

Design, Synthesis and Photostability of Novel 1,8-naphthalimide PAMAM Light-harvesting Dendrons

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Abstract This paper reports on the divergent synthesis, photophysical properties and photodegradation of novel PAMAM dendrons, core and peripherally functionalized with 1,8-naphthalimide fluorophores. The novel compounds were configured as light-harvesting antennae where the system surface is labeled with blue emitting 4-allyloxy-1,8-naphthalimide “donor” fluorophores capable of absorbing light and efficiently transferring the energy to a single yellow-green emitting 4-alkylamino-1,8-naphthalimide “acceptor” dye. The focal 1,8-naphthalimide fluorophores in the antennae were modified with a HALS fragment (2,2,6,6-tetramethylpiperidine or 1,2,2,6,6-pentamethylpiperidine) with a view to improve their photostability. Novel light-harvesting systems showed highly efficient energy transfer, depending on the volume of the core substituent. Due to the HALS fragments the chromophoric system of the novel antennae showed higher photostability, while the photostability of the PAMAM scaffold was found to be lower.

Keywords 1,8-Naphthalimide · Polyamidoamine · Light-harvesting · Hindered amine light stabilizers · Photostability · Photoinduced electron transfer

Abbreviation

PAMAM Polyamidoamine
HALS Hindered Amine Light Stabilizer
PET Photoinduced Electron Transfer

Introduction

Molecular systems capable of light-harvesting and efficiently transferring absorbed radiation unidirectionally over nanometer distances are currently of great interest [1–6]. Light-harvesting systems in natural world have the unique ability to absorb, transfer, and convert the solar energy with efficiency greater than 90%. The most attractive artificial light-harvesting systems are the dendritic assemblies because of their unique structures, reminiscent of the architecture of natural light-harvesting complexes [7–15]. The globular shape of dendritic architectures provides a large surface area that can be decorated with chromophores, resulting in a large absorption cross section and efficient capture of photons. Furthermore, because of their proximity, the various functional groups of dendritic systems may easily interact with one another producing a highly effective energy transfer [16].

The polyamidoamines (PAMAM) are a well know class of commercial dendrimers. The use of the flexible aliphatic PAMAM bone as a scaffold for light-harvesting antennae could give new systems with high efficiency of energy transfer [17, 18]. Particularly useful for PAMAM light-harvesting antennae are fluorophores such as 1,8-naphthalimide derivatives [19, 20]. Because of their strong fluorescence and good photostability, the 1,8-naphthalimide derivatives have found application in a number of areas [21–35].

The high photostability is important characteristic for the photodevices, such as light-harvesting antennae, with regard of their practical usage. Materials exposed to light undergo degradation which shortens their service life, mainly by a sequence of photo-oxidation. Hindered amine light stabilizers (HALS), such as 2,2,6,6-tetramethylpiperidines, inhibit autoxidation by transforming the parent

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amines to *N*-oxyl radicals, which stops oxidative degradation by the coupling of alkyl radicals [36–39].

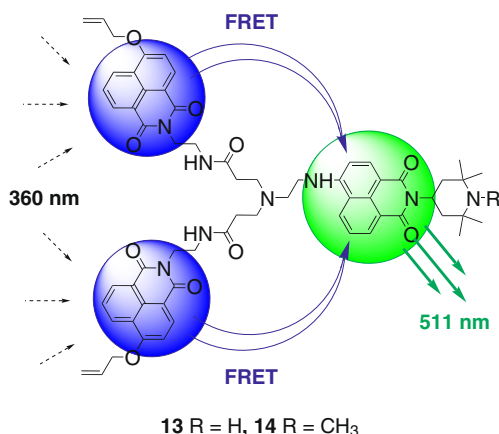
In this paper, we report on the design, synthesis and photophysical properties of novel fluorescence light-harvesting antennae based on PAMAM dendron, core and peripherally functionalized with 1,8-naphthalimide units (Scheme 1). In this systems the focal 1,8-naphthalimides contain a HALS fragment (2,2,6,6-tetramethylpiperidine or 1,2,2,6,6-pentamethylpiperidine) with a view to improve the core photostability.

In order to receive a more complete comparative picture for the photophysical properties and photostability of the novel light-harvesting antennae **13** and **14**, light-harvesting dendron **15**, peripherally decorated with blue emitting 4-allyloxy-1,8-naphthalimide units PAMAM dendron **16**, not containing focal “acceptor” 1,8-naphthalimide, and yellow-green emitting 4-*n*-buthylamino-*N*-*n*-buthyl-1,8-naphthalimide **17** were involved in the present study as reference compounds (Scheme 2).

Experimental

Materials

The starting 4-nitro-1,8-naphthalic anhydride **1** [40] and 4-bromo-1,8-naphthalic anhydride **10** [41] were prepared according to the reported procedure. The light-harvesting dendron **15** [19], PAMAM dendron **16** with peripheral blue emitting 1,8-naphthalimides [42] and 4-*n*-buthylamino-*N*-*n*-buthyl-1,8-naphthalimide **17** [43] were prepared as described before. 2,2,6,6-Tetramethylpiperidin-4-ylamine, formalin (37%), methylacrylate, ethylenediamine and allyl alcohol (Fluka, Merck), p.a. grade, were used without purification. All solvents (Fluka, Merck) were pure or of spectroscopy grade.



Scheme 1 Light-harvesting dendrons **13** and **14**

Methods

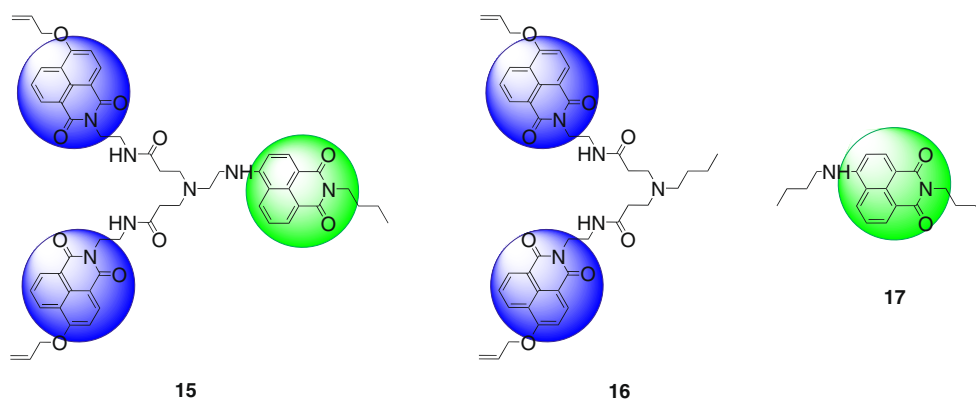
FT-IR spectra were recorded on a Varian Scimitar 1000 spectrometer. The ¹H NMR spectra (chemical shifts are given as δ in ppm) were recorded on a Bruker DRX-250 spectrometer, operating at 250.13 MHz. TLC was performed on silica gel, Fluka F60 254, 20×20, 0.2 mm. The melting points were determined by means of a Kofler melting point microscope. The UV–VIS absorption spectra were recorded on a spectrophotometer Lambda 25 (Perkin Elmer). The corrected excitation and fluorescence spectra were taken on a Perkin Elmer LS55 spectrofluorimeter. The fluorescence quantum yields (Φ_F) were measured relatively to Coumarin 6 ($\Phi_F=0.78$ in ethanol) [44]. The study on the photodegradation of the compounds was conducted in a solar simulator SUNTEST CPS equipment (Heraeus, Germany), supplied with an arc air-cooled Xenon lamp (Hanau, 1.1 kW, 765 W m⁻²), at ambient temperature. The irradiation was performed in DMF solution at concentration 10⁻⁵ mol l⁻¹.

Synthesis of amino functional 1,8-naphthalimide cores

4-(2-Aminoethyl)amino-*N*-(2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthalimide (**3**) A suspension of 4-nitro-1,8-naphthalic anhydride **1** (2 g, 8 mmol) and 2,2,6,6-tetramethylpiperidin-4-ylamine (1.4 ml, 8 mmol) in 20 ml of ethanol was refluxed with stirring for 8 h. The crude product that precipitated on cooling was filtered off and treated with 25 ml of 5% aqueous sodium carbonate. The solid phase was filtered off, washed with water and dried to give 2.59 g (83%) of pure 4-nitro-*N*-(2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthalimide **2** as yellow-brown crystals, m.p. 199–201 °C.

