Dyes and Pigments 81 (2009) 180–186

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

The synthesis of a novel 1,8-naphthalimide based PAMAM-type dendron and its potential for light-harvesting

Mark D. McKenna [a,1], Ivo Grabchev [b,*], Paula Bosch [a,**]

[a] Department of Photochemistry, Institute of Polymer Science and Technology – CSIC, C/Juan de la Cierva, 28006 Madrid, Spain
[b] Institute of Polymers, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

ARTICLE INFO

Article history:
Received 16 June 2008
Received in revised form
9 September 2008
Accepted 10 September 2008
Available online 30 September 2008

Dedicated to Professor Pierre Meallier from University Claude Bernard Lyon1, France with best wishes on the occasion of his 70th birthday.

Keywords:
Light-harvesting
Energy transfer
1,8-Naphthalimide
PAMAM
Fluorescence

ABSTRACT

The photophysical characteristics of a PAMAM-type dendron that utilizes a 4-ethoxy-1,8-naphthalimide donor and 4-piperidine-1,8-naphthalimide acceptor in nine organic solvents of different polarities were investigated using absorption and fluorescent spectroscopy. The 1,8-naphthalimide acceptor can be indirectly excited by the donor 1,8-naphthalimide at 372 nm whereby the only emission observed is that due to the acceptor at 517 nm; no acceptor emission at 435 nm was observed. The efficiency of energy transfer was ~98%.

1. Introduction

Dendrimers are monodisperse, three-dimensional macromolecular compounds with well defined structures possessing a number of end functional groups [1]. These functional groups are reactive, thereby allowing modification of such dendrimers. A great deal of attention has been paid to this class of macromolecules owing to their new forms of structure organization which combines the properties of low and high molecular weight compounds. Dendrimers have attracted a large amount of interest over the past few decades due to their utility as molecular scaffolding in a great many applications, e.g. liquid crystals, drug delivery systems, catalytic nanoreactors and light-harvesting systems [2]. This utilisation arises from the fact that dendrimers have the ability to concentrate a high number of end groups in high concentration in one molecule.

1,8-Naphthalimides and their 4-substituted derivatives constitute a very versatile class of compounds characterised by intensive fluorescence and a very good photostability, which find applications in a large variety of areas [3]. Some luminescent dendrimers have been recently described by the combination of the properties of 1,8-naphthalimides and dendrimers [4].

For effective light-harvesting to take place there should be a central core chromophore (acceptor) which is surrounded by a secondary chromophore (donor) [5]. Dendrons offer such a possibility, especially PAMAM-type dendrons, as it is possible to synthesize such dendrons in large quantities with high yields from readily available starting materials, with minimal need for purification [6].

In this paper we present the facile synthesis and photophysical characterization of a bi-chromophoric, 1,8-naphthalimide modified PAMAM-type dendron which exhibits a highly efficient energy-transfer process from the donor 4-ethoxy-1,8-naphthalimide to the acceptor 4-piperidine-1,8-naphthalimide.

2. Experimental

2.1. Materials

All reagents used were purchased from Aldrich, Fluka or Alfa Aesar and used without further purification. All solvents used in

* Corresponding author. Tel.: +399 2 9792293; fax: +359 2 8700309.
** Corresponding author. Tel.: +34 915 622 900; fax: +34 915 644 853.
E-mail addresses: grabchev@mail.polymer.bas.bg (I. Grabchev), director@ictp.csic.es (P. Bosch).
[1] Tel.: +34 915 622 900; fax: +34 915 644 853.

0143-7208/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2008.09.008

spectroscopic measurements were of analytical grade. Thin-layer chromatography was performed on precoated silica gel $60F_{254}$ aluminium sheets, and visualization carried out using UV light and a ninhydrin/butanol/ethanol solution, 1 g/50 ml/450 ml, TLC developer. Column chromatographic purification was carried out using Merck silica gel 60. NMR spectra were obtained using a Varian 500 MHz spectrometer. Electrospray mass spectroscopic measurements were carried out using a Hewlett–Packard Series 1100 MSD. UV/vis spectra were recorded on a Perkin Elmer Lambda 35 UV/VIS spectrometer and fluorescence excitation and emission spectra were recorded on a Perkin Elmer LS55 florescence spectrometer, all spectra were recorded using 1 cm pathlength synthetic quartz glass cells.

2.2. Synthesis

2.2.1. Synthesis of compound **2**

A dichloromethane solution (500 ml) of di-tertbutyl dicarbonate (8 g, 36.7 mmol) was added dropwise over 6 h to vigorously stirred dichloromethane (100 ml) solution of ethylenediamine (13.2 g, 220 mmol) at 0 °C. The reaction mixture was then left stirring overnight. The solvent was removed under a reduced pressure to give an oily liquid which was then dissolved in doubly distilled water (100 ml), filtered, and then extracted with dichloromethane (2×250 ml). The final product obtained was a viscous, colourless oil **2** (5.22 g, 32.6 mmol). Yield: 88.8%. ^{1}H NMR ($CDCl_3$, ppm): δ 5.29 (s br, 1H, Boc–NH–), δ 3.10–3.05 (q br, 2H, –NH–CH_2–), δ 2.74–2.68 (q br, 2H, –CH_2–NH_2), δ 1.36 (s, 9H, $(CH_3)_3$–). API-ES-MS (positive) m/z calcd: 160.1; found: 161.2 ($[M+H]^+$).

2.2.2. Synthesis of compound **3**

N-Boc-ethylenediamine **2** (5 g, 31 mmol) was dissolved in methanol (150 ml) under vigorous stirring; to this methyl acrylate (26.9 g, 310 mmol) dissolved in methanol (50 ml) was added slowly. The reaction mixture was left stirring for 3 days at room temperature. The solvent and the majority of the excess methyl acrylate were removed under reduced pressure at 60 °C using a rotary evaporator. A more rigorous purification was then carried out by subjecting the compound to a higher vacuum by using a mineral oil pump and the compound was placed in a heated vacuum desiccator at 60 °C. The resultant product was a viscous, slightly yellowish oil **3** (10.19 g, 30.6 mmol). Yield 98.7%. ^{1}H NMR ($CDCl_3$, ppm): δ 5.08 (s br, 1H, Boc–NH–), δ 3.66–3.65 (6H, CH_3–O–), δ 3.16–3.13 (q br, 2H, –NH–CH_2–), δ 2.73–2.71 (t, 4H, –N–$(CH_2–)_2$), δ 2.50–2.48 (t, 2H, –CH_2–N–$(CH_2–)_2$), δ 2.41–2.39 (t, 4H, –CH_2–CO_2Me), δ 1.42 (s, 9H, $(CH_3)_3$–). API-ES-MS (positive) m/z calcd: 332.2; found: 333.3 ($[M+H]^+$), 355.2 ($[M+Na]^+$).

