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Design and synthesis of a novel pH sensitive core and peripherally 1,8-naphthalimide-labeled PAMAM dendron as light harvesting antenna

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ABSTRACT

The system surface was labeled with blue emitting 1,8-naphthalimide "donor" dyes capable of absorbing light and efficiently transferring the energy to a single yellow-green emitting 1,8-naphthalimide "acceptor" dye. The overlap between the blue emission of the donor and the absorbance of the acceptor (focal dye) was >70%. Due to the energy transfer from the periphery to the focal 1,8-naphthalimide chromophore (67%) the core fluorescence ($\lambda_{ex} = 360$ nm) was enhanced >36 times. It was also found that the novel light harvesting system displayed sensitive fluorescence signaling over a wide pH scale, which was ascribed to photoinduced electron transfer from the dendron bone to the blue emitting periphery. In acidic media the electron transfer was "*switched off*" and, in turn, the periphery emission was "*switched on*", resulting in energy transfer enhancement to the focal chromophore up to 92%. This indicates the high potential of the novel light harvesting system as an efficient pH hemosensing material.

1. Introduction

Molecular systems capable of light harvesting and efficiently transferring absorbed radiation unidirectionally over nanometer distances are currently of great interest. Progress in the study of natural photosynthetic systems has provided the impetus to design artificial light harvesting assemblies based on a variety of architectures [1–9]. Dendritic light harvesting assemblies have also attracted much attention because of their unique structures and properties [10–15]. The globular shape of dendrimers provides a large surface area that can be decorated with chromophores, resulting in a large absorption cross-section and efficient capture of photons [16–20]. The polyamidoamine (PAMAM) is a class of commercial dendrimers. The design and modification of the PAMAM dendrimers with fluorescent units could give new and interesting properties. Constructing fluorophore-terminated amidoamine branches around a luminescent group could profitably alter the luminescence signals in the macromolecular structure and amplify the signals for sensing purposes [21–24].

Naphthalimide derivatives are a special class of environmentally sensitive fluorophores. The fluorescence of the 4-alkoxy- and 4-amino-1,8-naphthalimide derivates has been of great interest for several decades in connection with an array of technical, medical and electronic use. Because of their strong fluorescence and good photostability, 1,8-naphthalimide derivatives have found application in a number of areas including coloration of polymers [25,26], laser active media [27,28], potential photosensitive biological units [29], fluorescent markers in biology [30], anticancer agents [31] and analgesics [32] in medicine, light emitting diodes [33,34], photoinduced electron transfer sensors [35,36], fluorescence switchers [37,38], electroluminescent materials [39,40], liquid crystal displays [41,42] and ion probes [43]. Moreover, these properties are essential when employing such devices in real-time and on-line analysis.

Recently we have reported on the synthesis of a fluorescence light harvesting antenna based on core and peripherally 1,8-naphthalimide-labeled PAMAM dendron where the PAMAM dendron was bonded to the C-4 position of the focal yellow-green emitting 1,8-naphthalimide [44]. Also it was shown that such type of bonding involved the focal fluorophore in a photoinduced electron transfer process (PET), quenching the core emission of the system [24]. To avoid quenching of the core emission it was of interest to synthesize a novel light harvesting system where the focal fluorophore was dendronized in the 1,8-naphthalimide *N*-position (Scheme 1). In this system the PAMAM dendron periphery is decorated with blue emitting 4-allyloxy-1,8-naphthalimide units as a "donor" surface that is capable of absorbing light and efficiently transferring the energy to a focal "acceptor" yellow-green emitting 1,8-naphthalimide.

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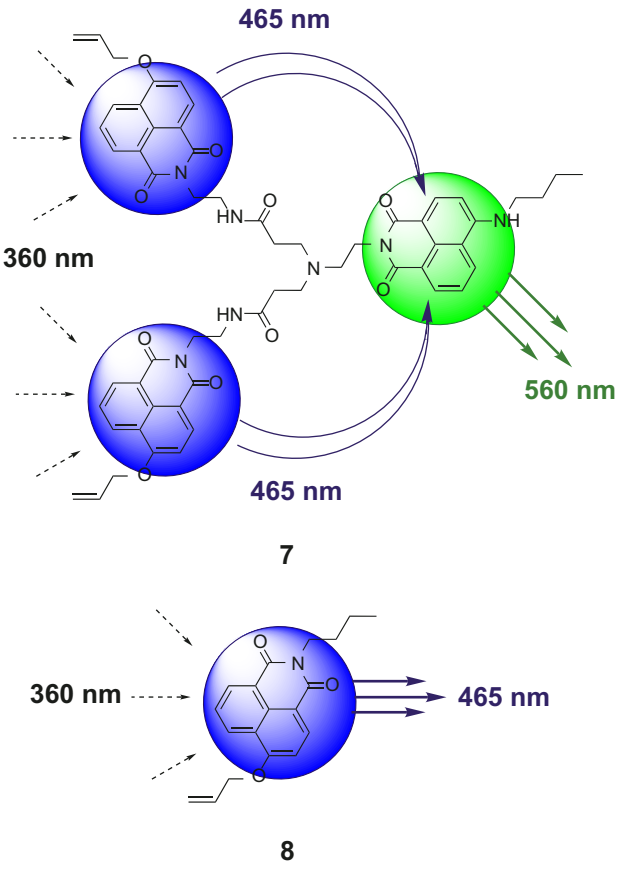


Scheme 1.

In order to receive a more complete comparative picture for the influence of both the branched (core) and peripheral fluorophores in the molecule of the light harvesting antenna **7** on its photophysical properties, the previously synthesized blue emitting 4-allyloxy-*N*-*n*-butyl-1,8-naphthalimide **8** (Scheme 1) was involved in the present study as a reference compound [45].

2. Experimental

2.1. Materials

The starting 4-bromo-1,8-naphthalic anhydride **1** was prepared according to the reported procedure [46]. Butylamine, ethylenediamine, allyl alcohol and methyl acrylate (Merck), p.a. grade, were used without purification. All solvents (Fluka, Merck) were pure or of spectroscopic grade.

2.2. Methods

FT-IR spectra were recorded on a Varian Scimitar 1000 spectrometer at 2 cm^{-1} resolution. The NMR spectra were recorded on a Bruker DRX-250 spectrometer, operating at 250.13 MHz and 62.90 MHz for ^1H and ^{13}C, respectively, using a dual 5 mm probe head. The chemical shifts (given as δ in ppm) were referenced to tetramethylsilane (TMS) standard. Experiments with 30° pulses, 1 s relaxation delays, 16 K time domain points, zero-filled to 64 K for protons and 32 K for carbons were performed. The distortionless enhancement by polarization transfer (DEPT) spectra were recorded under the conditions used for the ^{13}C NMR spectra at $\tau = (2^1J_{CH})^{-1} = 3.45$ μs. 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 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) [47].