To a solution of ethylenediamine (3.5 ml, 52 mmol) in 15 ml of DMF, 1.0 g (2.6 mmol) of 4-nitro-*N*-(2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthalimide **2** were added. The resulting mixture was stirred at room temperature for 48 h then poured into 100 ml of water. The precipitate was collected by filtration, washed with water and dried. Recrystallization from chlorobenzene afforded 0.77 g (75%) of 4-(2-aminoethyl)amino-*N*-(2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthalimide **3** as yellow-orange crystals (m.p. 157–160 °C; $R_f=0.26$ in methanol:chloroform=9/1).

FT-IR (KBr) cm⁻¹: 3380, 3318 and 3206 (ν_{NH} and ν_{NH_2}); 2844 (ν_{CH}); 1692 ($\nu_{\text{asN-C=O}}$); 1658 ($\nu_{\text{sN-C=O}}$). ¹H NMR (DMSO-*d*₆, 250.13 MHz) ppm: 8.68 (d, 1H, $J=8.6$ Hz, naphthalimide H-7); 8.37 (d, 1H, $J=7.2$ Hz, naphthalimide H-5); 8.20 (d, 1H, $J=8.6$ Hz, naphthalimide H-2); 7.65 (t, 1H, $J=7.9$ Hz, naphthalimide H-6); 6.75 (d, 1H, $J=8.8$ Hz, naphthalimide H-3); 6.62 (m 1H, ArNH); 5.53 (m, 1H, $\underline{\text{CH}}$ -piperidine); 3.42 (m, 2H, ArNH $\underline{\text{CH}_2\text{CH}_2\text{NH}_2}$); 3.14 (m, 2H, ArNH $\underline{\text{CH}_2\text{CH}_2\text{NH}_2}$); 2.87 (br.s, 2H,

Scheme 2 Reference compounds **15**, **16** and **17**

ArNHCH₂CH₂NH₂); 2.44 (m, 2H, CH₂-piperidine); 1.49 (d, 2H, *J*=11.9 Hz, CH₂-piperidine); 1.27 (s, 6H, 2 × CCH₃); 1.13 (s, 6H, 2 × CCH₃). Elemental analysis: Calculated for C₂₃H₃₀N₄O₂ (MW 394.51) C 70.02, H 7.66, N 14.20%; Found C 69.81, H 7.69, N 14.14%.

4-(2-Aminoethyl)amino-N-(1,2,2,6,6-pentamethylpiperidin-4-yl)-1,8-naphthalimide (5) A mixture of 4-nitro-*N*-(2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthalimide **2** (1.0 g, 2.6 mmol), 8.5 ml of formalin and 4.5 ml of formic acid (98%) was stirred under reflux for 4 h. After cooling the mixture was poured into 20 ml of water and alkalinized with 40% aqueous sodium hydroxide. The solid that precipitates was filtered off, washed with water and dried to give the pure 4-nitro-*N*-(1,2,2,6,6-pentamethylpiperidin-4-yl)-1,8-naphthalimide **4** as white crystals, m.p. 188–191 °C.

To a solution of ethylenediamine (2.7 ml, 40 mmol) in 15 ml of DMF, 0.9 g (2 mmol) of 4-nitro-*N*-(1,2,2,6,6-pentamethylpiperidin-4-yl)-1,8-naphthalimide **4** were added and the resulting mixture was stirred at room temperature for 48 h. The solid that precipitates after pouring the reaction mixture into 100 ml of water was collected by filtration, washed with water and dried. Recrystallization from chlorobenzene afforded 0.59 g (69%) of 4-(2-aminoethyl)amino-*N*-(1,2,2,6,6-pentamethylpiperidin-4-yl)-1,8-naphthalimide **5** as yellow-orange crystals (m.p. 148–153 °C; *R*_f=0.36 in methanol:chloroform=9/1).

FT-IR (KBr) cm⁻¹: 3378, 3326 and 3207 (νNH₂); 2920 and 2811 (νCH); 1686 (ν^{as}N–C=O); 1645 (ν^sN–C=O). ¹H NMR (DMSO-*d*₆, 250.13 MHz) ppm: 8.62 (d, 1H, *J*=8.5 Hz, naphthalimide H-7); 8.41 (d, 1H, *J*=7.4 Hz, naphthalimide H-5); 8.23 (d, 1H, *J*=8.6 Hz, naphthalimide H-2); 7.65 (dd, 1H, *J*=7.4 Hz, *J*=8.5 Hz, naphthalimide H-6); 6.73 (d, 1H, *J*=8.7 Hz, naphthalimide H-3); 5.87 (m, 1H, ArNH); 5.58 (m, 1H, CH-piperidine); 3.42 (m, 2H, ArNHCH₂CH₂NH₂); 3.04 (m, 2H, ArNHCH₂CH₂NH₂); 2.85 (br. s, 2H, ArNHCH₂CH₂NH₂); 2.38 (m, 5H, CH₂-

piperidine and NCH₃); 1.27 (d, 2H, *J*=12.1 Hz, CH₂-piperidine); 1.23 (s, 6H, 2 × CCH₃); 1.09 (s, 6H, 2 × CCH₃). Elemental analysis: Calculated for C₂₄H₃₂N₄O₂ (MW 408.54) C 70.56, H 7.90, N 13.71%; Found C 70.27, H 7.99, N 13.66%.

Synthesis of core functional 1,8-naphthalimide PAMAM dendrons

General preparation procedure for ester-functionalized 1,8-naphthalimides (6) and (7) To a solution of methyl acrylate (1.2 ml, 14 mmol) in 5 ml of methanol, a solution of amino-functionalized 1,8-naphthalimide core **3** (0.55 g, 1.4 mmol) or **5** (0.56 g, 1.4 mmol) in 10 ml of methanol was added dropwise for a period of 30 min. The reaction mixture was stirred for 3 days at room temperature and the excess of methyl acrylate was removed under vacuum, whereupon 0.77 g (97%) of the ester-functionalized derivative **6** or 0.79 g (98%) of the ester-functionalized derivative **7** were obtained as yellow-brown oil.

Ester-functionalized 1,8-naphthalimide (6) *R*_f=0.68 (methanol:chloroform=9/1). FT-IR (oil) cm⁻¹: 3312 (νNH); 2906 and 2848 (νCH); 1730 (νCOOCH₃); 1688 (ν^{as}N–C=O); 1650 (ν^sN–C=O). ¹H NMR (CHCl₃-*d*, 250.13 MHz) ppm: 8.54 (d, 1H, *J*=7.3 Hz, naphthalimide H-5); 8.44 (d, 1H, *J*=8.4 Hz, naphthalimide H-7); 8.38 (dd, 1H, *J*=8.7 Hz, naphthalimide H-2); 7.62 (dd, 1H, *J*=8.3 Hz, *J*=7.4 Hz, naphthalimide H-6); 6.71 (d, 1H, *J*=8.5 Hz, naphthalimide H-3); 6.32 (m, 1H, ArNH); 5.72 (m, 1H, CH-piperidine); 3.56 (s, 6H, 2 × OCH₃); 3.45 (m, 2H, ArNHCH₂); 2.85 (m, 4H, CH₂N(CH₂)₂); 2.76 (m, 2H, CH₂N(CH₂)₂); 2.61 (m, 3H, CH₂-piperidine and NH-piperidine); 2.49 (t, 4H, *J*=6.4 Hz, 2 × CH₂COOCH₃); 1.67 (m, 2H, CH₂-piperidine); 1.45 (s, 6H, 2 × CCH₃); 1.28 (s, 6H, 2 × CCH₃). Elemental analysis: Calculated for C₃₁H₄₂N₄O₆ (MW 566.69) C 65.70, H 7.47, N 9.89%; Found C 65.52, H 7.59, N 9.73%.