2.2.3. Synthesis of compound **4**

Compound **3** (10 g, 30 mmol) was dissolved in methanol (50 ml) and was then added slowly to a cooled (0 °C) methanol solution of ethylenediamine (54.09 g, 0.9 mol, 60.2 ml). The reaction mixture was left stirring for 10 days at room temperature. The solvent and the majority of the excess ethylenediamine were removed under reduced pressure at 60 °C using a rotary evaporator, with a rigorous purification being carried out by using a heated vacuum desiccator (60 °C) and a high vacuum mineral oil vacuum pump. The product obtained was a thick, viscous honey-like oil (11.41 g, 29.4 mmol). Yield 98%. ^{1}H NMR ($CDCl_3$, ppm): δ 7.41 (s br, 2H, CO–NH–CH_2–), δ 6.51 (t br, 1H, Boc–NH–), δ 3.28–3.24 (q, 4H, –CH_2–CH_2–NH_2), δ 3.16–3.12 (q, 2H, Boc–NH–CH_2–), δ 2.82–2.79 (t, 4H, –CH_2–CH_2–NH_2), δ 2.71–2.68 (t, 4H, –N–$(CH_2–)_2$), δ 2.51–2.48 (t, 2H, –CH_2–N–$(CH_2–)_2$), δ 2.32–2.29 (t, 4H, –CH_2–CO–NH–), δ 1.40 (s, 9H, $(CH_3)_3$–). API-ES-MS (positive) m/z calcd: 388.3; found: 389.2 ($[M+H]^+$), 390.2 ($[M+2H]^+$), 411.2 ($[M+Na]^+$).

2.2.4. Synthesis of compound **5**

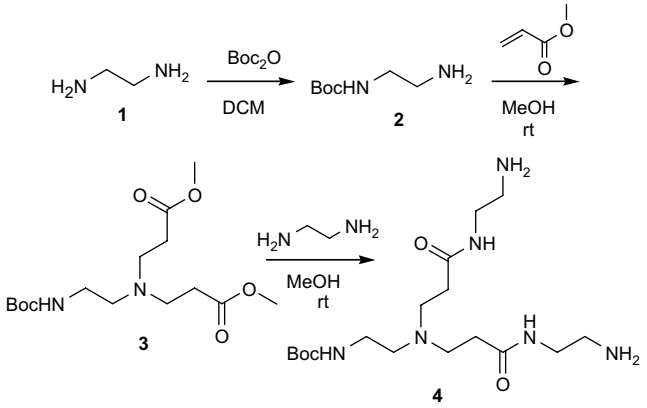
Compound **4** was added to a round bottomed flask (3.136 g, 8.07 mmol) to which 50 ml of ethanol was added and the mixture stirred until all the dendron was dissolved. 4-Bromo-1,8-naphthalic anhydride (5 g, 0178 mol) was added to the reaction mixture and the mixture refluxed overnight. The reaction mixture was left to cool and the resultant solid was collected by filtration and washed with cold ethanol to give compound **5** (6.796 g, 7.50 mmol). Yield = 92.9%. ^{1}H NMR ($CDCl_3$, ppm): δ 8.41–8.39 (dd, 2H, Ar), δ 8.24–8.22 (d, 2H, Ar), δ 8.15–8.13 (d, 2H, Ar), δ 7.82–7.80 (d, 2H, Ar), 7.65–7.61 (t, 2H, Ar), δ 7.53 (t br, 2H, CO–NH–CH_2–), δ 5.67 (t br, 1H, Boc–NH–), δ 4.23–4.20 (t, 4H, –CH_2–N–$(CO–)_2$), δ 3.68–3.64 (q, 4H, –CO–NH–CH_2–), δ 3.27–3.22 (q, 2H, Boc–NH–CH_2–), δ 2.60–2.57 (t, 4H, –N–$(CH_2–)_2$), δ 2.48–2.45 (t, 2H, –CH_2–N–$(CH_2–)_2$), δ 2.29–2.26 (t, 4H, –CH_2–CO–NH–), δ 1.41 (s br, 9H, $(CH_3)_3$–). API-ES-MS (positive) m/z calcd: 906.1; found: 905.2 $([M+H])^+$ $2 \times {}^{79}$Br, 907.2 $([M+H]^+)$ ^{79}Br + ^{81}Br, 909.2 $([M+H]^+)$ $2 \times {}^{81}$Br.

2.2.5. Synthesis of compound **6**

To a round bottomed flask compound **5** (2 g, 2.211 mmol) and 40 ml of ethanol were added. Finely ground KOH (1.6 g, 28.6 mmol) was then added and the reaction mixture refluxed overnight. The solvent was removed under reduced pressure, water (20 ml) was added, the mixture extracted with dichloromethane (4×30 ml), dried over sodium sulphate and the solvent removed under reduced pressure. The impure product was purified via column chromatography (dichloromethane:methanol 25:1 to 15:1) to give **6** (1.384 g, 1.654 mmol). Yield = 74.8%. ^{1}H NMR ($CDCl_3$, ppm): δ 8.30–8.29 (d, 2H, Ar), δ 8.23–8.20 (t, 4H, Ar), δ 7.60–7.58 (t br, 2H, CO–NH–CH_2–), δ 7.46–7.43 (t, 2H, Ar), δ 6.75–6.73 (d, 2H, Ar), δ 5.65 (s br, 1H, Boc–NH–), δ 4.20–4.15 (m, 8H, –CH_2–N–$(CO–)_2$ and Ar–O–CH_2–), δ 3.66–3.62 (q, 4H, –CO–NH–CH_2–), δ 3.24–3.23 (d br, 2H, Boc–NH–CH_2–), δ 2.63 (s br, 4H, –N–$(CH_2–)_2$), δ 2.49 (s br, 2H, –CH_2–N–$(CH_2–)_2$), δ 2.31 (s br, 4H, –CH_2–CO–NH–), δ 1.58–1.55 (t, 6H, –O–CH_2–CH_3), δ 1.40 (s, 9H, $(CH_3)_3$–). API-ES-MS (positive) m/z calcd: 836.4; found: 837.2 ($[M+H]^+$), 838.2 ($[M+2H]^+$), 859.2 ($[M+Na]^+$). UV/vis: $\lambda_{max} = 370$ nm. Fluorescence emission: $\lambda_{max} = 435$ nm.