2.3. Synthesis of fluorescent 1,8-naphthalimides

2.3.1. 4-Bromo-N-(2-aminoethyl)-1,8-naphthalimide (**2**)

To a stirred solution of 2.2 ml ethylenediamine (0.033 mol) in 12.6 ml of water, 1.84 g of 4-bromo-1,8-naphthalic anhydride **1** (0.005 mol) suspended in 5 ml of water was added portionwise at 75 °C over 10 min. The resulting suspension was kept at this temperature for 40 min and filtered off. The precipitate was collected, washed with water and dried in vacuum. The crude solid was extracted with boiling chloroform to give after evaporation of the solvent in vacuum 0.82 g (51%) pure 4-bromo-*N*-(2-aminoethyl)-1,8-naphthalimide **2** as pale yellow crystals (m.p. 151–152 °C; lit. [48] 150–151 °C).

IR (KBr) cm^{-1}: 3374 (νNH_2); 2920 (νCH); 1686 ($\nu^{as}N–C{=}O$); 1644 ($\nu^{s}N–C{=}O$). ^1H NMR ($CDCl_3$-*d*, 250.13 MHz) ppm: 8.65 (dd, 1H, $J = 7.3$ Hz, $J = 1.1$ Hz, naphthalimide H-5); 8.56 (dd, 1H, $J = 8.5$ Hz, $J = 1.1$ Hz, naphthalimide H-7); 8.40 (d, 1H, $J = 7.9$ Hz, naphthalimide H-3); 8.05 (d, 1H, $J = 7.9$ Hz, naphthalimide H-2); 7.84 (dd, 1H, $J = 8.5$ Hz, $J = 7.3$ Hz, naphthalimide H-6); 4.27 (t, 2H, $J = 6.6$ Hz, $NCH_2CH_2NH_2$); 3.07 (t, 2H, $J = 6.7$ Hz, $NCH_2CH_2NH_2$).

2.3.2. 4-n-Butylamino-N-(2-aminoethyl)-1,8-naphthalimide (**3**)

To a solution of *n*-butylamine (0.99 ml, 0.001 mol) and 4-bromo-*N*-(2-aminoethyl)-1,8-naphthalimide **2** (0.8 g, 0.0025 mol) in 15 ml of DMF, 0.1 g of $CuSO_4 \cdot 5H_2O$ was added. The resulting mixture was stirred at 90 °C for 12 h. After cooling to room temperature, the solution was poured into 50 ml of water, and the precipitate was collected by filtration, washed with water and dried. Silica gel chromatography (ethanol:chloroform = 9:1) afforded 0.43 g (55%) of 4-*n*-butylamino-*N*-(2-aminoethyl)-1,8-naphthalimide **3** as yellow-orange crystals (m.p. 158–162 °C).

IR (KBr) cm^{-1}: 3282 and 3194 (νNH_2); 2946 and 2810 (νCH); 1664 ($\nu^{as}N–C{=}O$); 1620 ($\nu^{s}N–C{=}O$). ^1H NMR (DMSO-d_6, 250.13 MHz) ppm: 8.72 (d, 1H, $J = 8.4$ Hz, naphthalimide H-5); 8.43 (d, 1H, $J = 7.2$ Hz, naphthalimide H-7); 8.26 (d, 1H, $J = 8.5$ Hz, naphthalimide H-2); 7.67 (dd, 1H, $J = 8.3$ Hz, $J = 7.3$ Hz, naphthalimide H-6); 6.77 (d, 1H, $J = 8.4$ Hz, naphthalimide H-3); 5.16 (m, 1H, NH); 4.18 (m, 2H, $NCH_2CH_2NH_2$); 3.41 (m, 2H, $ArNHCH_2$); 2.91 (t, 4H, $J = 7.2$ Hz, $NCH_2CH_2NH_2$); 1.69 (m, 2H, $CH_2CH_2CH_2CH_3$); 1.43 (m, 2H, $CH_2CH_2CH_2CH_3$); 0.95 (t, 3H, $J = 7.3$ Hz, $CH_2CH_2CH_2CH_3$). ^{13}C NMR (DMSO-d_6, 62.90 MHz) ppm: 160.5 (2 × N–C=O); 152.1, 138.1, 131.1, 130.1, 127.1, 120.7, 118.9, 117.2 and 114.3 (Ar CH and Ar C); 50.9 ($(CO)_2NCH_2CH_2NH_2$); 46.1 ($(CO)_2NCH_2CH_2NH_2$); 43.7 ($ArNCH_2CH_2CH_2CH_3$); 29.8 ($NCH_2CH_2CH_2CH_3$); 20.6 ($NCH_2CH_2CH_2CH_3$); 13.5 (CH_3). Elemental analysis: Calculated for $C_{18}H_{21}N_3O_2$ (MW 311.38) C 69.43, H 6.80, N 13.49%; Found C 69.69, H 6.72, N 13.61%.

2.3.3. Ester-functionalized 1,8-naphthalimide (**4**)

To a solution of methyl acrylate (1.1 ml, 0.013 mol) in 5 ml of methanol, a solution of 4-*n*-butylamino-*N*-(2-aminoethyl)-1,8-naphthalimide **3** (0.4 g, 0.0013 mol) 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 the ester-functionalized derivative **4** was obtained as yellow-brown oil (0.6 g, 95%).

IR (oil) cm^{-1}: 3318 (νNH); 2930 (νCH); 2832 (νCH_3); 1726 ($\nu COOCH_3$); 1682 ($\nu^{as}N–C{=}O$); 1634 ($\nu^{s}N–C{=}O$). ^1H NMR ($CDCl_3$-*d*,

250.13 MHz) ppm: 8.57 (dd, 1H, $J = 7.3$ Hz, $J = 1.1$ Hz, naphthalimide H-5); 8.45 (d, 1H, $J = 8.4$ Hz, naphthalimide H-2); 8.07 (dd, 1H, $J = 8.5$ Hz, $J = 1.1$ Hz, naphthalimide H-7); 7.61 (dd, 1H, $J = 8.4$ Hz, $J = 7.3$ Hz, naphthalimide H-6); 6.72 (d, 1H, $J = 8.4$ Hz, naphthalimide H-3); 5.22 (m, 1H, NH); 4.23 (t, 2H, $J = 7.3$ Hz, $(CO)_2NCH_2CH_2N$); 3.57 (s, 6H, $2 \times OCH_3$); 3.41 (m, 2H, $ArNHCH_2$); 2.91 (t, 4H, $J = 7.2$ Hz, $2 \times NCH_2CH_2CO$); 2.78 (t, 2H, $J = 7.3$ Hz, $(CO)_2NCH_2CH_2N$); 2.49 (t, 4H, $J = 7.2$ Hz, $2 \times NCH_2CH_2CO$); 1.81 (m, 2H, $CH_2CH_2CH_2CH_3$); 1.53 (m, 2H, $CH_2CH_2CH_2CH_3$); 1.03 (t, 3H, $J = 7.3$ Hz, $CH_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$-*d*, 62.90 MHz) ppm: 171.8 ($2 \times COOCH_3$); 159.3 ($2 \times N–C{=}O$); 151.9, 138.0, 130.7, 128.9, 127.2, 121.1, 119.3, 116.9 and 113.8 (Ar CH and Ar C); 53.1 ($(CO)_2NCH_2CH_2N$); 50.8 ($2 \times OCH_3$); 49.3 ($2 \times NCH_2CH_2CO$); 45.2 ($(CO)_2NCH_2CH_2N$); 43.4 ($ArNCH_2CH_2CH_2CH_3$); 33.1 ($2 \times NCH_2CH_2CO$); 30.7 ($NCH_2CH_2CH_2CH_3$); 21.1 ($NCH_2CH_2CH_2CH_3$); 13.7 (CH_3). Elemental analysis: Calculated for $C_{26}H_{33}N_3O_6$ (MW 483.56) C 64.58, H 6.88, N 8.69%; Found C 64.86, H 6.79, N 8.57%.