Ester-functionalized 1,8-naphthalimide (7) $R_f=0.74$ (methanol:chloroform=9/1). FT-IR (oil) cm^{-1} : 3334 (νNH); 2930 and 2816 (νCH); 1728 (νCOOCH_3); 1680 ($\nu^{\text{as}}\text{N}-\text{C}=\text{O}$); 1644 ($\nu^{\text{s}}\text{N}-\text{C}=\text{O}$). ^1H NMR (CHCl_3 -*d*, 250.13 MHz) ppm: 8.56 (d, 1H, $J=7.4$ Hz, naphthalimide H-5); 8.42 (d, 1H, $J=8.4$ Hz, naphthalimide H-7); 8.28 (dd, 1H, $J=8.6$ Hz, naphthalimide H-2); 7.64 (dd, 1H, $J=8.3$ Hz, $J=7.4$ Hz, naphthalimide H-6); 6.69 (d, 1H, $J=8.6$ Hz, naphthalimide H-3); 6.02 (m, 1H, ArNH); 5.68 (m, 1H, CH-piperidine); 3.52 (s, 6H, $2 \times \text{OCH}_3$); 3.41 (m, 2H, ArNHCH₂); 2.83 (m, 4H, CH₂N(CH₂)₂); 2.72 (m, 2H, CH₂N(CH₂)₂); 2.63 (m, 2H, CH₂-piperidine); 2.53 (m, 4H, $2 \times \text{CH}_2\text{COOCH}_3$); 2.34 (s, 3H, NCH₃); 1.67 (m, 2H, CH₂-piperidine); 1.41 (s, 6H, $2 \times \text{CCH}_3$); 1.32 (s, 6H, $2 \times \text{CCH}_3$). Elemental analysis: Calculated for C₃₂H₄₄N₄O₆ (MW 580.71) C 66.18, H 7.64, N 9.65%; Found C 65.89, H 7.55, N 9.82%.

General preparation procedure for amidoamine-functionalized 1,8-naphthalimides (8) and (9) To a solution of ethylenediamine (5.2 ml, 78 mmol) in 5 ml of methanol, a solution of ester-functionalized 1,8-naphthalimide **6** (0.73 g, 1.3 mmol) or **7** (0.75 g, 1.3 mmol) in 20 ml of methanol was added dropwise at 5 °C for a period of 30 min. The reaction mixture was stirred for 168 h at room temperature. Then the solvent and the ethylenediamine excess were distilled under vacuum. After the final traces of excess ethylenediamine were removed azeotropically using a 9:1 toluene/methanol (v/v) solution, the amidoamine-functionalized 1,8-naphthalimides **8** (0.78 g, 96%) and **9** (0.76 g, 92%) were obtained as yellow-brown oil.

Amidoamine-functionalized 1,8-naphthalimide (8) $R_f=0.24$ (*n*-propanol:ammonium hydroxide=1/1). FT-IR (oil) cm^{-1} : 3388 and 3260 (νNH and νNH_2); 2924 and 2904 (νCH); 1696 ($\nu^{\text{as}}\text{N}-\text{C}=\text{O}$); 1654 ($\nu^{\text{s}}\text{N}-\text{C}=\text{O}$); 1633 ($\nu\text{NH}-\text{C}=\text{O}$). ^1H NMR ($\text{DMSO-}d_6$, 250.13 MHz) ppm: 8.56 (d, 1H, $J=8.4$ Hz, naphthalimide H-5); 8.42 (d, 1H, $J=7.3$ Hz, naphthalimide H-7); 8.27 (d, 1H, $J=8.5$ Hz, naphthalimide H-2); 7.69 (dd, 1H, $J=8.4$ Hz, $J=7.4$ Hz, naphthalimide H-6); 7.45 (m, 2H, $2 \times \text{NHCO}$); 6.81 (d, 1H, $J=8.5$ Hz, naphthalimide H-3); 6.37 (m, 1H, ArNH); 5.57 (m, 1H, CH-piperidine); 3.45 (m, 6H, ArNHCH₂ and $2 \times \text{CH}_2\text{CONH}$); 3.31 (br.s, 4H, $2 \times \text{NH}_2$); 2.79 (m, 6H, CH₂N(CH₂)₂ and CH₂-piperidine); 2.67 (m, 2H, CH₂N(CH₂)₂); 2.45 (m, 8H, $2 \times \text{NHCH}_2\text{CH}_2\text{NH}_2$ and $2 \times \text{NHCH}_2\text{CH}_2\text{NH}_2$); 1.51 (m, 2H, CH₂-piperidine); 1.29 (s, 6H, $2 \times \text{CCH}_3$); 1.15 (s, 6H, $2 \times \text{CCH}_3$). Elemental analysis: Calculated for C₃₃H₅₀N₈O₄ (MW 622.80) C 63.64, H 8.09, N 17.99%; Found C 63.46, H 7.99, N 18.13%.

Amidoamine-functionalized 1,8-naphthalimide (9) $R_f=0.28$ (*n*-propanol:ammonium hydroxide=1/1). FT-IR (oil) cm^{-1} :

3390 and 3304 (νNH and νNH_2); 2912 and 2822 (νCH); 1684 ($\nu^{\text{as}}\text{N}-\text{C}=\text{O}$); 1646 ($\nu^{\text{s}}\text{N}-\text{C}=\text{O}$); 1628 ($\nu\text{NH}-\text{C}=\text{O}$). ^1H NMR ($\text{DMSO-}d_6$, 250.13 MHz) ppm: 8.66 (d, 1H, $J=8.5$ Hz, naphthalimide H-5); 8.44 (d, 1H, $J=7.1$ Hz, naphthalimide H-7); 8.26 (d, 1H, $J=8.6$ Hz, naphthalimide H-2); 7.68 (t, 1H, $J=7.8$ Hz, naphthalimide H-6); 7.53 (m, 2H, $2 \times \text{NHCO}$); 6.79 (d, 1H, $J=8.6$ Hz, naphthalimide H-3); 6.57 (m, 1H, ArNH); 5.64 (m, 1H, CH-piperidine); 3.45 (m, 2H, ArNHCH₂); 3.22 (m, 4H, $2 \times \text{CH}_2\text{CONH}$); 2.95 (br.s, 4H, $2 \times \text{NH}_2$); 2.74 (m, 6H, $3 \times \text{NCH}_2$); 2.67 (m, 2H, CH₂-piperidine); 2.52 (m, 4H, $2 \times \text{NHCH}_2\text{CH}_2\text{NH}_2$); 2.30 (m, 7H, $2 \times \text{NHCH}_2\text{CH}_2\text{NH}_2$ and NCH₃); 1.54 (m, 2H, CH₂-piperidine); 1.28 (s, 6H, $2 \times \text{CCH}_3$); 1.18 (s, 6H, $2 \times \text{CCH}_3$). Elemental analysis: Calculated for C₃₄H₅₂N₈O₄ (MW 636.83) C 64.12, H 8.23, N 17.60%; Found C 63.90, H 8.12, N 17.74%.

Synthesis of light-harvesting dendrons

General preparation procedure for light-harvesting 1,8-naphthalimide dendrons (13) and (14) To a solution of 4-bromo-1,8-naphthalic anhydride **10** (0.55 g, 2 mmol) in 60 ml of boiling methanol, a solution of amino-terminated 1,8-naphthalimide dendron **8** (0.49 g, 1 mmol) or **9** (0.50 g, 1 mmol) in 50 ml of methanol was added dropwise under stirring over a period of 2 h. The resulting solution was refluxed for 8 h. After cooling the orange precipitate was filtered off, treated with 50 ml of 5% aqueous sodium hydroxide to give after filtration and drying a solid product of intermediate dendrons **11** or **12**. The solid was suspended in solution of 0.112 g of KOH (2 mmol) in 20 ml of allyl alcohol and the reaction mixture was refluxed under stirring for a period of 18 h. After cooling to room temperature, the solid was filtered off and the filtrate was poured into 20 ml of water. The crude product that precipitated after dilution in water was collected by filtration and dried. Silica gel chromatography (*n*-propanol:ammonium hydroxide=1:1) afforded 0.23 g (48%) of antenna **13** (m.p. 159–163 °C) or 0.31 g (64%) of antenna **14** (m.p. 135–140 °C) as yellow crystals.