2.2.6. Synthesis of compounds **7** and **8**

Compound **6** (1.2 g, 1.434 mmol) was placed into a round bottom flask to which dichloromethane (25 ml) and trifluoroacetic acid (6 ml) were added. The mixture was stirred vigorously and the reaction was followed by TLC (15:1 DCM:MeOH). On completion of reaction the excess trifluoroacetic acid and dichloromethane were removed under reduced pressure to give **7**. Ethanol (25 ml) and triethylamine (0.23 g, 2.151 mmol, 0.32 ml) were added to a round bottom flask along with **7**, and the mixture was stirred for half

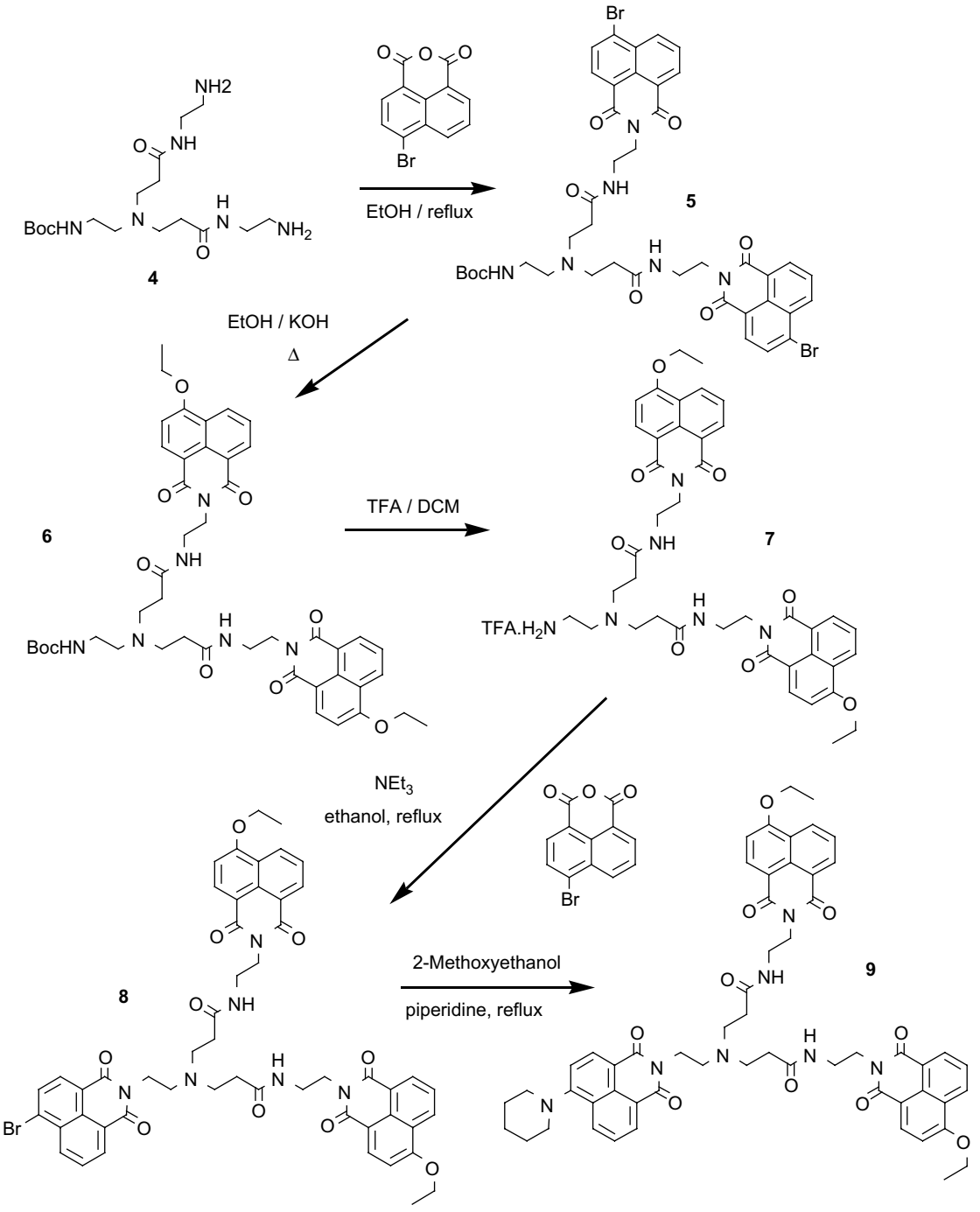


Scheme 1. Synthesis of PAMAM dendron.