2.3.4. Amidoamine-functionalized 1,8-naphthalimide (**5**)

To a solution of ethylenediamine (4.8 ml, 0.072 mol) in 5 ml of methanol, a solution of 1,8-naphthalimide **4** (0.6 g, 0.0012 mol) in 15 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 80 ml of toluene was added and methanol was distilled under vacuum along with the part of the toluene. The amino-functionalized dendron **5** was obtained as yellow-brown oil (0.58 g, 90%) after decantation of excess ethylenediamine and toluene.

IR (oil) cm^{-1}: 3315, 3224 (νNH_2); 3180 (νNH); 2920 and 2894 (νCH); 1698 ($\nu^{as}N–C{=}O$); 1650 ($\nu^{s}N–C{=}O$); 1632 ($\nu NH–C{=}O$). ^1H NMR (DMSOl-d_6, 250.13 MHz) ppm: 8.71 (d, 1H, $J = 8.4$ Hz, naphthalimide H-5); 8.42 (d, $J = 7.2$ Hz, 1H, naphthalimide H-7); 8.26 (d, 1H, $J = 8.7$ Hz, naphthalimide H-2); 7.88 (br s, 2H, $2 \times$ NHCO); 7.75 (m, 1H, ArNH); 7.67 (t, 1H, $J = 7.7$ Hz, naphthalimide H-6); 6.77 (d, 1H, $J = 8.6$ Hz, naphthalimide H-3); 4.06 (m, 2H, $J = 7.3$ Hz, $(CO)_2NCH_2$); 3.05 (m, 6H, $2 \times NHCH_2CH_2NH_2$ and $ArNHCH_2CH_2CH_2CH_3$); 2.75 (m, 6H, $3 \times NCH_2$); 2.60 (m, 4H, $2 \times NHCH_2CH_2NH_2$); 2.23 (m, 4H, $2 \times CH_2CO$); 1.69 (m, 2H, $CH_2CH_2CH_2CH_3$); 1.43 (m, 2H, $CH_2CH_2CH_2CH_3$); 0.95 (t, 3H, $J = 7.4$ Hz, $CH_2CH_2CH_2CH_3$). ^{13}C NMR (DMSO-d_6, 62.90 MHz) ppm: 166.6 ($2 \times NH–C{=}O$); 160.1 ($N–C{=}O$); 152.1, 137.8, 131.5, 129.1, 125.9, 120.9, 118.1, 117.1 and 114.0 (Ar CH and Ar C); 55.8 ($(CO)_2NCH_2CH_2N$); 52.8 ($2 \times NCH_2CH_2CONH$); 43.1 ($ArNCH_2CH_2CH_2CH_3$); 42.7 ($2 \times NCH_2CH_2NH_2$); 42.1 ($(CO)_2NCH_2CH_2N$); 41.6 ($2 \times NCH_2CH_2NH_2$); 30.9 ($2 \times NCH_2CH_2CONH$); 29.8 ($NCH_2CH_2CH_2CH_3$); 20.8 ($NCH_2CH_2CH_2CH_3$); 14.1 (CH_3). Elemental analysis: Calculated for $C_{28}H_{41}N_7O_4$ (MW 539.67) C 62.32, H 7.66, N 18.17%; Found C 62.03, H 7.74, N 18.28%.

2.3.5. Synthesis of light harvesting 1,8-naphthalimide dendron (**7**)

To a solution of 4-bromo-1,8-naphthalic anhydride **1** (0.5 g, 0.0018 mol) in 20 ml of boiling methanol, a solution of amino-terminated 1,8-naphthalimide dendron **5** (0.5 g, 0.0009 mol) in 15 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 yellow-orange precipitate was filtered off, washed with fresh methanol and dried in vacuum to afford 0.49 g (52%) of 4-bromo-1,8-naphthalimide peripherally functionalized dendron **6**. The solid was suspended in solution of 0.06 g KOH (0.001 mol) in 20 ml of allyl alcohol and the reaction mixture was refluxed under stirring for a period of 20 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 (ethanol:chloroform = 9:1) afforded 0.16 g (34%) of 4-allyloxy-1,8-naphthalimide peripherally functionalized dendron **7** as yellow crystals (m.p. 112–115 °C).

IR (KBr) cm^{-1}: 3334 (νNH); 2922 and 2906 (νCH); 1698 ($\nu^{as}N–C{=}O$); 1654 ($\nu^{s}N–C{=}O$); 1633 ($\nu NH–C{=}O$). ^1H NMR ($CDCl_3$-*d*, 250.13 MHz) ppm: 8.37 (dd, 1H, $J = 7.2$ Hz, $J = 1.9$ Hz, focal naphthalimide H-5); 8.28 (m, 3H, focal naphthalimide H-7 and $2 \times$ peripheral naphthalimide H-5); 8.23 (d, 2H, $J = 8.3$ Hz, $2 \times$ peripheral naphthalimide H-2); 8.13 (dd, 2H, $J = 8.4$ Hz, $J = 1.2$ Hz, $2 \times$ peripheral naphthalimide H-7); 8.01 (d, 1H, $J = 8.5$ Hz, focal naphthalimide H-2); 7.68 (m, 2H, $2 \times$ NHCO); 7.50 (t, 1H, $J = 7.8$ Hz, focal naphthalimide H-6); 7.38 (t, 2H, $J = 8.3$ Hz, $2 \times$ peripheral naphthalimide H-6); 6.72 (d, 2H, $J = 8.3$ Hz, $2 \times$ peripheral naphthalimide H-3); 6.58 (d, 1H, $J = 8.4$ Hz, focal naphthalimide H-3); 6.10 (m, 2H, $2 \times OCH_2CH{=}CH_2$); 5.51 (dd, 2H, $J_{trans} = 17.1$ Hz, $J = 1.4$ Hz, $2 \times$ allyl $HCH{=}$); 5.41 (d, 2H, $J_{cis} = 10.5$ Hz, $2 \times$ allyl $HCH{=}$); 5.26 (m, 1H, $2 \times$ ArNH); 4.62 (d, 4H, $J = 6.7$ Hz, $2 \times OCH_2CH{=}CH_2$); 4.18 (m, 6H, $3 \times (CO)_2NCH_2$); 3.55 (m, 4H, $2 \times CONHCH_2$); 3.33 (m, 2H, $ArNHCH_2$); 2.80 (t, 4H, $J = 6.5$ Hz, $CH_2N(CH_2)_2$); 2.72 (t, 2H, $J = 6.7$ Hz, $CH_2N(CH_2)_2$); 2.37 (t, 4H, $J = 6.5$ Hz, $2 \times CH_2CONH$); 1.77 (m, 2H, $CH_2CH_2CH_2CH_3$); 1.52 (m, 2H, $CH_2CH_2CH_2CH_3$); 1.02 (t, 3H, $J = 7.3$ Hz, $CH_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$-*d*, 62.90 MHz) ppm: 170.1 ($2 \times NH–C{=}O$); 161.5 (focal naphthalimide $2 \times N–C{=}O$); 160.1 (peripheral naphthalimide $4 \times N–C{=}O$); 157.6 (peripheral naphthalimide $2 \times$ Ar–C–O); 149.6 (focal naphthalimide Ar–C–NH); 133.9, 133.3, 133.0, 131.1, 129.9, 128.4, 127.0, 126.1, 124.8, 123.1, 122.5, 121.2, 120.1, 116.9, 113.1 and 108.6 (Ar CH and Ar C); 133.6 ($2 \times$ allyl CH); 117.1 ($2 \times$ allyl CH_2); 71.2 ($2 \times$ allyl OCH_2); 52.1 ($(CO)_2NHCH_2CH_2N$); 50.6 ($2 \times CONHCH_2CH_2N(CO)_2$); 46.3 ($2 \times CONHCH_2CH_2N(CO)_2$); 44.1 ($ArNCH_2CH_2CH_2CH_3$); 41.2 ($(CO)_2NHCH_2CH_2N$); 40.7 ($2 \times NCH_2CH_2CONH$); 31.8 ($2 \times NCH_2CH_2CONH$); 28.7 ($NCH_2CH_2CH_2CH_3$); 21.0 ($NCH_2CH_2CH_2CH_3$); 13.9 ($CH_3$). Elemental analysis: Calculated for $C_{58}H_{57}N_7O_{10}$ (MW 1012.11) C 68.83, H 5.68, N 9.69%; Found C 68.49, H 5.76, N 9.57%.