Light-harvesting 1,8-naphthalimide dendron (13) $R_f=0.53$ (*n*-propanol:ammonium hydroxide=1/1). FT-IR (KBr) cm^{-1} : 3334 (νNH); 2912 and 2890 (νCH); 1692 ($\nu^{\text{as}}\text{N}-\text{C}=\text{O}$); 1648 ($\nu^{\text{s}}\text{N}-\text{C}=\text{O}$). ^1H NMR (CDCl_3 -*d*, 250.13 MHz) ppm: 8.37 (m, 2H, $2 \times$ peripheral naphthalimide H-5); 8.28 (m, 5H, $2 \times$ peripheral naphthalimide H-2 and focal naphthalimide H-7, H-5, H-2); 8.13 (d, 2H, $J=8.3$ Hz, $2 \times$ peripheral naphthalimide H-7); 7.64 (t, 1H, $J=7.9$ Hz, focal naphthalimide H-6); 7.49 (t, 2H, $J=7.9$ Hz, $2 \times$ peripheral naphthalimide H-6); 7.15 (m, 2H, $2 \times \text{CONH}$); 6.68 (m, 3H, $2 \times$ peripheral naphthalimide H-3 and ArNH); 6.50 (d,

1H, $J=8.4$ Hz, focal naphthalimide H-3); 6.18 (m, 2H, $2 \times \text{OCH}_2\text{CH}=\text{CH}_2$); 5.72(m, 1H, CH -piperidine); 5.54 (d, 2H, $J_{\text{trans}}=17.3$ Hz, $2 \times \text{trans-allyl HCH}=\text{}$); 5.45 (d, 2H, $J_{\text{cis}}=10.4$ Hz, $2 \times \text{cis-allyl HCH}=\text{}$); 4.72 (d, 4H, $J=5.3$ Hz, $2 \times \text{OCH}_2\text{CH}=\text{CH}_2$); 4.14 (m, 4H, $2 \times (\text{CO})_2\text{NCH}_2$); 3.55 (m, 4H, $2 \times \text{CONHCH}_2$); 3.40 (m, 2H, ArNHCH_2); 2.77 (m, 6H, $3 \times \text{NCH}_2$); 2.62 (t, 2H, $J=12.8$ Hz, CH_2 -piperidine); 2.39 (m, 5H, $2 \times \text{CH}_2\text{CONH}$ and NH -piperidine); 1.69 (d, 2H, $J=9.9$ Hz, CH_2 -piperidine); 1.41 (s, 6H, $2 \times \text{CCH}_3$); 1.26 (s, 6H, $2 \times \text{CCH}_3$). Elemental analysis: Calculated for $\text{C}_{63}\text{H}_{66}\text{N}_8\text{O}_{10}$ (MW 1095.25) C 69.09, H 6.07, N 10.23%; Found C 68.78, H 6.01, N 10.34%.

Light-harvesting 1,8-naphthalimide dendron (14) $R_f=0.55$ (*n*-propanol:ammonium hydroxide=1/1). FT-IR (KBr) cm^{-1} : 3352 (νNH); 2924 and 2818 (νCH); 1696 ($\nu^{\text{as}}\text{N}-\text{C}=\text{O}$); 1652 ($\nu^{\text{s}}\text{N}-\text{C}=\text{O}$). ^1H NMR (CDCl_3 -*d*, 250.13 MHz) ppm: 8.41 (m, 2H, $2 \times$ peripheral naphthalimide H-5); 8.27 (m, 5H, $2 \times$ peripheral naphthalimide H-2 and focal naphthalimide H-7, H-5, H-2); 8.19 (d, 2H, $J=8.4$ Hz, $2 \times$ peripheral naphthalimide H-7); 7.57 (t, 1H, $J=7.9$ Hz, focal naphthalimide H-6); 7.44 (t, 2H, $J=7.9$ Hz, $2 \times$ peripheral naphthalimide H-6); 7.12 (m, 2H, $2 \times \text{CONH}$); 6.74 (d, 2H, $J=8.4$ Hz, $2 \times$ peripheral naphthalimide H-3); 6.61(m, 1H, and ArNH); 6.42 (d, 1H, $J=8.4$ Hz, focal naphthalimide H-3); 6.15 (m, 2H, $2 \times \text{OCH}_2\text{CH}=\text{CH}_2$); 5.51 (m, 3H, $2 \times \text{trans-allyl HCH}=\text{}$ and CH -piperidine); 5.41 (d, 2H, $J_{\text{cis}}=10.5$ Hz, $2 \times \text{cis-allyl HCH}=\text{}$); 4.70 (d, 4H, $J=5.3$ Hz, $2 \times \text{OCH}_2\text{CH}=\text{CH}_2$); 4.00 (m, 4H, $2 \times (\text{CO})_2\text{NCH}_2$); 3.52 (m, 4H, $2 \times \text{CONHCH}_2$); 3.34 (m, 2H, ArNHCH_2); 2.90 (t, 2H, $J=12.4$ Hz, CH_2 -piperidine); 2.74 (m, 6H, $3 \times \text{NCH}_2$); 2.36 (m, 7H, $2 \times \text{CH}_2\text{CONH}$ and NCH_3); 1.57 (d, 2H, $J=11.0$ Hz, CH_2 -piperidine); 1.32 (s, 6H, $2 \times \text{CCH}_3$); 1.15 (s, 6H, $2 \times \text{CCH}_3$). Elemental analysis: Calculated for $\text{C}_{64}\text{H}_{68}\text{N}_8\text{O}_{10}$ (MW 1109.27) C 69.30, H 6.18, N 10.10%; Found C 69.03, H 6.12, N 9.97%.

Results and discussion

Design and synthesis of light-harvesting 1,8-naphthalimide dendrons

Recently, we have synthesized two 1,8-naphthalimide PAMAM based light-harvesting dendrons with yellow-green fluorescence [19, 20]. We chose 1,8-naphthalimide fluorophores for the fluorescence modification of PAMAM due to their good photostability and high fluorescence efficiency. The high photostability of the 1,8-naphthalimides raises the question whether these light-harvesting systems are photostable too? This was the reason to investigate the photostability of the reference light-

harvesting dendron **15** in DMF solution by irradiation in a SUNTEST equipment. The changes in the absorption spectra of antenna **15** after irradiation for 2, 4 and 6 h are presented in a Fig. 1.

As seen (Fig. 1), the photodegradation of core 1,8-naphthalimide (band with maximum at about 440 nm) was considerably faster if compared to those of peripheral 1,8-naphthalimides (band with maximum at about 365 nm). Within 4 h the focal fluorophore loses completely its absorption capacity as a result of photodegradation of the dye chromophoric system probably due to the energy transfer from the peripheral units. In order to improve the core photostability we synthesized novel light-harvesting antennae with 1,8-naphthalimide “acceptor” dyes, linked to the hindered amine radical scavenger fragments such as 2,2,6,6-tetramethylpiperidine and 1,2,2,6,6-pentamethylpiperidine. They are well known as hindered amine light stabilizers (HALS) considerably increasing the photostability of the fluorescent compounds [36–39].

The novel light-harvesting antennae were prepared in three basic steps: synthesis of amino-functionalized yellow-green emitting 1,8-naphthalimide cores **3** and **5** (Scheme 3), PAMAM dendronization of the amino functional cores to yellow-green emitting PAMAM dendrons **8** and **9** (Scheme 4) and finally, peripheral decoration of the yellow-green emitting PAMAM dendrons with blue emitting 4-allyloxy-1,8-naphthalimide moieties to the desired antennae **13** and **14** (Scheme 5).

Synthesized compounds were characterized and identified by their melting points, TLC (R_f values), elemental analysis data, UV–VIS, fluorescence, FT-IR and ^1H NMR spectroscopy. For instance, in the ^1H NMR (CDCl_3 -*d*, 250.13 MHz) spectra of novel antennae, a resonance at 6.78 ppm for **13** and at 6.74 ppm for **14** was observed (peaks A in Fig. 2). This is characteristic for the proton in

