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The design and synthesis of a novel 1,8-naphthalimide PAMAM light-harvesting dendron with fluorescence "off-on" switching core

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ABSTRACT

A novel polyamidoamine dendron core, peripherally functionalized with 1,8-naphthalimide fluorophores, was configured as a light harvesting antenna in which the system surface was labelled with blue emitting 4-allyloxy-1,8-naphthalimide "donor" dyes capable of both absorbing light and efficiently (96%) transferring the energy to a single, yellow-green emitting 4-*N*-methylpiperazinyl-1,8-naphthalimide "acceptor" dye. The 1,8-naphthalimide core was designed on the "fluorophore-spacer-receptor" format and was able to function as a fluorescence photoinduced electron transfer sensor. Two different photoinduced electron transfer effects were observed in the new antenna namely that from the receptor to the core fluorophore and that from the polyamidoamine backbone to the peripheral 1,8-naphthalimides. Althogh the core emission intensity of the system was enhanced $>$ four times by reducing the pH from 10 to 2, the fluorescence enhancement of the system in acidic medium, excited within the periphery (λ_{ex} = 360 nm), was approximately twice that of the core fluorescence enhancement after direct excitation of the focal 1,8-naphthalimide (λ_{ex} = 420 nm), because of more efficient energy transfer. The observed "off-on" switching of the core fluorescence over a wid pH scale indicates that the novel light harvesting antenna would be able to act as a highly efficient fluorescent sensor.

1. Introduction

The design of artificial light harvesting materials is an important goal, considering the need for effective use of renewable energy sources [1,2]. Nature has already evolved an effective pathway for harvesting sunlight and efficiently transferring it into useful chemical energy. The remarkable character of this photosynthetic system is that the energy of any photon absorbed by antenna complexes is transferred at >90% efficiency. Progress in the study of natural photosynthetic systems has provided the impetus to design artificial light harvesting assemblies based on a variety of architectures [3–15]. Dendritic light harvesting assemblies have also attracted much attention because of their unique structures, which are reminiscent of those of natural light-harvesting complexes [16–28]. Collecting light by antenna systems may also be useful for signal amplification in luminescence sensors. Systems capable of sensing guest molecules or ions are currently of great interest [29,30] The photoinduced electron transfer (PET) using the "fluorophore-spacer-receptor" format is the most commonly exploited approach for the design of fluorescent sensors and switchers [31]. Accordingly, the components are selected so that PET from the receptor to the fluorophore quenches the fluorescence of the system; however, in the presence of a guest, which binds to the receptor engaging its lone pair of electrons, PET communication between the receptor and the fluorophore gets cut off and the fluorescence of the system is recovered. In other words, the presence of a guest is signalled by fluorescence enhancement of the system [32].

Because of their strong fluorescence and good photostability, 1,8-naphthalimide derivatives have found application in several areas, such as fluorescent dyes for polymer materials [33,34], laser active media [35,36], fluorescent markers in biology [37], anticancer agents [38] and analgesics [39] in medicine, fluorescence switchers and sensors [40,41], light emitting diodes [42,43], electroluminescent materials [44,45], liquid crystal displays [46,47] and ion probes [48].

Polyamidoamines (PAMAMs) are a novel class of industrial dendrimer with very well-defined chemical structures. They consist of three major architectural components namely a core, branch and terminal (end) groups. The core and/or peripheral modification of the PAMAM dendrimers with fluorophore units could provide new fluorescent dendritic architectures with valuable properties [49–51]. The present authors have recently reported the synthesis and photophysical properties of some novel PAMAM derivatives which were periphery functionalized with 1,8-naphthalimide units [52–54]. The fluorescence properties of these novel compounds were studied as a function of pH and PET from the PAMAM

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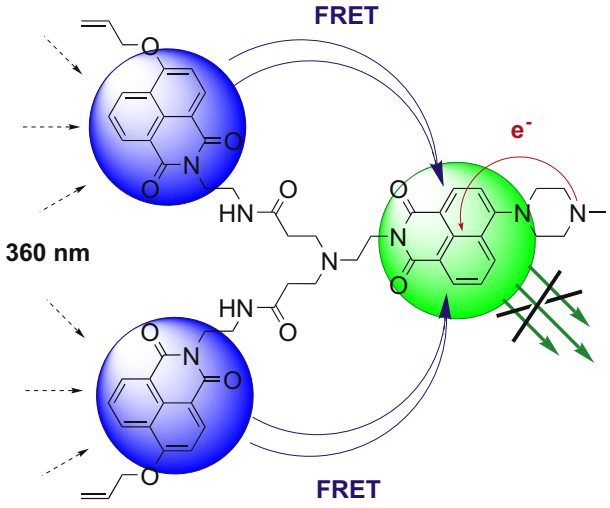
backbone to the 1,8-naphthalimide fluorophores was observed, making them of potential use as chemosensing materials. This paper concerns the design, synthesis and photophysical properties of a novel fluorescent light harvesting antenna based on a core and peripherally 1,8-naphthalimide functionalized PAMAM dendron. The periphery of the novel light harvesting dendron was imbibed with blue emitting 4-allyloxy-1,8-naphthalimide units as a "donor" surface capable of absorbing light and efficiently transferring the energy to a focal 4-(*N*-methylpiperazinyl)-1,8-naphthalimide "acceptor" (Scheme 1). The yellow-green emitting 1,8-naphthalimide core of the system is designed on "fluorophore-spacer-receptor" format to act as a fluorescence PET based sensor.