3. Results and discussion

3.1. Design and synthesis of light harvesting 1,8-naphthalimide-labeled PAMAM dendron

The PAMAM dendron **7**, core and peripherally labeled with 1,8-naphthalimide units, was designed as a fluorescent light harvesting antenna. We chose 1,8-naphthalimide for the fluorescence modification of PAMAM in a view of its chemical stability and high fluorescent efficiency. A requirement for efficient energy transfer is that there be a spectral overlap between the emission of the peripheral donor dyes and the absorbance of the focal acceptor chromophore. It is well known that absorption and fluorescence characteristics of the 1,8-naphthalimides depend on the nature of the substituent at C-4 position of the 1,8-naphthalimide ring. 4-Alkylamino-1,8-naphthalimide derivatives are yellow-green emitting fluorophores with maximal absorption in the blue region at about $\lambda_A = 430–440$ nm, where the emission of 4-alkoxy-1,8-naphthalimides appears. Consistent with the requirement, 4-alkoxy- and 4-alkylamino-1,8-naphthalimides are suitable fluorescence donor–acceptor pairs for light harvesting systems. In this study 4-allyloxy- and 4-buthylamino-1,8-naphthalimide derivatives were used as their spectral overlap was more than 70%. The absorbance of the PAMAM 1,8-naphthalimide core functional dendron **5** and the emission of the reference compound 4-allyloxy-*N*-*n*-butyl-1,8-naphthalimide **8** are depicted in Fig. 1.

The synthesis of amino-terminated 1,8-naphthalimide dendron **5** was performed in four steps following Scheme 2. First, 4-bromo-*N*-(2-aminoethyl)-1,8-naphthalimide **2** was obtained by reaction of 4-bromo-1,8-naphthalic anhydride **1** with ethylenediamine in water at 75 °C as described before [48]. The intermediate **2** was

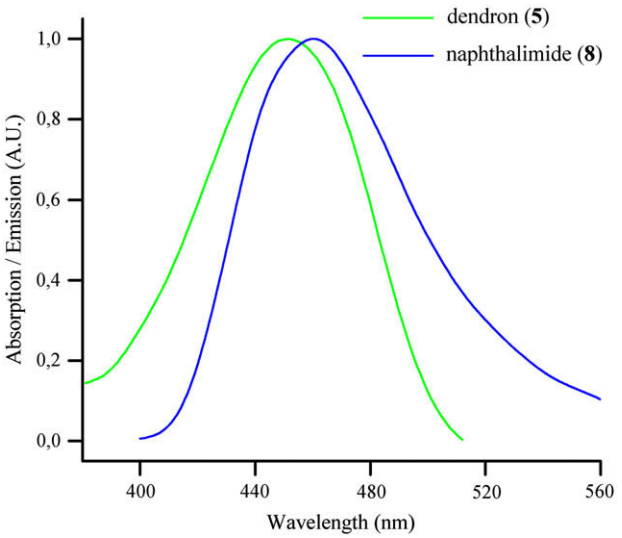


Fig. 1. Normalized absorption of dendron **5** (green line) and emission of naphthalimide **8** (blue line) in ethanol solution.

subsequently converted into the yellow-green emitting dendron core **3** by reaction with *n*-butylamine in DMF at 90 °C for 5 h in the presence of $CuSO_4 \cdot 5H_2O$.

The ester-terminated and amino-terminated 1,8-naphthalimide dendrons **4** and **5** were synthesized by a divergent strategy involving an initial Michael addition of methyl acrylate to the 4-*n*-butylamino-*N*-(2-aminoethyl)-1,8-naphthalimide **3** followed by exhaustive amidation of the resulting diester **4** with a large excess of ethylenediamine to afford the amidoamine-functionalized 1,8-naphthalimide **5** with reactive amine groups of its periphery.

The light harvesting antenna **7** was synthesized in two steps as shown in Scheme 3. The intermediate 4-bromo-1,8-naphthalimide peripherally functionalized dendron **6** was obtained by reaction of 4-bromo-1,8-naphthalic anhydride **1** with amidoamine-functionalized 1,8-naphthalimide **5**, possessing two primary terminal amine groups, under reflux in methanol solution. In order to obtain a blue emitting periphery of the desired antenna **7**, the bromine atoms in the intermediate **6** were subsequently nucleophilically substituted with alkoxy groups under reflux of intermediate **6** in allyl alcohol in the presence of finely ground potassium hydroxide.

The structure and purity of the synthesized compounds were characterized and confirmed by conventional techniques – melting point, TLC (R_f value), elemental analysis data, UV–vis, fluorescence, FT-IR, ^{1}H and ^{13}C NMR spectroscopy. For instance, in the ^{1}H NMR ($CDCl_3$-*d*, 250.13 MHz) spectrum of antenna **7** a resonance at 6.72 ppm was observed. This is characteristic for the proton in position C-3 of the periphery 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 core "yellow-green" 1,8-naphthalimide moiety (6.58 ppm). Furthermore, the ^{1}H NMR spectrum contained peaks in range of 6.10–4.62 ppm, attributed to the protons for the peripheral allyloxy groups.