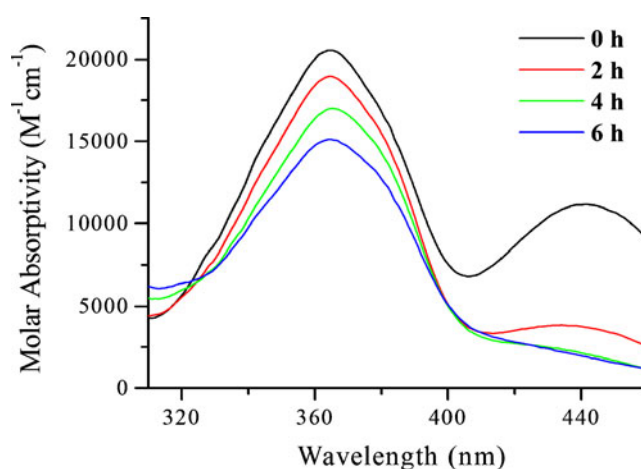
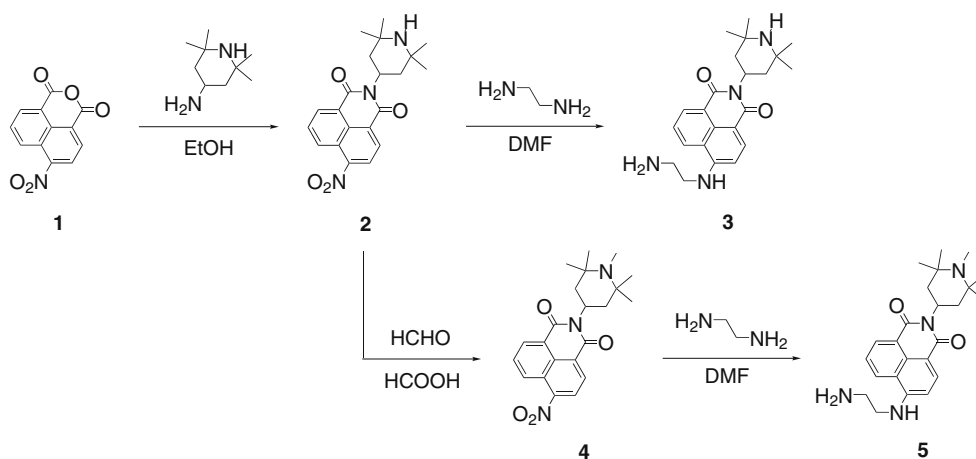


Fig. 1 Absorption spectra of antenna **15** recorded at concentration 10^{-5} mol l^{-1} in DMF solution after irradiation in SUNTEST equipment

Scheme 3 Synthesis of 1,8-naphthalimide cores **3** and **5**

position C-3 of the peripheral blue emitting 1,8-naphthalimide ring, substituted in position C-4 with an electron-donating alkoxy group. This resonance is different from the corresponding resonance for the yellow-green emitting 1,8-naphthalimide core—6.50 ppm for **13** and 6.42 ppm for **14** (peaks **B** in Fig. 2). Furthermore, the ^1H NMR spectra contain peaks in range of 6.18–4.70 ppm, attributed to the protons for the peripheral allyloxy groups.

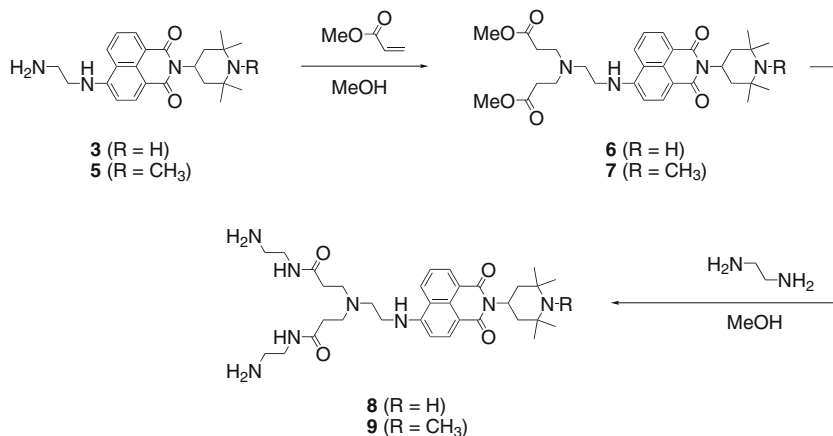
Photophysical characterization of the fluorophores

It is well known that the light absorption in the 1,8-naphthalimide molecule generates a charge transfer interaction between the substituent at a C-4 position and the imide carbonyl groups [18–20]. Data presented in Table 1 show that the different alkylamino substituents at the 1,8-naphthalimide C-4 position (compounds **3**, **5–9**) have a small effect on the energy and the shape of the dyes' absorption bands. Also a typical bathochromic shift of the longest-wavelength band with increasing the solvent polarity was observed. Any specific effects in protic solvent (ethanol) were not observed, which indicates lack

of intermolecular H-bond formation in the dyes' ground state.

The molar absorptivities of the longest-wavelength absorption maximum in chloroform solution, presented in Table 1, are common for the 1,8-naphthalimide derivatives [21–35]. All compounds under study have a molar extinction coefficients (ϵ) in the long-wavelength absorption band higher than $10,000 \text{ l mol}^{-1} \text{ cm}^{-1}$, indicating that this is a charge transfer (CT) band, due to (π, π^*) character of the $S_0 \rightarrow S_1$ transition.

The absorption spectra of the light harvesting dendrons **13** and **14** contained, as expected, two absorption bands corresponding to absorption of the peripheral and core 1,8-naphthalimide chromophores (Fig. 3). The band with maximum at about 365 nm is typical for the 4-allyloxy-1,8-naphthalimides [18–20], while the band with maximum at about 430 nm is usual for the 4-alkylamino-1,8-naphthalimides. Furthermore the molar extinction coefficient values of the peripheral absorption of light-harvesting antennae **13** and **14** are about two times higher than those of the core fluorophores, suggesting no ground state interaction between the peripheral 1,8-naphthalimide units.

Scheme 4 Synthesis of amino-terminated PAMAM dendrons **8** and **9**

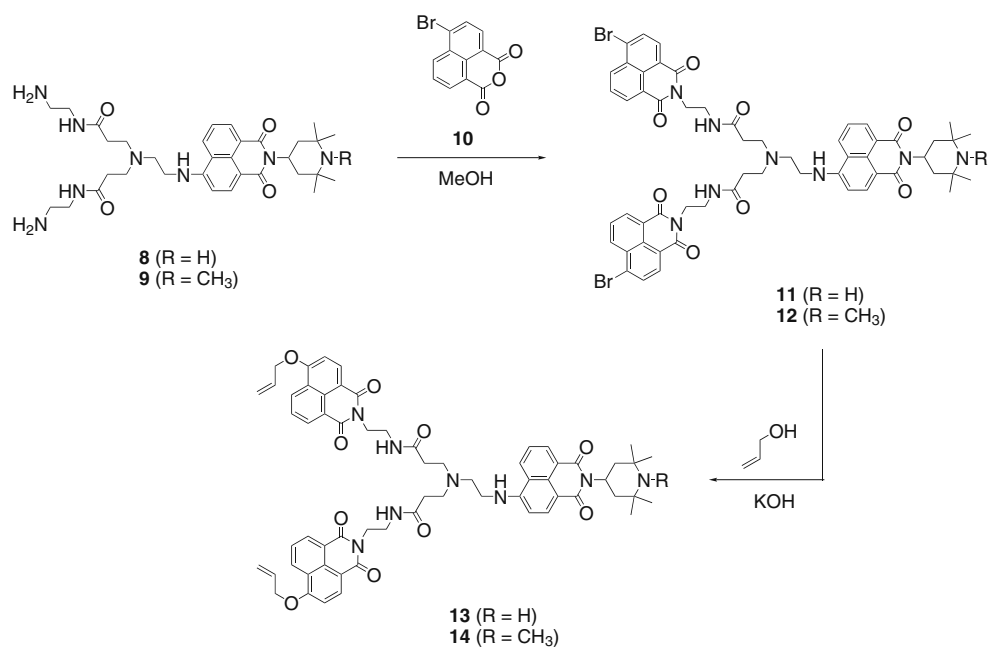
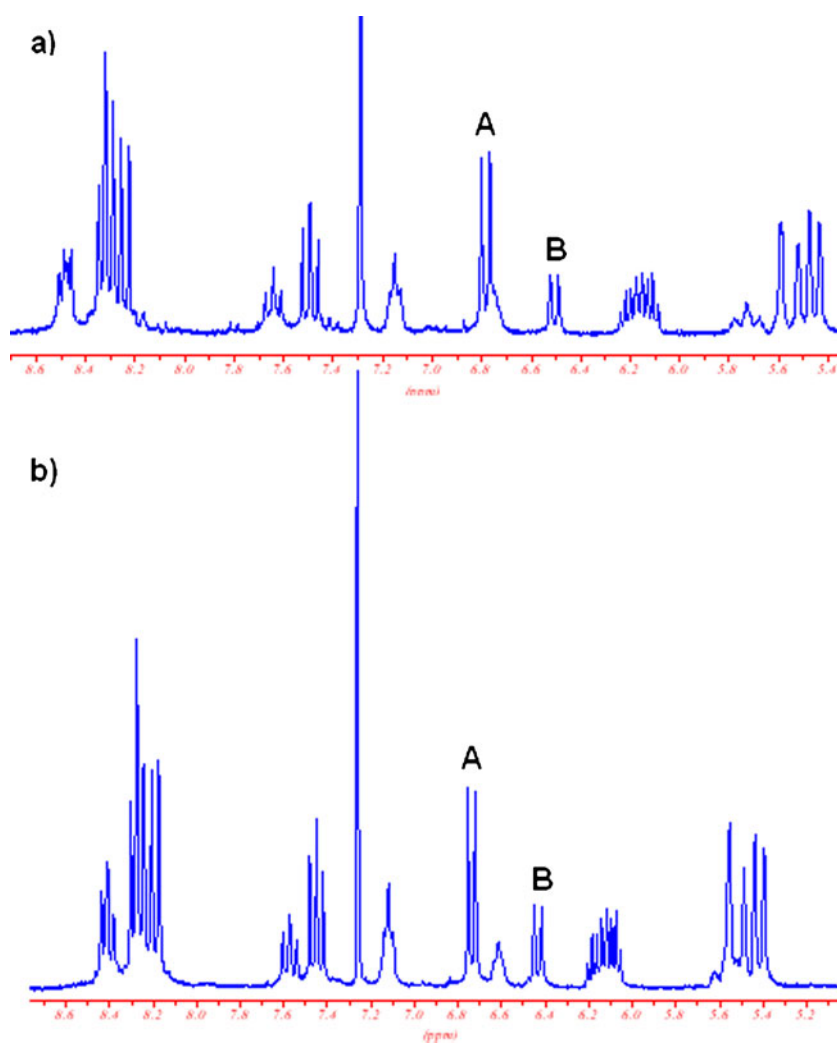
Scheme 5 Synthesis of light harvesting antennae **13** and **14****Fig. 2** ¹H NMR (CDCl₃-*d*, 250.13 MHz) spectra of antennae **13** (a) and **14** (b) in a range of about 8.80–5.20 ppm