an hour. 4-Bromo-1,8-naphthalic anhydride (0.5 g, 1.805 mmol) was then added and the reaction mixture refluxed overnight. After removing the solvent under reduced pressure, the crude product was purified via column chromatography, dichloromethane:methanol 25:1 to 18:1, to give a pale yellow solid **8** (1.018 g, 1.022 mmol). Yield = 71.3%. ^{1}H NMR ($CDCl_3$, ppm): δ 8.49–8.47 (d, 1H, Ar), δ 8.44–8.43 (d, 1H, Ar), δ 8.28–8.27 (d, 1H, Ar), δ 8.26–8.25 (d, 1H, Ar), δ 8.19–8.14 (q, 2H, Ar), δ 7.95–7.92 (m, 3H, Ar and CO–NH–CH_2–), δ 7.64–7.61 (t, 2H, Ar), δ 7.06–7.04 (d, 2H, Ar), δ 4.20–4.16 (q, 4H, –O–CH_2–CH_3), δ 4.06–4.04 (t, 4H, –CH_2–N–(CO–)$_2$), δ 3.89–3.86 (t, 2H, –(OC)$_2$–N–CH_2–), δ 3.33 (H_2O + –CO–NH–CH_2), δ 2.63–2.60 (t, 4H, –N–(CH_2–)$_2$), δ 2.51–2.49 (DMSO + CH_2–N–(CH_2–)$_2$), δ 2.11–2.08 (t, 4H, –CH_2–CO–NH–), δ 1.45–1.42 (t, 6H, –O–CH_2–CH_3). API-ES-MS (positive) *m*/*z* calcd: 994.3; found: 995.2 ($[M+H]^+$) ^{79}Br, 996.0 ($[M+2H]^+$) ^{79}Br, 997.0 ($[M+H]^+$) ^{81}Br, 998.0 ($[M+2H]^+$) ^{81}Br, 1017.2 ($[M+Na]^+$) ^{79}Br, 1019.0 ($[M+Na]^+$) ^{81}Br.

2.2.7. Synthesis of compound **9**

Compound **8** (250 mg, 0.251 mmol) was placed into a round bottom flask with 20 ml of 2-methoxyethanol. The mixture was stirred, piperidine was added (0.214 g, 2.51 mmol, 0.24 ml), and the reaction mixture was heated to 105 °C and the complexion of reaction was followed by TLC (dichloromethane:methanol 17:1). After the solvent was removed under reduced pressure, the crude product was purified via column chromatography, dichloromethane:methanol 25:1 to 17:1. A somewhat orange compound **9**



Scheme 2. Synthesis of a PAMAM-type dendron **9**.

(214 mg, 0.214 mmol) was obtained. Yield = 85.3%. ^{1}H NMR ($CDCl_3$, ppm): δ 8.40–8.38 (dd, 1H, Ar), δ 8.31–8.27 (m, 4H, Ar), δ 8.21–8.20 (d, 2H, Ar), δ 8.12–8.10 (dd, 2H, Ar), δ 7.76–7.74 (t, 2H, CO–NH–CH_2–), δ 7.58–7.55 (dd, 1H, Ar), δ 7.39–7.36 (dd, 2H, Ar), δ 6.96–6.97 (d, 1H, Ar), δ 6.70–6.69 (d, 2H, Ar), δ 4.19–4.17 (t, 6H, –CH_2–N–$(CO–)_2$ and –$(OC)_2$–N–CH_2–), δ 4.15–4.10 (q, 4H, Ar–O–CH_2–), δ 3.50–3.46 (q, 4H, –CO–NH–CH_2–), δ 3.11 (s br, 4H, –$(CH_{2pip})_2$–N–), δ 2.82–2.79 (t, 4H, –N–$(CH_2–)_2$), δ 2.74–2.72 (t, 2H, –CH_2–N–$(CH_2–)_2$), δ 2.39–2.36 (t, 4H, –CH_2–CO–NH–), δ 1.85–1.81 (quin, 4H, –$(CH_{2pip}–CH_2)_2$–N–), δ 1.67 (s br, 2H, –CH_2–$CH_{2pip}CH_2$–), δ 1.56–1.53 (t, 6H, –O–CH_2–CH_3). API-ES-MS (positive) *m/z* calcd: 999.4; found: 1000.2 ($[M + H]^+$), 1001.2 ($[M + 2H]^+$), 1022.2 ($[M + Na]$).

2.2.8. Synthesis of compound **10**

Compound **2** (5.22 g, 32.6 mmol) was added to a round bottom flask and ethanol was added (50 ml). After a few minutes stirring 4-bromo-1,8-naphthalic anhydride (9.94 g, 35.9 mmol) was added and the reaction mixture refluxed for 2 h, after which the reaction was allowed to cool to room temperature. The precipitated solid **11** was filtered and washed with cold ethanol and dried under vacuum at 40 °C to give an off-white solid (12.53 g, 29.9 mmol). Yield = 91.7%. ^{1}H NMR ($CDCl_3$, ppm): δ 8.63–8.60 (dd, 1H, Ar), δ 8.53–8.50 (dd, 1H, Ar), δ 8.38–8.36 (d, 1H, Ar), δ 8.01–7.98 (d, 1H, Ar), δ 7.83–7.78 (dd, 1H, Ar), δ 4.98 (s br, 1H, Boc–NH–), δ 4.35–4.31 (2H, Boc–NH–CH_2–CH_2–), δ 3.55–3.49 (q, 2H, Boc–NH–CH_2–CH_2–), δ 1.27 (s, 9H, Boc). API-ES-MS (positive) *m/z* calcd: 418.1; found: 441.1 ($[M + Na]^+$) ^{79}Br, 443.1 ($[M + Na]^+$) ^{81}Br.