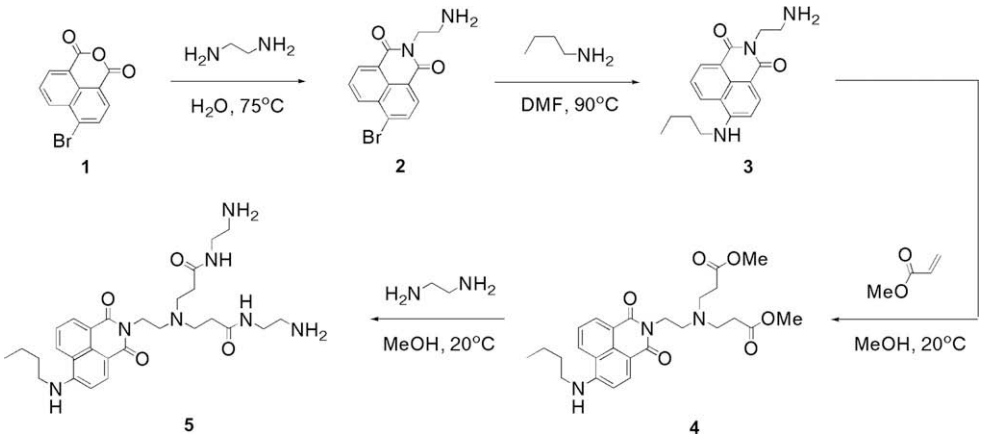
3.2. Photophysical characterization of the dyes

It is well known that the light absorption properties of the 1,8-naphthalimide derivatives are basically related to the polarization of their chromophoric system and may be influenced by the environmental effect of the media. The absorption spectra of compounds **3**–**8** were measured in solvents of different polarity such as ethanol and chloroform. The absorption data of the examined compounds are listed in Table 1.

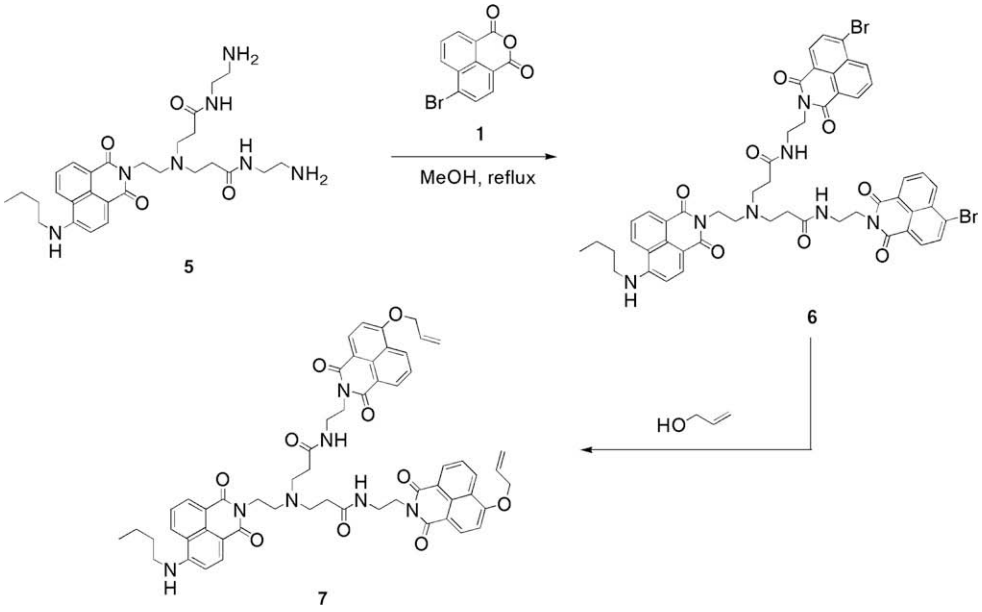
Compounds **3**–**5** showed typical absorption bands for the 4-aminosubstituted 1,8-naphthalimides with well pronounced maximum at 429–434 nm in chloroform and at 439–443 nm in ethanol, while the absorption spectrum of light harvesting system **7**, as expected, contains two bands (Fig. 2) corresponding to the absorption location of the peripheral 4-allyoxy-1,8-naphthalimide donors (reference compound **8**) and the focal 4-amino-1,8-naphthalimide acceptor unit (compound **5**). A typical bathochromic shift of the longest-wavelength band with increasing the solvent polarity was observed (Table 1). No specific effect in protic ethanol was observed, which indicates a lack of intermolecular H-bond formation in the dyes' ground state.

The molar extinction coefficients (ε) of the compounds under study in the long-wavelength band of the absorption spectra are higher than 10,000 l mol^{-1} cm^{-1} (Table 1), indicating that this is a charge transfer (CT) band, due to (π,π^*) character of the $S_0 \rightarrow S_1$ transition. Also the molar extinction coefficient value of the peripheral absorption of the light harvesting antenna **7** is about 2-fold higher than that of the reference blue emitting 1,8-naphthalimide **8**, suggesting no ground state interaction between the peripheral 1,8-naphthalimide units. The molar extinction coefficient (ε) of the focal 1,8-naphthalimide chromophore in antenna **7** has approximately the same value as that of the yellow-green emitting PAMAM core 1,8-naphthalimide dendron **5**.

The steady-state fluorescence characteristics of the 1,8-haphthalimides **3**–**5** and light harvesting antenna **7** such as fluorescence (λ_F) maxima, Stokes shift ($\nu_A - \nu_F$) and quantum yield of



Scheme 2.



Scheme 3.

fluorescence (Φ_F) were measured in chloroform and ethanol and are presented in Table 2.

In solution the periphery of antenna **7** displays blue fluorescence, while the core of dendron **7** and compounds **3**–**5** are yellow-green emitting due to the charge transfer in the 1,8-naphthalimide moieties from the electron-donating alkoxy (blue fluorescence) or alkylamino (yellow-green fluorescence) substituent at C-4 position to the electron-accepting carbonyl groups. The fluorescence Franck Condon (FC) transitions λ_F in ethanol solution as expected are bathochromically shifted with respect to those in chloroform. In all cases, the shape and the maximum of the fluorescence band do not depend on the excitation wavelength and the excitation spectra are identical to the corresponding absorption ones.

The Stoke's shift ($\nu_A - \nu_F$) is an important parameter for the fluorescent compounds and indicates differences in properties and structure of fluorophores in the ground state S_0 and the first excited state S_1. The Stoke's shifts (cm^{-1}) were calculated by Eq. (1).

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

The Stoke's shift values of the compounds under study ranged between 4.217 and 5.817 cm^{-1} for the blue emitting dendron periphery **7** as well as between 3.699 and 4.498 cm^{-1} for the yellow-green focal chromophore **7** and yellow-green emitting compounds **3**–**5** correspond to the results for other 1,8-naphthalimide derivatives [49,50] and these values do not indicate remarkable changes in the geometry of the first singlet excited state due to the excitation.