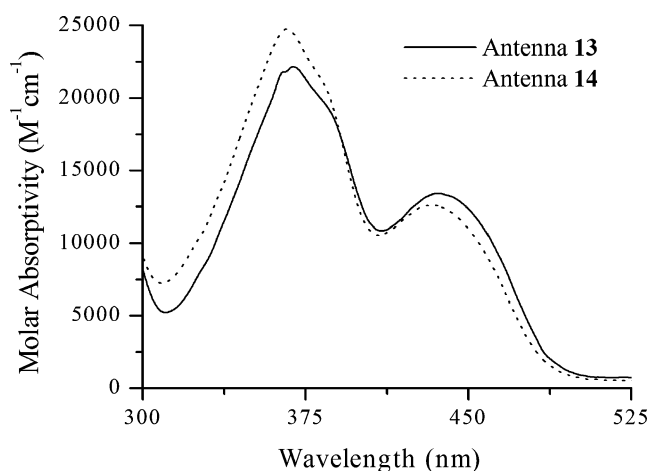
Table 1 Absorption data of fluorescent 1,8-naphthalimides **3**, **5–9** and antennae **13** and **14** in different solvents

Compound	DMF	Ethanol	Chloroform	
	λ_A (nm)	λ_A (nm)	λ_A (nm)	ϵ (l mol ⁻¹ cm ⁻¹)
3	442	442	430	14,478
5	440	438	428	14,598
6	442	446	436	13,914
7	442	440	430	13,159
8	440	442	432	12,861
9	442	440	434	13,326
13	368	370	368	22,175
	440	446	438	13,388
14	366	370	366	24,774
	442	438	434	12,595

This fact clearly shows the greater ability of periphery to capturing photons from the environment in comparison to the single focal chromophore in the examined antennae.

The fluorescence characteristics, such as fluorescence (λ_F) maximum, Stokes shift ($\nu_A - \nu_F$) and fluorescence quantum yield (Φ_F) of the 1,8-naphthalimides **3**, **5–9** and antennae **13** and **14** in different solvents are presented in Table 2.

In solution the fluorescent compounds **3**, **5–9** showed yellow-green fluorescence, typical for the 1,8-naphthalimides substituted in C-4 position with alkylamines. The fluorescence spectra of the light harvesting antennae **13** and **14** in solution, obtained after excitation within the spectral region of maximal absorption of the peripheral fluorophore ($\lambda_{ex}=360$ nm), showed two emission bands, corresponding to the emission bands of the donor and acceptor 1,8-naphthalimide fragments in the donor-

**Fig. 3** Absorption spectra of light harvesting dendrons **13** and **14** recorded in chloroform at concentration 10^{-5} mol l⁻¹

acceptor systems. As a result of the energy transfer, the blue emission intensity of the antennae periphery (donating 1,8-naphthalimide moieties) was strongly decreased in respect to the emission intensity of the reference blue emitting dendron **16**, not containing a focal (accepting) 1,8-naphthalimide. This is illustrated in Fig. 4, where are depicted the fluorescence spectra of antennae **13** and **14** and reference dendron **16** at the same optical density, excited within the maximal absorption of the peripheral 4-allyloxy-1,8-naphthalimides ($\lambda_{ex}=360$ nm).

By applying the Eq. 1 [17], where F_{DA} is the normalized to the optical density fluorescence intensity of the donor in the presence of acceptor (light harvesting antennae) and F_D is the normalized to the optical density fluorescence intensity of the donor without acceptor (model compound **16**), the efficiency of the energy transfer E_T in the light harvesting antennae was calculated to 92% for **13**, 80% for **14** and 94% for the reference antenna **15**.

$$E_T = 1 - F_{AD}/F_D \quad (1)$$

The E_T values of the examined antennae showed increase of the energy transfer with the volume decrease of the substituent, attached in *N*-position of the core 1,8-naphthalimide. This indicates that the average distance between the peripheral and core 1,8-naphthalimide units is increased with increasing the volume of the core substituents, which is related to the reduced ability of the flexible PAMAM dendron for back folding effect in the antennae with larger core volume.

Due to the high energy transfer and the greater ability of periphery to capturing photons from environment in respect to the single core (extinction coefficient in the antennae periphery is higher than that of the core, Fig. 3), the emission intensity of the core in the light harvesting systems **13** and **14**, excited by energy transfer from the peripheral units ($\lambda_{ex}=360$ nm), is higher than that of the core emission intensity, excited within the maximal absorption of the focal fluorophore ($\lambda_{ex}=420$ nm). This phenomenon is illustrated in Fig. 5, where are depicted fluorescence spectra of antennae **13** and **14** excited in periphery ($\lambda_{ex}=360$ nm) and directly in the core ($\lambda_{ex}=420$ nm), corrected for the lamp output difference at these wavelengths.

The Stoke's shift values of the compounds under study between $3,452$ cm⁻¹ and $4,698$ cm⁻¹ in different solvents correspond to the results for other 1,8-naphthalimide derivatives [19, 20] and these values do not indicate remarkable changes in the geometry of the first singlet excited state due to the excitation.

The ability of the molecules to emit the absorbed light energy is characterized quantitatively by the fluorescence quantum yield (Φ_F). The quantum yields of fluorescence were calculated using Coumarin 6 ($\Phi_F=0.78$ in ethanol) as a

Table 2 Fluorescence characteristics of 1,8-naphthalimides **3**, **5–9** and antennae **13** and **14** in different solvents

Compound	DMF		Ethanol		Chloroform		Φ_F^a
	λ_F (nm)	$\nu_A - \nu_F$ (cm ⁻¹)	λ_F (nm)	$\nu_A - \nu_F$ (cm ⁻¹)	λ_F (nm)	$\nu_A - \nu_F$ (cm ⁻¹)	
3	536	3,967	547	4,342	515	3,839	0.56
5	535	4,035	544	4,449	510	3,756	0.53
6	538	4,037	544	4,040	518	3,630	0.50
7	534	3,897	542	4,277	520	4,025	0.48
8	536	4,070	540	4,105	520	3,950	0.51
9	534	3,897	541	4,243	524	3,957	0.45
13	443	4,601	445	4,555	433	4,079	0.11
	534	4,000	538	3,835	516	3,452	
14	442	4,698	446	4,605	435	4,333	0.08
	535	3,932	540	4,312	513	3,548	

^a Quantum yield of fluorescence after excitation at $\lambda_{ex}=420$ nm (in the core)

standard according to Eq. 2, where A_{ref} , S_{ref} , n_{ref} and A_{sample} , S_{sample} , n_{sample} represent the absorbance at the excited wavelength, the integrated emission band area and the solvent refractive index of the standard and the sample, respectively.

$$\Phi_F = \Phi_{ref} \left(\frac{S_{sample}}{S_{ref}} \right) \left(\frac{A_{ref}}{A_{sample}} \right) \left(\frac{n_{sample}^2}{n_{ref}^2} \right) \quad (2)$$

As can be seen from the data in Table 2, the quantum yield of fluorescence of 1,8-naphthalimides **6–9** are lower in comparison with the data for compounds **3** and **5**, not containing tertiary amine, attached directly to the 4-amino moiety. As we reported before this phenomenon is due to the photoinduced electron transfer (PET) process from the tertiary PAMAM amine receptor to the 4-amino-1,8-naphthalimide fluorophore through the ethylene spacer [43]. Furthermore, as demonstrated experimentally by de Silva et

al. [45] only the receptor that is directly attached to the 4-amino moiety is capable of quenching the fluorophores excited state. Thus the fluorescence of the focal 4-amino-1,8-naphthalimide fluorophore is quenched (Scheme 6).

