [15], suggesting no ground state interaction between the 1,8-naphthalimide chromophoric units [16]. The studies on some 1,8-naphthalimide labelled PAMAM derivatives of zero generation have given similar results [9a].

Table 2
Photophysical characteristics of dendrimers D1–D4 in *N*,*N*-dimethylformamide

	D1	D2	D3	D4
λ_A (nm)	333	347	408	439
ε (l mol^{-1} cm^{-1}	171300	76200	189400	189300
λ_F (nm)	451	–	521	524
$\nu_A - \nu_F$ (cm^{-1})	7857		5316	3695
Φ_F	0.006	–	0.28	0.32
f	3.52	–	3.60	3.01

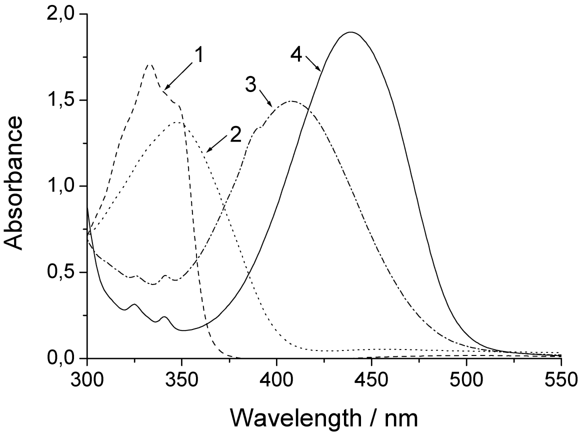


Fig. 2. Absorption spectra of dendrimers D1–D4 in *N*,*N*-dimethylformamide solution.

The shift in the CT bands for dendrimers D3 and D4 in the different organic solvents is caused by the solvatochromic effect of the solvents used. Such bathochromic shifts have already been demonstrated for several monomeric 1,8-naphthalimide derivatives substituted by different alkoxy or amino electron-donating groups at C-4 position [12c,12e,13,17].

Of particular interest is the fluorescence of dendrimers. Each of these four dendrimers comprise a 1,8-naphthalimide fluorophore units with different substituents in C-4 position. The fluorescence behavior of the dendrimers D1–D4 is very different (Tables 1 and 2). As the electron accepting nitro groups in D2 quench the fluorescence the experiments to obtain data on its fluorescence failed. No fluorescent emission has also been observed in the case of 4-nitro-1,8-naphthalimide-labelled PAMAM of zero generation [9a] and in that of 4-nitro-1,8-naphthalimides that are not bonded to the PAMAM molecules [10c]. The non substituted 1,8-naphthalimide labelled PAMAM (D1) has a blue fluorescence with well-pronounced maxima at 451 nm in chloroform and 451 nm in *N*,*N*-dimethylformamide solution. Dendrimers D3 and D4 have a yellow–green fluorescence, with maxima in the 520–524 nm region. In this case it is seen that the substituents at C4 position and the polarity of the solvents have negligible influence upon the position of the fluorescence maxima. The fluorescence maxima appear at the similar wavelength as those assigned to 1,8-naphthalimides unbounded to the

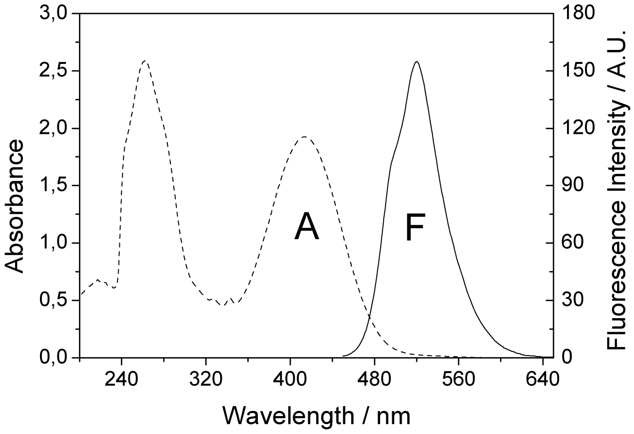


Fig. 3. Absorption (A) and fluorescence (F) maxima of dendrimer D3 in chloroform solution.

PAMAM molecules [11b,11f,12e,15a]. The same behavior of PAMAM of zero generation comprising the same 1,8 naphthalimide fluorophores in their periphery has been recently described [9a]. Fig. 3 presents as an example the absorption and fluorescence spectra of 4-piperidino-1,8-naphthalimide labelled PAMAM dendrimer D3 in chloroform solution. The fluorescence curve is approximately a mirror image of its absorption spectrum in the long-wavelength region, which indicates that the molecular structure of the 1,8-naphthalimide fluorophore is maintained in the exited state and that fluorescence emission prevails. The overlap between absorption and fluorescence spectra is low and the re-absorption and aggregation effect are negligible in the concentration 10^{-6} M l^{-1}. The absorption and emission spectra in both organic solvents are very similar.