Table 1
Absorption maxima and molar extinction coefficients of antenna **7**, yellow-green emitting 1,8-naphthalimides **3**–**5** and blue emitting 1,8-naphthalimide **8** in solvents of different polarity

Compound	Chloroform[a]			Ethanol[a]		
	λ_{A1} (nm)	λ_{A2} (nm)	ε ($l\,mol^{-1}\,cm^{-1}$)	λ_{A1} (nm)	λ_{A2} (nm)	ε ($l\,mol^{-1}\,cm^{-1}$)
3	–	429	17.022	–	439	15.230
4	–	430	14.111	–	440	14.993
5	–	434	12.536	–	448	10.003
7	369	434	29.177, 12.201	366	449	21.852, 10.170
8	360	–	12.313	363	–	13.478

[a] λ_{A1} and λ_{A2} represent the peripheral and core absorption, respectively.

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 standard [47] 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 solution refractive index of the standard and the sample, respectively.

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

The fluorescence spectrum of the light harvesting antenna **7** in ethanol 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

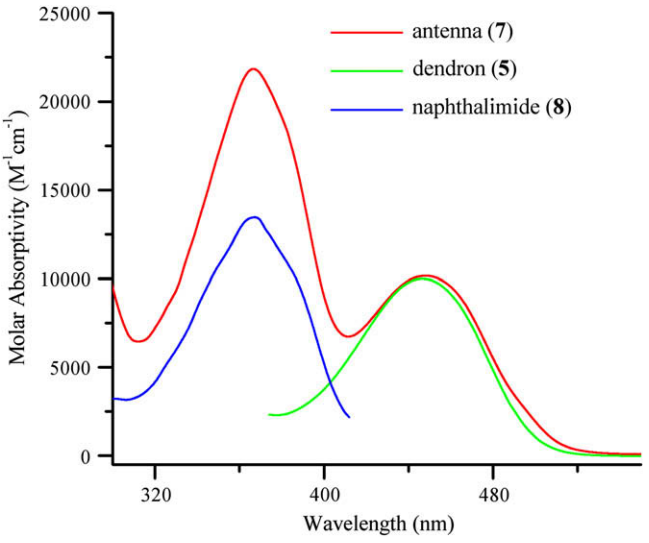


Fig. 2. Absorption spectra of antenna **7** (red line), periphery (compound **8**, blue line) and core (compound **5**, green line) in ethanol solution.

Table 2
Fluorescence characteristics of antenna **7** and 1,8-naphthalimides **3**–**5** and **8** in ethanol solution

Compound	Chloroform			Ethanol		
	λ_F (nm)	$\nu_A - \nu_F$ (cm^{-1})	Φ_F	λ_F (nm)	$\nu_A - \nu_F$ (cm^{-1})	Φ_F
3	517	3.758	0.49	547	4.498	0.32
4	521	4.062	0.39	546	4.412	0.27
5	519	3.774	0.38	544	3.939	0.26
7	437	4.217	0.21[a]	465	5.817	0.12[a]
	517	3.699	0.36[b]	560	4.414	0.25[b]
8	438	4.947	0.59	464	6.180	0.41

[a] Quantum yield of fluorescence of antenna **7** at $\lambda_{ex} = 360$ nm.
[b] Quantum yield of fluorescence of antenna **7** at $\lambda_{ex} = 460$ nm.

emission bands of the donor and acceptor 1,8-naphthalimide fragments in the donor–acceptor system **7** (Fig. 3).

Under excitation at $\lambda_{ex} = 360$ nm (within the maximal absorption of the peripheral fluorophore) the 1,8-naphthalimide core dendron **5** showed a subtle emission in the yellow-green spectral region, while the core fluorescence intensity of the donor–acceptor system **7** in the same region is more than 36 times higher due to the energy transfer from the periphery to the focal chromophore (Fig. 4).

Fig. 5 represents the emission spectra of light harvesting antenna **7** under excitation in periphery ($\lambda_{ex} = 360$ nm) and direct at the core ($\lambda_{ex} = 460$ nm). The emission intensity of the core, excited by energy transfer from peripheral units ($\lambda_{ex} = 360$ nm) is 1.77 times higher than that of the core emission intensity, excited within the maximal absorption of the focal fluorophore ($\lambda_{ex} = 460$ nm). The difference of the harvested and direct core emission clearly demonstrates the great ability of the light harvesting system **7** to transfer energy from its periphery to the core. This observation indicates that the light harvesting antenna is more efficient than the core dye at capturing photons from environment.

In contrast, when the fluorescence spectra of light harvesting system **7** were normalized at the same optical density, the core emission intensity of the system excited at $\lambda_{ex} = 360$ nm decreased and became lower than that recorded at $\lambda_{ex} = 460$ nm (Fig. 6) due to the loss of energy during the transfer from periphery to the core. On the basis of the curves plotted in Fig. 6 the calculated efficiency of the energy transfer in the light harvesting system **7** was 67%.

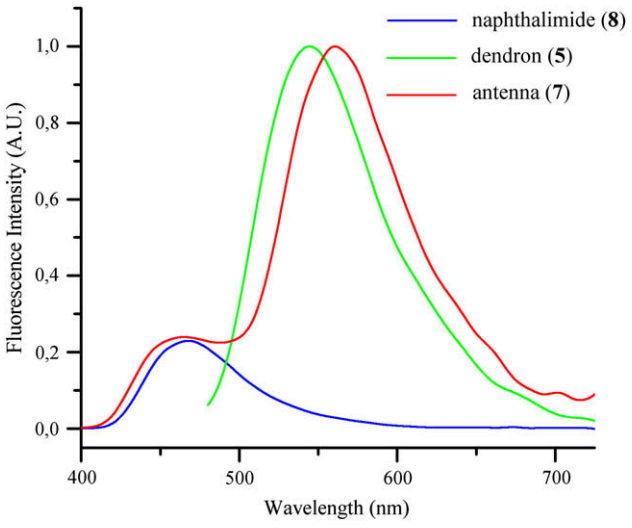


Fig. 3. Normalized emission spectra of periphery at $\lambda_{ex} = 360$ nm (compound **8**, blue line), core at $\lambda_{ex} = 460$ nm (compound **5**, green line) and antenna **7** at $\lambda_{ex} = 360$ nm (red line) in ethanol at concentration 10^{-5} mol l^{-1}.

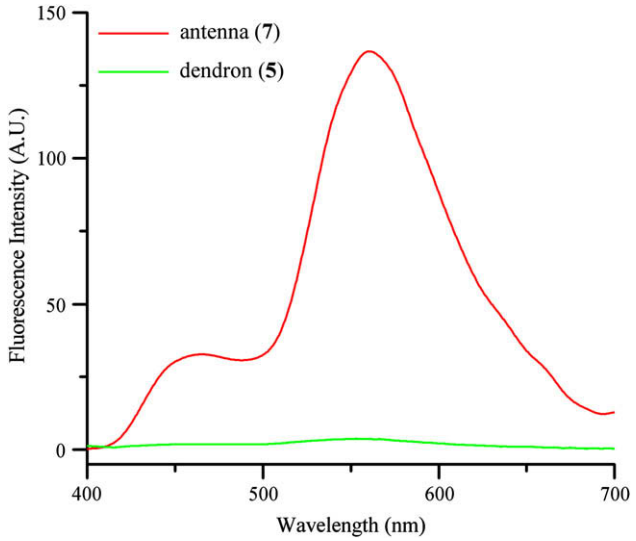


Fig. 4. Fluorescence spectra ($\lambda_{ex} = 360$ nm) of yellow-green emitting 1,8-naphthalimide **5** (green line) and donor–acceptor system **7** (red line) in ethanol at concentration 10^{-5} mol l^{-1}.