The data in Table 2 also show an extremely low quantum yield of fluorescence of the focal 1,8-naphthalimides in antennae **13** and **14**. The unusually low quantum yield of the core 1,8-naphthalimide in PAMAM light harvesting antennae was observed and attributed to a possible photoinduced electron transfer (PET) from the dendron bone to the focal fluorophore in the work of McKenna et al. [18]. However in the same study the core 1,8-naphthalimide has been dendronized in *N*-position, and as such, the tertiary amine in the dendron bone could not effectively take place in a PET process to the focal fluorophore [20]. This fact together with the much lower quantum yields of antennae **13** and **14** than those of the respective PAMAM

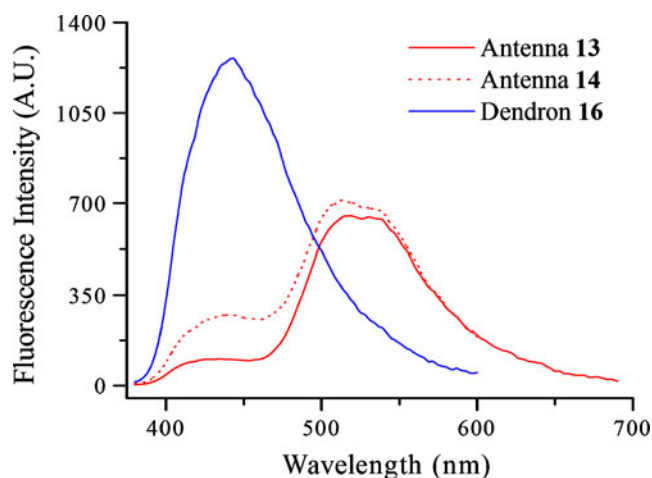


Fig. 4 Normalized to the same optical density fluorescence spectra of antennae **13** and **14** (red lines) and reference blue emitting dendron **16** (blue line) in chloroform solution, excited at 360 nm

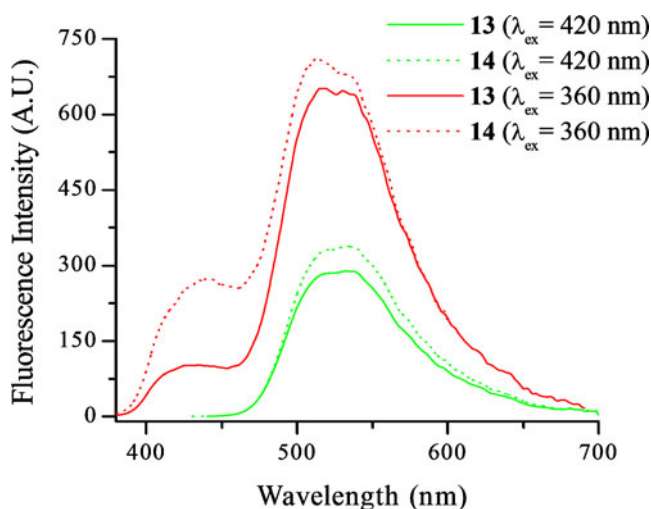
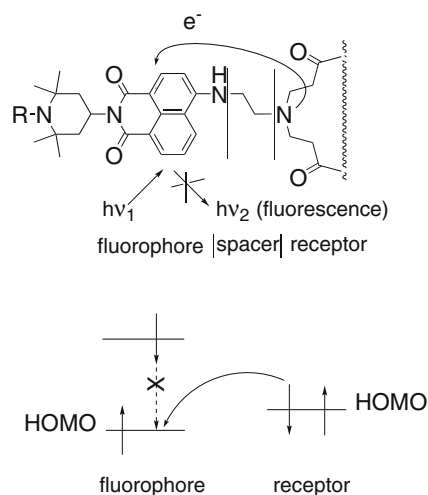


Fig. 5 Fluorescence spectra of antennae **13** and **14** in chloroform, excited in periphery ($\lambda_{ex}=360$ nm) and core ($\lambda_{ex}=420$ nm)

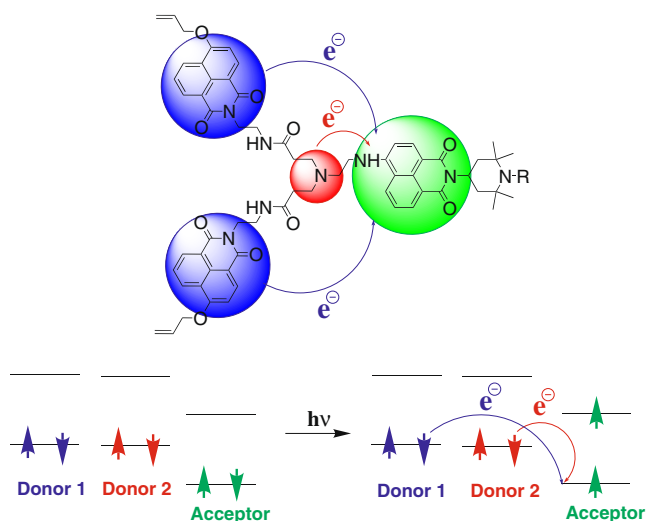


Scheme 6 The fluorescence quenching of the focal 4-amino-1,8-naphthalimide in compounds **6-9**

dendronized 1,8-naphthalimides **6-9**, not containing blue emitting periphery, suggest that the primary quenching element in antennae **13** and **14** are the peripheral units. In other words, if the antennae quenching is due to a PET effect, the process should mainly go from the peripheral 4-alkoxy-1,8-naphthalimides to the excited state of the focal 4-alkylamino-1,8-naphthalimide (Scheme 7).

Photodegradation of the antennae

The basic goal of this work was to obtain novel light-harvesting dendrons **13** and **14** containing more photostable core than that of the reference antenna **15**. This was the reason to investigate the photostability of the light-harvesting dendrons **13**, **14** and **15** in DMF solution by irradiation in a SUNTEST equipment. The changes in the



Scheme 7 The fluorescence quenching of the focal 4-amino-1,8-naphthalimide in antennae **13** and **14**

absorption spectra of antenna **13** as a function of the time of irradiation are presented in Fig. 6. As can be seen, after irradiation for a period of 60 min, the core absorption intensity decreased (band with maximum at about 440 nm) as a result of photodegradation, while the peripheral absorption intensity (band with maximum at about 365 nm) increased.

This phenomenon can be explained with the fact, that the molar extinction coefficient of the peripheral units in dendron **16** is higher than that of the periphery in antenna **13** (Fig. 7), suggesting higher prohibition for the $S_0 \rightarrow S_1$ transition of 4-allyloxy-1,8-naphthalimides in antenna **13** in comparison with those in dendron **16**. After degradation of the core in antenna **13** the prohibition for the $S_0 \rightarrow S_1$ transition in the peripheral 4-allyloxy-1,8-naphthalimides is decreased and their absorption intensity increased to the value that is typical for the blue-emitting dendron **16**.

A reason for the lower photostability of the core in the examined antennae could be the energy transfer from the periphery to the focal chromophore. To verify this assumption 4-*n*-butylamino-*N*-*n*-butyl-1,8-naphthalimide **17**, not containing blue-emitting (donating) periphery, was involved in the present study as reference compound. The correlation between the time of irradiation and the changes in the core absorption maxima of antennae **13-15** and reference 1,8-naphthalimide **17** are presented in Fig. 8, where A_0 and A are the core absorbance before and after the irradiation respectively.