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):

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

The Stokes shift calculated for D1, D3 and D4 is in the region 3652–8153 cm^{-1} in chloroform and 3695–7857 cm^{-1} in *N*,*N*-dimethylformamide solution. Much larger Stokes shifts 7857, 8153 cm^{-1}, are observed in the case of dendrimer D1 nearly double than those observed for D3 and D4 indicating that the conformational changes in the naphthalimide structure for D3 and D4 are small. In this case the amino substituents probably stabilize the planarity of the chromophoric 1,8-naphthalimide system. The same Stokes shift values have been obtained for low molecular weight 1,8-naphthalimides having different substituents at C-4 position [11b,11f,15b].

An important characteristic of the fluorophores is the oscillator strength (f), it reveals the effective number of electrons whose transition from ground S_0 to excited S_1 state gives the absorption area in the spectrum. Values for oscillator strength can be calculated using Eq. (2) [18]:

$$f = 4.32 \times 10^{-9} \Delta\nu_{1/2} \varepsilon_{\max} \qquad (2)$$

where $\Delta\nu_{1/2}$ is the width of the absorption band (in cm^{-1}) at $1/2\varepsilon_{\max}$.

The values obtained for f are: 3.01–3.52 in *N*,*N*-dimethylformamide and 3.69–3.92 in chloroform solution. The highest values in chloroform correlate well with the hypochromic effect of the dendrimers in this solvent. On the other hand the very high f values for the dendrimers in both organic solvents confirm the suggestion that in the ground state 1,8-naphthalimide chromophoric units do not interact with each other. In this case the values obtained for the oscillator strength are the sum of the oscillator strength for each 1,8-naphthalimide units bonded to the dendrimer macromolecules. Our previous investigation shows that the monomeric 1,8-naphthalimide derivatives have oscillator strength values in the range 0.15–0.30 depending on the experimental conditions [11f,12g].

The fluorescence efficiency of dendrimer D1, D3 and D4 is estimated from their quantum fluorescence yield Φ_F obtained from the absorption and fluorescence spectra. The data presented in Tables 1 and 2 shows that the Φ_F is lower for D1 in both organic solvents. This is due to the absence of an electron donor at C-4 position in the 1,8-naphthalimide ring. Therefore the polarization of the chromophoric system is different. The very low Φ_F values and great Stokes shift evidence the conformation changes in this 1,8-naphthalimide occurring the transition from the excited S_1 to the ground S_0 state. In this case the nonradioactive deactivation prevails. The quantum yield for D3 and D4 depends on the nature of the solvents. In *N*,*N*-dimethylformamide D3 and D4 have higher Φ_F which is probably due to the better planar stabilization of the chromophoric 1,8-naphthalimide system. In this case the emissionless deactivation during $S_1 \rightarrow S_0$ transition is less thus increasing the quantum yield of fluorescence. In both organic solvents the dendrimer D4 has a higher Φ_F that D3 determined by the stronger electron donor ability of the secondary amine groups. Similar dependences exhibit the values for monomer 1,8-naphthalimides having the same substitutents at C-4 position [11a, 11f,15], which proves that 1,8-naphthalimide comprised in the dendrimers do not interact with each other. The values of the quantum yield are very low if compared with those of similar monomeric 1,8-naphthalimides [11f,15a]. This phenomenon is probably caused by the photo-induced electron transfer from the amino groups of the central part of PAMAM to the 1,8-naphthalmide units [9a,19].

3.4. Photodegradation of dendrimers in N,N-dimethylformamide solution

Photodegradation of the PAMAM dendrimers was measured comparing the maxima of the absorption spectra of the solution before and after exposure.

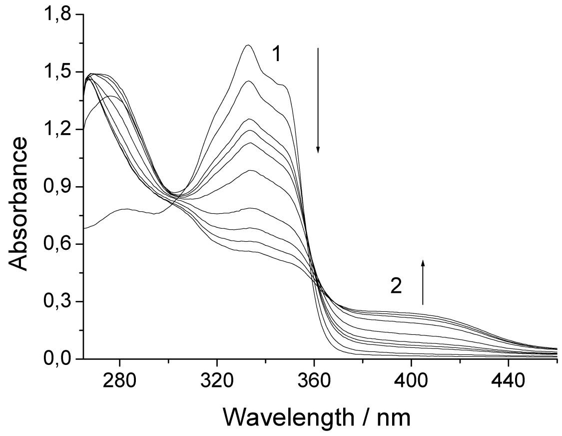


Fig. 4. Absorption spectra of dendrimer D1 in *N*,*N*-dimethylformamide solution during the irradiation from $t = 0$ to $t = 10$ h.

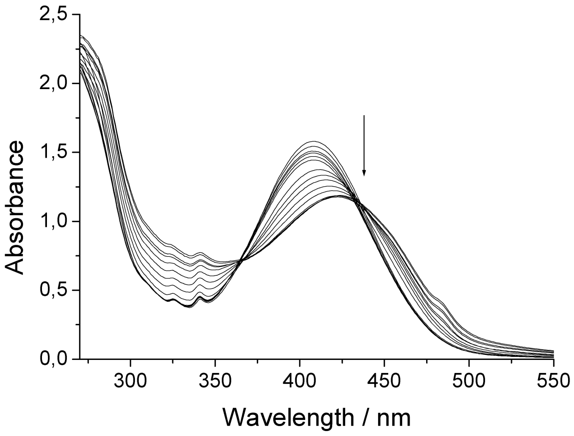


Fig. 6. Absorption spectra of dendrimer D3 in *N*,*N*-dimethylformamide solution during the irradiation from $t = 0$ to $t = 10$ h.