At the same time the emission intensity of the periphery (blue emitting 1,8-naphthalimide donor fragments) in the light harvesting system **7** was decreased by 98% with respect to the emission of reference blue emitting 4-allyoxy-*N*-*n*-butyl-1,8-naphthalimide **8** at the same optical density (Fig. 7).

The reason for this phenomenon along with the energy transfer discussed above could be the possible photoinduced electron transfer (PET) from the PAMAM bone to the periphery of antenna **7**. The PAMAM architecture contains a tertiary amine proton receptor able to involve the system in a PET process. In this particular case, it was predicted that the PET process (an electron transfer from the receptor to the excited state of the fluorophore) would quench fluorescence emission of the 1,8-naphthalimide units. The protonation of the tertiary amine in the fluorophore-amine conjugates would increase the oxidation potential of the receptor, and as such, thermodynamically disallow the electron transfer [51,52]. Thus, we expect the fluorescence signal of the light system **7** to be a function of pH.

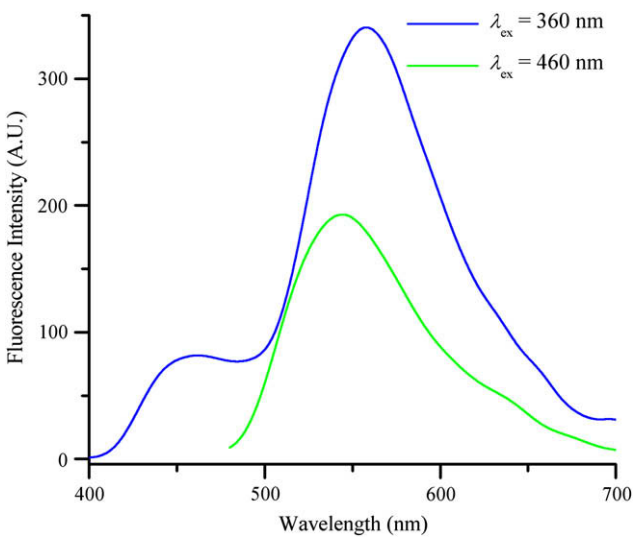


Fig. 5. Emission spectra of antenna **7** in ethanol excited in periphery ($\lambda_{ex} = 360$ nm) and core ($\lambda_{ex} = 460$ nm).

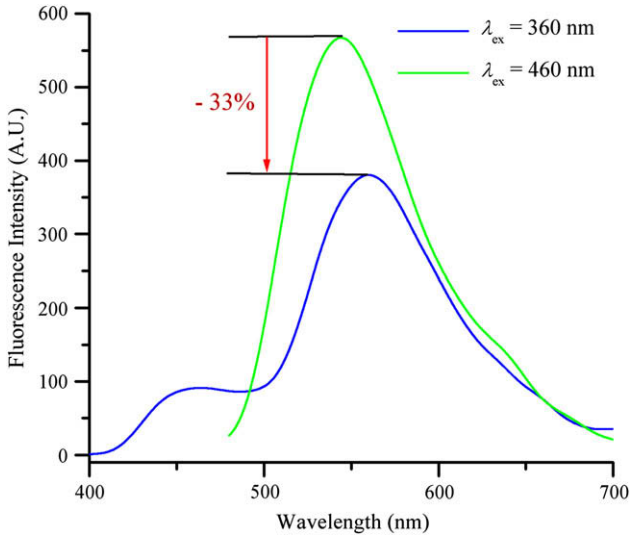


Fig. 6. Emission spectra of antenna **7** excited in periphery ($\lambda_{ex} = 360$ nm) and core ($\lambda_{ex} = 460$ nm), recorded at the same optical density.

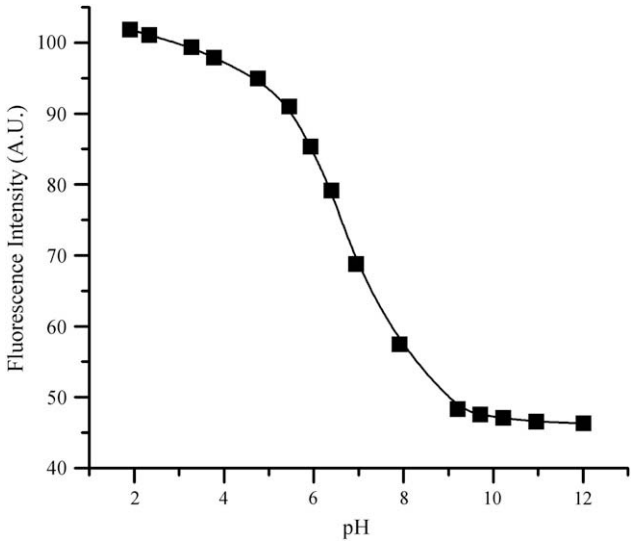


Fig. 8. Effect of pH on the fluorescence intensity ($\lambda_{ex} = 360$ nm) of antenna **7** in water/ethanol (4:1, v/v).

3.3. *Influence of pH on the fluorescence characteristics of the dyes*

As can be seen from the data presented in Table 2, the quantum yield of fluorescence of light harvesting antenna **7** excited at 460 nm is approximately 2-fold higher with respect to that of the same system excited under 360 nm. These results suppose PET sensor properties of the antenna **7** due to electron transfer from the tertiary amine in the dendron bone to the peripheral blue emitting fluorophores that quench the excited state of the latter. This is in good correlation with the relatively lower energy transfer in the PAMAM antenna **7** compared to other types of dendronized light harvesting systems [10–15]. This was the reason to investigate the photophysical behaviour of the 1,8-naphthalimides **3**–**5** and **7** in water/ethanol (4:1, v/v) at different pH values.

In a water/ethanol (4:1, v/v) solution, the reference yellow-green emitting 1,8-naphthalimides **3**–**5** show imperceptible changes in their emission intensity (I_F) as a function of pH ($\lambda_{ex} = 460$ nm). The fluorescence enhancement ($FE = I_{F_{max}}/I_{F_{min}}$) of compounds **3**–**5** was negligible (FE = 1.10–1.17), which is in agreement with the low activity of the 1,8-naphthalimide *N*-bonded "upper" receptor as described by de Silva et al. [51].

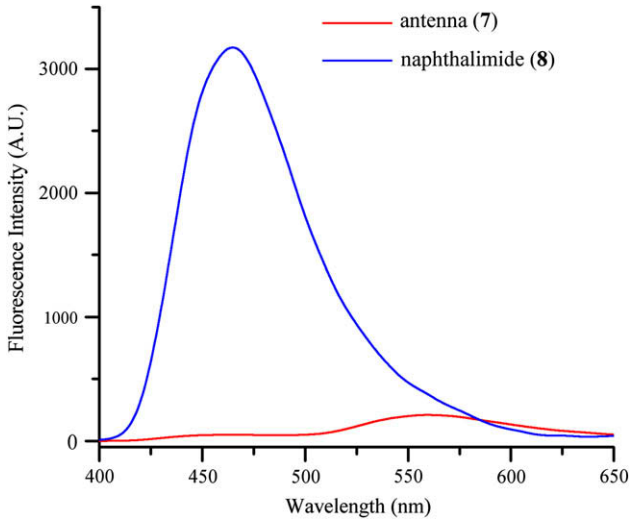


Fig. 7. Fluorescence spectra at $\lambda_{ex} = 360$ nm of blue emitting 1,8-naphthalimide **8** (blue line) and donor–acceptor system **7** (red line) in ethanol, recorded at the same optical density.