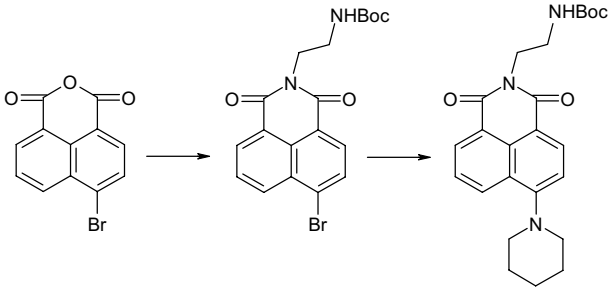
Compound **11** (500 mg, 1.19 mmol) was put into a round bottom flask and 2-methoxyethanol (40 ml) was added, the mixture was then stirred. Piperidine (1.02 g, 1.19 mmol) was then added and the reaction mixture was heated to 105 °C and complexion of reaction was followed by TLC (DCM:ethyl acetate 8:2). On completion of reaction the solvent was removed under reduced pressure. The impure compound was purified by column chromatography (DCM:ethyl acetate 10:0 to 8:2) to give a fluorescent yellow solid (399 mg, 0.94 mmol). Yield = 79.0%. ^{1}H NMR ($CDCl_3$, ppm): δ 8.57–8.56 (dd, 1H, Ar), δ 8.50–8.48 (d, 1H, Ar), δ 8.39–8.37 (dd, 1H, Ar), δ 7.68–7.65 (dd, 1H, Ar), δ 7.17–7.16 (d, 1H, Ar), δ 5.05 (s br, 1H, –NH–Boc), δ 4.36–4.34 (t, 2H, –CH_2–CH_2–NH–Boc), δ 3.53–3.50 (q, 2H, –CH_2–CH_2–NH–Boc), δ 3.23–3.21 (t, 4H, –N–$(CH_{2pip})_2$–), δ 1.90–1.86 (quin, 4H, –N–$(CH_2–CH_{2pip})_2$–), δ 1.74–1.71 (m, 2H, –CH_2–$CH_{2pip}CH_2$–). API-ES-MS (positive) *m/z* calcd: 423.2; found: 424.3 ($[M + H]^+$), 425.3 ($[M + 2H]^+$). UV/vis: λ_{max} = 413 nm. Fluorescence emission: λ_{max} = 518 nm.

3. Results and discussion

3.1. Synthesis of antenna dendron **9**

The synthesis of the PAMAM-type dendron was began by firstly carrying out the synthesis of the dendritic scaffold **4** (Scheme 1). This was undertaken by the mono-Boc protection of ethylenediamine, and then via normal PAMAM dendrimer synthesis, i.e. the Michael addition of methyl acrylate to mono-protected ethylenediamine, followed by exhaustive amidation of the resulting esters with a large excess of ethylenediamine to give an amine terminated dendron in near quantitative yield. The resultant combination of free amino groups and a BOC protected amino group then allows selective additions of 1,8-naphthalimde chromophores.

The next step was the introduction of the two 1,8-naphthalimde derivatives to the dendron **4** (Scheme 2). The first was introduced by refluxing dendron **4** with 4-bromo-1,8-naphthalic anhydride in ethanol solution. The solid precipitate was filtered and washed with cold ethanol to give **5**. This compound was then refluxed overnight in ethanol with finely ground KOH to give **6**. Compound **6** was dissolved in dichloromethane (DCM) to which trifluoroacetic acid was added and the mixture was allowed to stir at room temperature. The reaction was followed by TLC and on complete disappearance of the starting material dichloromethane and trifluoroacetic acid were removed under reduced pressure to give **7**. To an ethanol solution of **7**, triethylamine and 4-bromo-1,8-naphthalic anhydride were then added to give **8**. Compound **8** was added to 2-methoxyethanol and stirred. Piperidine was then added and the mixture heated to 100 °C overnight. The crude product was purified by column chromatography to give compound **9**.



Scheme 3. Synthesis of model fluorophore **10**.

The model fluorophore **10** was synthesized by the reaction of 4-bromo naphthalic anhydride and *N*-Boc-ethylenediamine **2** in 2-methoxyethanol and the respective nucleophilic substitution of the bromo atom by piperidine [7] (Scheme 3).

3.2. Photophysical characteristics of antenna dendron **9**

The photophysical properties and the colour characteristics of 1,8-naphthalimides are strongly dependent on the polarization of molecules. Irradiation induced polarization of 1,8-naphthalimide molecules causes an electron donor–acceptor interaction in the chromophoric system between the substituent at C-4 and the imide carbonyl groups. In general the derivatives with alkoxy groups are colourless and have a blue emission [8], while the amino substituted 1,8-naphthalimides have a yellow colour and green fluorescence [9].

The spectral characteristics of antenna dendron **9** depend on the polarization and interaction of 1,8-naphthalimide derivatives, which is provoked by solvent polarity and by possible intramolecular energy transfer. We have investigated the absorption (λ_A) and fluorescence (λ_F) maxima, the extinction coefficient (ε), Stokes shift ($\nu_A - \nu_F$), and fluorescence quantum yield (Φ_F) in organic solvents of different polarity. It can be seen from the data in Table 1 that the absorption maxima of antenna dendron **9** in nine organic solvents are in the ultra-violet region with the maxima in the range of 366–372 nm, which correspond to an ethoxy substituted 1,8-naphthalimide unit, and emit a yellow-green

Table 1
Photophysical characteristics of antenna dendron **9** (see text).

Solvents	Dielectric constant ε	λ_A nm	ε dm^3 mol^{-1} cm^{-1}	λ_F nm	$\nu_A - \nu_F$ cm^{-1}	Φ_F
Methanol	32.70	372	22 000	539	8329	0.009
Ethanol	24.55	371	22 300	536	8297	0.013
Acetonitrile	37.50	370	22 700	538	8440	0.016
N,*N*-dimethylformamide	37.78	370	22 600	536	8370	0.010
Acetone	20.70	368	21 300	532	8377	0.054
Dichloromethane	8.93	371	22 000	522	7797	0.327
Chloroform	4.81	372	20 400	517	7529	0.365
Tetrahydrofuran	7.58	367	24 300	523	8127	0.324
1,4-Dioxane	2.21	366	24 500	513	7829	0.328

fluorescence with maxima at 517–539 nm corresponding to the 4-piperidine 1,8-naphthalimide unit.

Fig. 1 presents an example of absorption and fluorescence spectra of **9** in chloroform solution. The figure shows that the absorption maximum appears at 372 nm and is attributed to the ethoxy substituted 1,8-naphthalimide units. The 4-piperidine-1,8-naphthalimide absorbs in the visible region at 420 nm. As the two absorption maxima are relatively closely located ($\Delta\lambda = 48$ nm), the total spectrum results from their overlapping. In this case the spectrum shoulder occurring in the visible region can be assigned to absorbance by 4-piperidine-1,8-naphthalimide unit.

The data in Table 1 and the plot of Fig. 2 show that the solvent polarity does not significantly influence the position of the absorption maxima, while in more polar solvents the fluorescence maxima is bathochromicaly shifted. As the dipole moment of the molecule is enhanced upon excitation due to electron density redistribution, the excited molecule is more stabilized in polar solvents because of the stronger interactions with the solvent dipoles. This effect causes the bathochromic shift in the fluorescence maxima and a positive solvatochromism (Fig. 2).