As seen (Fig. 8), in DMF solution photostability of the reference 1,8-naphthalimide **17** is lower in respect to the photostability of the focal 4-allylamino-1,8-naphthalimides in antennae **13**, **14** and **15**. This clearly shows that the lower core photostability in relation to the peripheral photostability in the examined antennae is not due to the energy transfer to the focal dye. The higher photostability of core

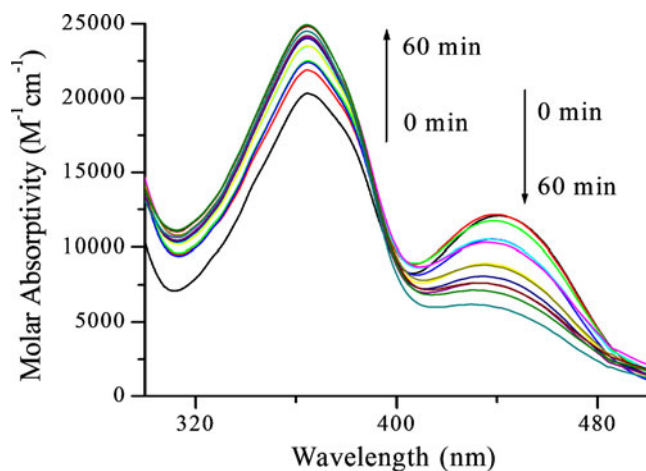


Fig. 6 Changes in the absorption spectra of antenna **13** after irradiation for 60 min, recorded in DMF solution at concentration $10^{-5} \text{ mol l}^{-1}$

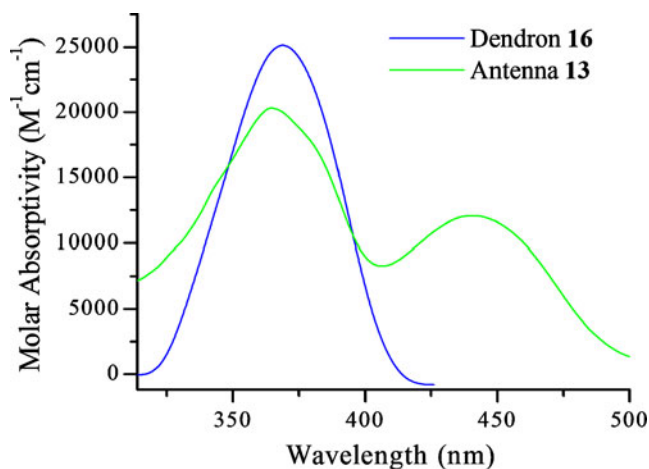


Fig. 7 Absorption spectra of reference dendron **16** and light harvesting antenna **13** recorded in DMF at concentration 10^{-5} mol l^{-1}

1,8-naphthaimides in the antennae than the photostability of reference 1,8-naphthaimide **17** probably is due to the absorption of a part of the dangerous energy form the near UV-region by peripheral 1,8-naphthaimides.

Data plotted in Fig. 8 clearly show that the core photostability of antennae **13** and **14** by virtue of the HALS (tetramethylpiperidine) fragment is higher than the core photostability of antenna **15**, not containing a tetramethylpiperidine moiety. The study also showed that the core photostability of antenna **14**, containing *N*-substituted piperidine moiety, is relatively lower in respect to that of the *N*-free piperidine core in antenna **13** due to the reduced ability of the piperidine nitrogen to form *N*-oxyl radicals.

The higher core photostability of the synthesized light-harvesting antennae **13** and **14** gave as an opportunity to study the PAMAM bone photodegradation. This was the

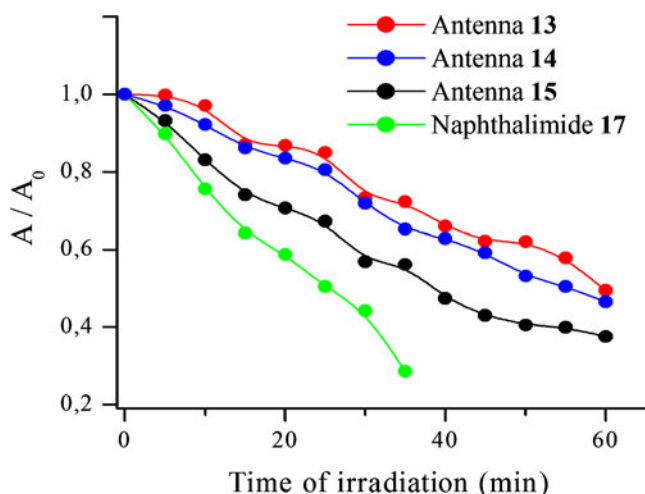


Fig. 8 Core photodegradation of antennae **13-15** and reference 1,8-naphthaimide **17** in DMF solution at concentration 10^{-5} mol l^{-1}

reason to investigate the fluorescence properties of the synthesized antennae as a function of the time of irradiation. The fluorescence spectra of a model antenna **13** in DMF solution after irradiation for 30 min in a SUNTEST equipment are presented in Fig. 9. As a result of irradiation the fluorescence intensity of the periphery (donor emission band at about 440 nm) increased, suggesting decrease of the energy transfer in antenna **13**.

As can be seen from Fig. 8, after irradiation for the first 10 min the core chromophoric system in antenna **13** was relatively stable, notwithstanding that at the same time the energy transfer obviously decreased (Fig. 9). This fact clearly shows that the average distance between the core and peripheral units in antenna **13** increased, which is due to the photodegradation of a PAMAM scaffold, keeping together the donor and acceptor fluorophores in one molecule. Further irradiation caused extremely decrease of the energy transfer in antenna **13** and after 30 min it was less than 10% due to the both effects—photodegradation of the PAMAM bone and about 10% photodestruction of the antenna core (as seen from Fig. 8).

It is evident that the low photostability of the PAMAM light-harvesting antennae is mainly due to the low photostability of the dendron bone. This suggests that the efforts for improvement the photostability of the PAMAM photo-devices should be directed to the enhanced photostability of the PAMAM scaffold.

Conclusions

Two novel light-harvesting antennae **13** and **14** with improved core photostability due to the incorporation of a HALS (2,2,6,6-tetramethylpiperidine or 1,2,2,6,6-pentam-

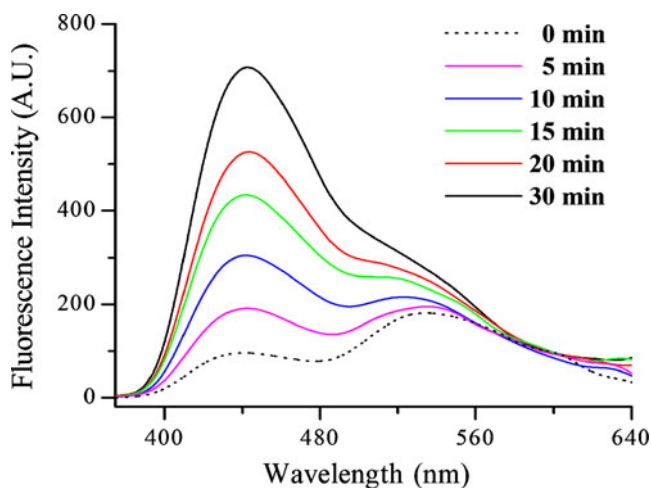


Fig. 9 Normalized to the optical density fluorescence spectra of antenna **13** in DMF solution at concentration 10^{-5} mol l^{-1} , after irradiation for 30 min in SUNTEST equipment

ethylpiperidine) fragment in the focal chromophore have been synthesized. Absorption and fluorescence characteristics of the synthesized donor-acceptor systems were determined and discussed. The novel antennae showed a highly efficient energy transfer from the peripheral units to the focal chromophore depending on the volume of the substituent in *N*-position of the core 1,8-naphthalimide. The efficiency of energy transfer for antenna **13** was calculated to be 92%, while in the antenna **14** was 80%, which is related to the reduced ability of the flexible PAMAM dendron for back folding effect in the antennae with larger core volume. The core chromophoric system in the novel antennae **13** and **14** showed higher photostability than the core photostability in the reference antenna **15**, not containing a HALS fragment. However the PAMAM bone photostability was found to be rather low, which indicates that the photostabilization of PAMAM photodevices should be focused on the PAMAM scaffold photostabilization.

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