Fig. 4 shows the change of absorption spectra of D1 in DMF during the irradiations. Two isobestic points and a new absorption maximum in the visible region which was centered about 400 nm have been observed. That means that photoproducts are generated which can absorb in the visible region. In this case the solution changes its color from colorless to yellow with intense green fluorescence. The fluorescence spectra of dendrimer D1 in *N*,*N*-dimethylformamide after the irradiation are shown in Fig. 5. The spectra are taken at two excitation wavelengths. At $\lambda_{\mathrm{EXT}} = 330$ nm the fluorescent spectrum has not a well pronounced maximum. Hence, the photoproduct does not absorb at this wavelength. While at $\lambda_{\mathrm{EXT}} = 400$ nm the fluorescence spectrum has two well pronounced maxima at 492 and 518 nm. This is an indication that a new green fluorescent product is being obtained with the photodegradation of D1.

Fig. 6 shows two isobestic points and a bathochromic shift of the maximum of the absorption spectrum of D3 during irradiation. Fig. 7 shows the change in the intensity of absorbance of dendrimer D3 (curve A/A_0) as a function of the irradiation time. It has been found that the photodegradation of the dendrimer follows a pseudo first order reaction. The linear decrease of the absorption values can be explained by the gradual photodestruction of 1,8-naphthalimide fluorophores bonded to the PAMAM dendrimers. The Fig. 7 also shows the shifting of the absorption maxima (curve λ_{MAX}). At the beginning (in the first 400 min) of the irradiation no change of the absorption maximum has been observed and after that the absorption maximum is shifted from 408 to 424 nm. All these data suggest an interaction of the peripheral naphthalimide units from the dendrimer molecules with the photoproducts. The latter are likely to react with the amino groups at C-4 position enhancing the electron donating ability of the amino substituent.

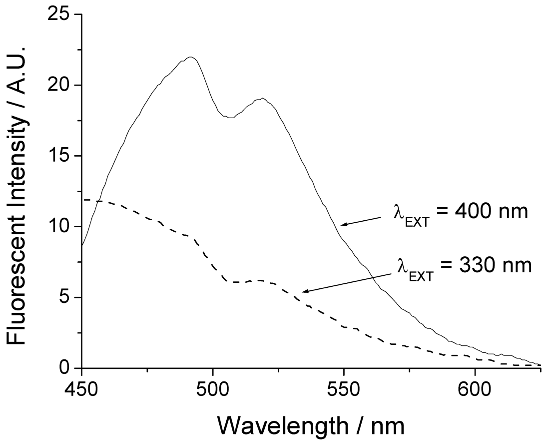


Fig. 5. Fluorescence spectra of dendrimer D1 after irradiation in *N*,*N*-dimethylformamide. The excitation wavelength are at $\lambda_{\mathrm{EXT}} = 330$ and 400 nm.

The nature of the photoproducts obtained by light irradiation requires special studies, which are beyond the scope of the present paper.

4. Conclusions

Four new 1,8-naphthalimide labelled PAMAM dendrimers from second generation have been synthesized with

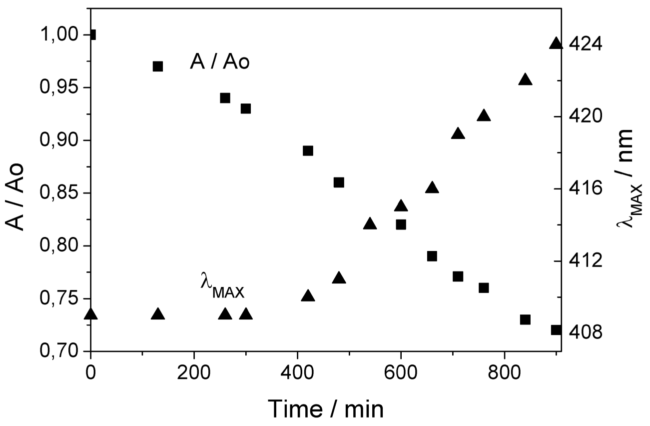


Fig. 7. Photodegradation (A/A_0) and change of the absorption of the fluorescence maximum (λ_{MAX}) during the irradiation of dendrimer D3 in *N*,*N*-dimethylformamide solution.

good yields and purities. The photophysical investigation in organic solvents shows that the color and fluorescence depends from the substituent in position C-4 in the chromophoric system. The 1,8-naphthalimide units do not interact with each other in DMF and chloroform. The photochemical investigation have shown that the dendrimers under study are relatively photostable in *N*,*N*-dimethylformamide solution. In the case of D1, some photoproducts generated can absorb in the visible region while in the case of D3 photoproducts can interact with the chromophoric naphthalimide system thus shifting the maximum of absorption towards higher wavelengths.

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