The molar extinction coefficients ε (at absorption maxima) of **9** are approximately two-fold higher than that of the 4-ethoxy substituted 1,8-naphthalimides [8]. This confirms the presence of two ethoxy substituted 1,8-naphthalimide units in the dendron molecule.

Stokes shift is a parameter indicating the difference in the properties and structure of the ground state (S_0) and the first excited singlet state (S_1) of the chromophore system. The calculated values for the Stokes shift of the antenna dendron **9** (Table 1) are much higher than the values obtained for the PAMAM dendrimers with peripheral 1,8-naphthalimide units [10] and 1,8-naphthalimides containing the same substituents [7,9]. This effect is determined by the prevailing influence of the 4-alkoxy substituted 1,8-naphthalimide upon the position of absorption maximum in the spectra of the antenna dendron **9**. Yellow-green fluorescence, caused by the 4-piperidine-1,8-naphthalimide, dominates the fluorescent spectra, while the blue fluorescence typical of the 4-ethoxy-1,8-naphthalimides is missing. The possible intramolecular energy transfer between the donor and acceptor naphthalimides can explain this fact.

The fluorescence quantum yield of antenna dendron **9** in organic solvents of different polarities has been calculated on the basis of the absorption and fluorescence spectra using Eq. (1):

$$\Phi_F = \Phi_{st}\frac{S_u}{S_{st}}\frac{A_{st}}{A_u}\frac{n_{Du}^2}{n_{Dst}^2} \quad (1)$$

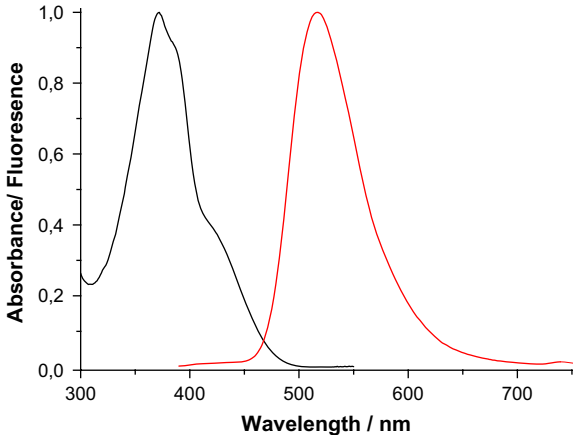


Fig. 1. Normalized absorption and fluorescence spectra of **9** in chloroform solution ($c = 10^{-5}$ mol l^{-1}), $\lambda_{EXT} = 372$ nm.

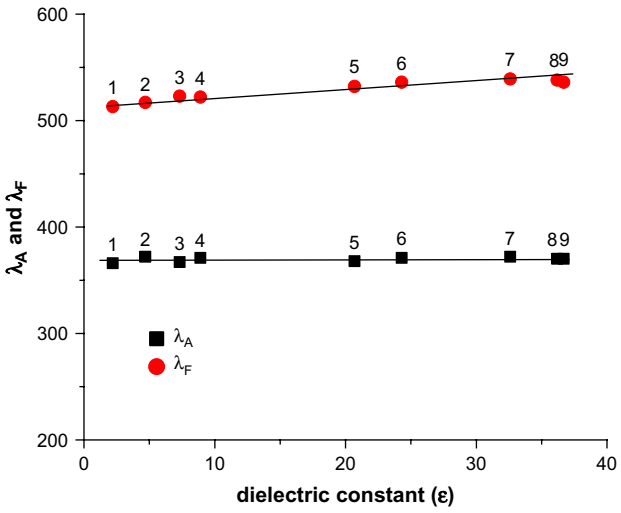


Fig. 2. Absorption (λ_A) and fluorescence (λ_F) maxima of antenna **9** as a function of the dielectric constant (ε): 1-tetrahydrofuran, 2-chloroform, 3-dichloromethane, 4-dioxan, 5-acetone, 6-ethanol, 7-methanol, 8-acetonitrile, and 9-DMF at $c = 10^{-5}$ mol l^{-1}.

where Φ_{st} is the quantum yield of the reference, A_{st} and A_u represent the absorbance of the reference and the sample, respectively; S_{st} and S_u are the integrals of the emission of the reference and the sample, respectively; and n_{Dst} and n_{Du} are the refractive index of the reference and the sample, respectively.

The data obtained are presented in Table 1 and their dependence on the polarity of organic solvents is plotted in Fig. 3. It can be seen that in polar organic solvents the quantum yields are low ($\Phi_F = 0.009$–0.016), while in non-polar media the respective quantum yields are higher ($\Phi_F = 0.324$–0.365). This significant difference is due to the possible photoinduced electron transfer (PET) occurring from the dendron core to the 1,8-naphthalimide units, which is quenched in non-polar media causing restoration of the fluorescence emission [11].

3.3. Antenna effect of dendron **9**

Chloroform solution of antenna dendron **9** ($c = 10$–5 mol l^{-1}) was prepared as well as solutions of similar concentrations of

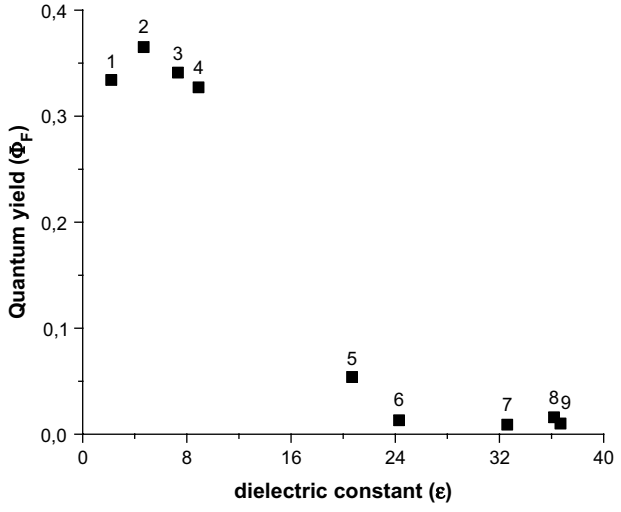


Fig. 3. Dependence of quantum fluorescence yield of antenna dendron **9** on dielectric constant (ε): 1-tetrahydrofuran, 2-chloroform, 3-dichloromethane, 4-dioxan, 5-acetone, 6-ethanol, 7-methanol, 8-acetonitrile, and 9-DMF at $c = 10^{-5}$ mol l^{-1}.