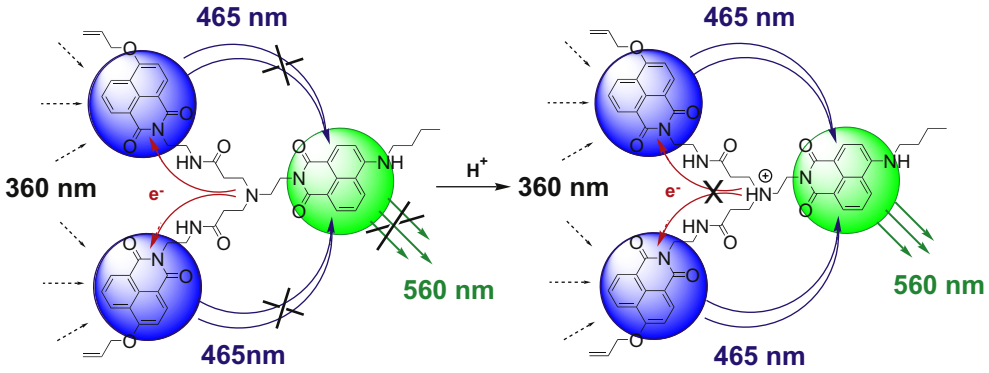
In contrast to the above results, in alkaline solution for light harvesting system **7** a weak core emission between 480 and 700 nm was observed under excitation at 360 nm (within the maximal absorption of the peripheral fluorophore). After careful titration to pH *ca.* 2.0 the emission intensity had enhanced more than two times (FE = 2.2). These changes are of such magnitude that they can be considered as representing two different "states", where the fluorescence emission is "*switched off*" in alkaline solutions and "*switched on*" in acidic solutions (Fig. 8).

Visible changes in the fluorescence intensity of the light harvesting dendron **7** as a function of pH were observed only under excitation within the spectral region of maximal absorption of the peripheral fluorophores ($\lambda_{ex} = 360$ nm). This is an indication that the amine receptor is engaged in PET quenching of the peripheral blue emitting 1,8-naphthalimide excited state, that hinders the energy transfer to the yellow-green core. Upon protonation of this amine the quenching process is substantially removed and the energy transfer is completely restored (Scheme 4).

The fluorescence spectra of antenna **7** in water/ethanol (4:1, v/v) as a function of pH, recorded under excitation at antenna core ($\lambda_{ex} = 460$ nm) and periphery ($\lambda_{ex} = 360$ nm), are depicted in Fig. 9. As can be seen the energy transfer in the light harvesting system **7** at pH = 3.3 increased by 24% in relation to that at pH = 6.9 and in acidic media became 92%.

Obviously, the reduction potential of the 4-allyloxy-1,8-naphthalimide fluorophores (peripheral units) is higher than that of the 4-amino-1,8-naphthalimides (compounds **3**–**5**). That is why the PET process from the tertiary amine in dendron bone ("upper" receptor) is thermodynamically more favorable to the periphery of the system. This observation comes into line with the work of Badugu [53], where the influence of the "upper" receptor on the fluorescence behaviour of 4-alkoxy- and 4-alkylamino-1,8-naphthalimides was studied.

The light harvesting system **7** is thus efficient "off-on" switcher for pH. This switching process was also found to be reversible. Taking the part of the graph in Fig. 8 located between pH 3 and 9, the pK_a value of the light harvesting dendron **7** have been calculated by Eq. (3) [52].



Scheme 4.

$$\log\left[(I_{F_{max}} - I_F)/(I_F - I_{F_{min}})\right] = \mathrm{pH} - \mathrm{p}K_a \quad (3)$$

The calculated pK_a value of 6.45 for the light harvesting system **7** is consistent with the data for compounds of similar nature that were developed before [51,54,55].

4. Conclusions

A novel PAMAM dendron **7**, core and peripherally functionalized with 1,8-naphthalimide fluorophores, was synthesized for the first time based on a divergent approach. The novel compound **7** was designed as light harvesting antenna capable of absorbing light by its periphery and efficiently transferring the energy to a single acceptor dye in the focal point of the system. Absorption and fluorescence characteristics of the donor–acceptor system were determined and discussed. The overlap between the blue emission of the peripheral donor dyes and the absorbance of the acceptor 1,8-naphthalimide dye in the focal point of the system was more than 90%. After excitation within the spectral region of maximal absorption of the peripheral fluorophores ($\lambda_{ex} = 360$ nm) the blue emission intensity of the periphery was decreased by 98%, while the yellow-green core fluorescence was enhanced more than 36 times with respect to the fluorescence intensity of the reference yellow-green emitting 1,8-naphthalimide **5**. This indicates an efficient energy transfer between the periphery and focal point in the donor–acceptor system. However, the determined energy transfer (67%) was not very high due to a photoinduced electron transfer from the dendron bone to the blue emitting periphery. In acidic media, after protonation of the amine receptor in the dendron bone, the oxidation potential of the latter was increased, and as such, thermodynamically disallowed the electron transfer. Consequently the periphery emission was "*switched on*" and the energy transfer to the focal chromophore was increased up to 92%. These results show the high potential of the novel light harvesting system as efficient pH chemosensing material.

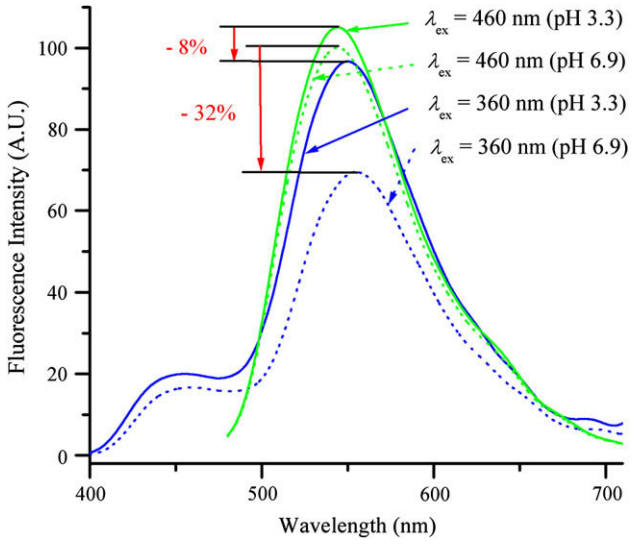


Fig. 9. Emission spectra of antenna **7** in water/ethanol (4:1, v/v) at different pH values, recorded at the same optical density.

Acknowledgements

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