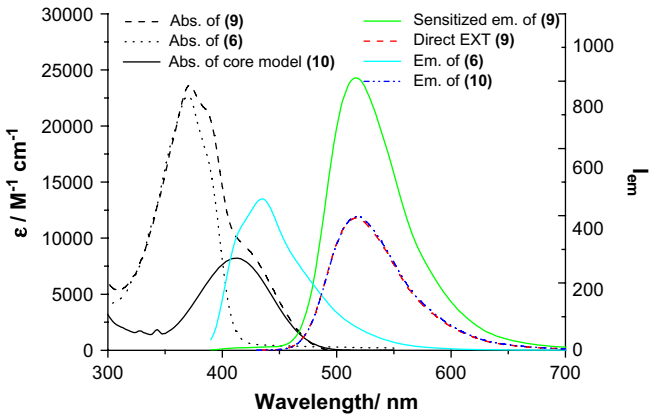


Fig. 4. Absorption and fluorescence spectra of **6**, **9** and **10** in chloroform solution ($c = 10^{-5}$ mol l^{-1}).

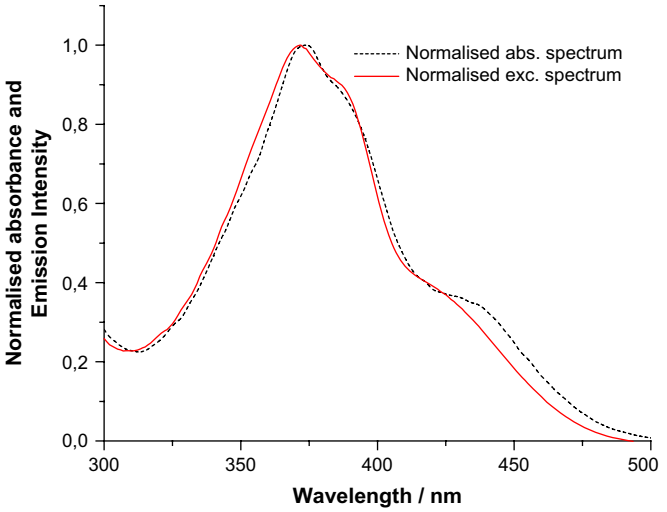


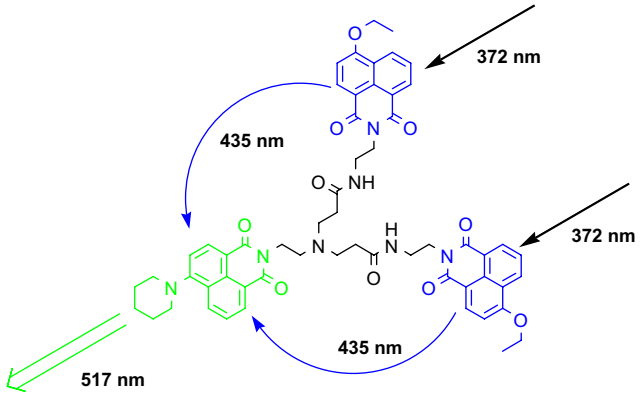
Fig. 5. Normalized absorption and excitation spectra of antenna dendron **9** ($c = 10^{-5}$ mol l^{-1}).

compound **6**. The latter compound contains only two 4-ethoxy-1,8-naphthalimide units and can be treated as a model of the donor part of the antenna molecule, and monomeric compound **10**, which can be treated as a model of the acceptor 4-piperidine-1,8-naphthalimide unit. These solutions were then used to record the absorption and emission spectra of the fully loaded antenna dendron **9**, and the donor model **6** and the acceptor model **10**. All these absorption and fluorescence spectra are plotted in Fig. 4.

The comparison of the emission spectra of antenna dendron **9** and compound **6** shows clearly that the antenna dendron is excited at the wavelength corresponding to the absorption maximum of the donor 4-ethoxy-1,8-naphthalimide ($\lambda_{EXT} = 372$ nm). The only fluorescence emission is the one due to the donor 4-piperidino-1,8-naphthalimide ($\lambda_{Fl} = 517$ nm). No emission has been recorded at 435 nm, which whereat emits only the dendron containing just donor **6**. These results demonstrate that the entire energy absorbed by the donor 4-ethoxy-1,8-naphthalimide is transferred as a fluorescence emission to the acceptor 4-piperidine-1,8-naphthalimide (Scheme 4).

It shows how upon addition of the 4-piperidino-1,8-naphthalimide to the dendron the fluorescence has changed from blue to green which corresponds to fluorescence solely from the 4-piperidine-1,8-naphthalimide moiety.

When comparing the unquenched donor emission of compound **6** and the quenched emission of antenna dendron **9**, it has been found that the energy-transfer efficiency is 98% [12]. This result has been also confirmed by comparing the normalized absorption and excitation spectra of compound **9** (Fig. 5) [13], although it is known that both these methods of determining the energy-transfer efficiency are less accurate at near quantitative values [14].



Scheme 4. Proposed mechanism of energy transfer of dendron **9**.

4. Conclusion

For the first time an effective antenna dendron has been synthesized from two differently substituted 1,8-naphthalimide fluorophore units employing a relatively simple procedure. The photophysical characteristics of the compound have been determined in nine solvents of different polarities. The values for the quantum fluorescent yield obtained in polar solvents are lower than those registered in non-polar solvents. This fact demonstrates the medium dependent properties of the newly synthesized molecule. The 98% energy transfer from the donor 4-ethoxy-1,8-naphthalimide units to the acceptor 4-piperidine-1,8-naphthalimide unit observed for all organic solvents shows the antenna capacities of the dendron. This opens opportunities to use this simple dendron as an effective energy-transfer system.

Acknowledgment

This work was supported by the bilateral cooperation between the Bulgarian Academy of Science and Instituto de Ciencia y Tecnología de Polímeros – CSIC, Spain, and M.D.McK. wishes to thank the MEC for the concession of his contract as part of the I3P programme.

References

[1] (a) Baars Mwp L, Meijer EW. Top Curr Chem 2000;210:131;
(b) Inoue K. Prog Polym Sci 2000;25:453;
(c) Vögtle F, Gesterman S, Hasse R, Schwiert H, Windisch B. Prog Polym Sci 2000;25:987.
[2] (a) Meijer EW, van Genderen MHP. Nature 2003;426:128;
(b) Han H, Gorka M, Vögtle F, Vicinelli V, Ceroni P, Maestri M, et al. Angew Chem Int Ed 2002;41:3595;
(c) Gilat SL, Adronov A, Fréchet JMJ. Angew Chem Int Ed Engl 1999;38:1422;
(d) Gilat S, Adronov A, Fréchet J. J Org Chem 1999;64:7474;
(e) Froehling P. Dyes Pigments 2001;48:187;
(f) Pan J, Zhu W, Li S, Xu J, Tian H. Eur J Org Chem 2006:986;
(g) Hu X, Damjanović A, Ritz T, Schulten K. Proc Natl Acad Sci USA 1998;95:5935.
[3] (a) Mitchell K, Brown R, Yuan D, Chang S-C, Utech R, Lewis D. J Photochem Photobiol A Chem 1998;115:157;
(b) Ramachamdram B, Sankaran N, Karmaka R, Saha S, Samanta A. Tetrahedron 2000:567041;
(c) Gunnlaugsson T, Kruger P, Lee T, Parkesh R, Pfeffer F, Hussey G. Tetrahedron Lett 2003;44:6575;
(d) Grabchev I, Chovelon J-M, Qian X. J Photochem Photobiol A Chem 2003;158:37;
(e) de Silva A, Nimal Gunaratne HQ, Habib-Jiwan J-L, McCoy C, Rice T, Soumillion J-P. Angew Chem Int Ed Engl 1995;34:1728;
(f) Cosnard F, Wintgens V. Tetrahedron Lett 1998;39:2751;

(g) Liu B, Tian H. J Math Chem 2005;15:2681;
(h) Lin B, Tian H. Chem Commun 2005:3156;
(i) Banthia S, Sarkar M, Samanta A. Res Chem Intermed 2005;31:25;
(j) Chovelon J-M, Grabchev I. Spectrochim Acta Part A 2007;67:87.
[4] (a) Grabchev I, Qian X, Bojinov V, Xiao Y, Zhang W. Polymer 2002;43:5731;
(b) Grabchev I, Bojinov V, Chovelon J-M. Polymer 2003;44:4721;
(c) Grabchev I, Chovelon J-M, Bojinov V, Ivanova G. Tetrahedron 2003;59:9591;
(d) Grabchev I, Chovelon J-M, Qian X. New J Chem 2003;27(337):10;
(e) Grabchev I, Soumillion J-P, Muls B, Ivanova G. Photochem Photobiol Sci 2004;3:1032;
(f) Grabchev I, Betcheva R, Bojinov V, Staneva D. Eur Polym J 2004;40:1249;
(g) Sali S, Grabchev I, Chovelov J-M, Ivanova G. Spectrochim Acta Part A 2006;65:591;
(h) Grabchev I, Staneva D, Betcheva R. Polym Degrad Stab 2006;91:2257;
(i) Grabchev I, Chovelon J-M, Nedelcheva A. J Photochem Photobiol A Chem 2006;183:9.
[5] (a) Adronov A, Fréchet JMJ. Chem Commun 2000:1701;
(b) Nantalaksakul A, Reddy DR, Bardeen CJ, Thayumanavan S. Photosynth Res 2006;87:133;
(c) Balaban TS. Acc Chem Res 2005;38:612;
(d) Yilmaz MD, Bozdemir OA, Akkaya EU. Org Lett 2006;8:2871;
(e) Takahashi M, Morimoto H, Miyake K, Yamashita M, Kawai H, Sei Y, et al. Chem Commun 2006:3084;
(f) Takahashi M, Morimoto H, Miyake K, Kawai H, Sei Y, Yamaguchi K, et al. New J Chem 2008;32:545.
[6] (a) Tomalia DA, Baker H, Dewald J, Hall M, Kallos G, Martin S, et al. Polym J (Tokio) 1985;17:117;
(b) Tomalia DA, Baker H, Dewald J, Hall M, Kallos G, Martin S, et al. Macromolecules 1986;19:2466;
(c) Aoi K, Itoh K, Okada M. Macromolecules 1997;30:8072;
(d) King ASH, Martin IK, Tywman LJ. Polym Int 2006;55:798.
[7] Konstantinova T, Meallier P, Grabchev I. Dyes Pigments 1993;22:191.
[8] (a) Grabchev I, Konstantinova T. Dyes Pigments 1997;33:197;
(b) Grabchev I, Petkov Ch, Bojinov V. Macromol Chem Eng 2002;287(12):904.
[9] Alexiou M, Tychopoulous V, Chorbanian S, Tyman J, Brawn R, Brittain R. J Chem Soc Perkin Trans 2 1990:837.
[10] Grabchev I, Guittonneau S. J Photochem Photobiol A Chem 2006;179:28.
[11] (a) de Silva AP, Gunatatne NQN, Gunnlauggson T, Huxley AJM, McCoy CP, Radmancher JT, et al. Chem Rev 1997;97:1515;
(b) de Silva AP, McCaughan B, McKiney BOF, Querol M. Dalton Trans 2003:1902.
[12] Schenning APHJ, Peeters E, Meijer Ew. J Am Chem Soc 2000;122:4489.
[13] Stryer L, Haughland RP. Proc Natl Acad Sci USA 1967;58:719.
[14] Adronov A, Gilatb SL, Frechet JMJ, Ohta K, Neuwahl FVR, Fleming Gr. J Am Chem Soc 2000;122:1175.