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, a periphery decorated with blue emitting 4-allyloxy-1,8-naphthalimide units PAMAM dendron **11**, not containing a "focal" (acceptor) 1,8-naphthalimide dye fragment, was involved in the present study as a reference compound (Scheme 1).

2. Experimental

2.1. Materials

The starting 4-bromo-1,8-naphthalic anhydride **1** [55] and 4-bromo-*N*-(2-aminoethyl)-1,8-naphthalimide **2** [54] were prepared according to the reported procedure. *N*-Methylpiperazine, ethylenediamine, allyl alcohol and methyl acrylate (Merck), p.a. grade, were used without purification. All solvents (Fluka, Merck) were pure or of spectroscopy grade.



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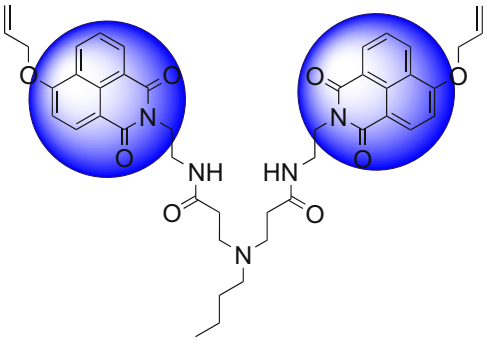

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Scheme 1.

2.2. Methods

FT-IR spectra were recorded on a Varian Scimitar 1000 spectrometer. The ^{1}H NMR spectra were recorded on a Bruker DRX-250 spectrometer, operating at 250.13 MHz, using a dual 5 mm probe head. The chemical shifts (given as δ in ppm) were referenced to tetramethylsilane (TMS) standard. TLC was performed on silica gel, Fluka F60 254, 20 × 20, 0.2mm. 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 (Φ_F = 0.78 in ethanol, λ_{ex} 420 nm) [56] and p-methoxybenzylidenephthalide (Φ_F = 0.14 in ethanol, λ_{ex} 360 nm) [57].

2.3. Synthesis of fluorescent 1,8-naphthalimides

2.3.1. 4-(N-Methylpiperazinyl)-N-(2-aminoethyl)-1,8-naphthalimide(3)

To a solution of *N*-methylpiperazine (1.2 g, 12 mmol) and 4-bromo-*N*-(2-aminoethyl)-1,8-naphthalimide **2** (1.0 g, 3 mmol) 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 4 h. After cooling to room temperature, the reaction mixture was poured into 50 ml of water and the precipitate was collected by filtration, washed with water and dried. Silica gel chromatography (*n*-propanol:ammonium hydroxide = 1:1) afforded 0.48 g (47%) of 4-(*N*-methylpiperazinyl)-*N*-(2-aminoethyl)-1,8-naphthalimide **3** as yellow crystals (m.p. 171–173 °C).

IR (KBr) cm^{-1}: 3242 and 3086 (νNH_2); 2876 and 2808(νCH); 1678 ($\nu^{as}N–\underline{C=O}$); 1630 ($\nu^{s}N–\underline{C=O}$). ^{1}H NMR (DMSO-$d_6$, 250.13 MHz) ppm: 8.43 (m, 2H, naphthalimide H-5 and H-7); 8.15 (d, 1H, J = 8.5 Hz, naphthalimide H-2); 7.77 (dd, 1H, J = 8.3 Hz, J = 7.3 Hz, naphthalimide H-6); 7.30 (d, 1H, J = 8.4 Hz, naphthalimide H-3); 4.11 (m, 2H, $N\underline{CH_2}CH_2NH_2$); 3.77 (br.s, 2H, NH_2); 3.24 (m, 6H, $NCH_2\underline{CH_2}NH_2$ and 2 × piperazine $ArN\underline{CH_2}$); 2.62 (m, 4H, 2 × piperazine $CH_3N\underline{CH_2}$); 2.32 (s, 3H, $N\underline{CH_3}$). Elemental analysis: Calculated for $C_{19}H_{22}N_4O_2$ (MW 338.4) C 67.44, H 6.55, N 16.56%; Found C 67.08, H 6.63, N 16.44%.

2.3.2. Ester-functionalized 1,8-naphthalimide (4)

To a solution of methyl acrylate (1.3 g, 14 mmol) in 5 ml of methanol, a solution of 4-(*N*-methylpiperazinyl)-*N*-(2-aminoethyl)-1,8-naphthalimide **3** (0.48 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 day at room temperature and the excess of methyl acrylate was removed under vacuum, whereupon the ester-functionalized derivative **4** was obtained as yellow oil (0.57 g, 90%).

IR (oil) cm^{-1}: 2920 and 2810 (νCH); 1722 ($\nu\underline{CO}OCH_3$); 1688 ($\nu^{as}N–\underline{C=O}$); 1646 ($\nu^{s}N–\underline{C=O}$). ^{1}H NMR (DMSO-$d_6$, 250.13 MHz) ppm: 8.47 (d, 1H, J = 7.4 Hz, naphthalimide H-5); 8.43 (d, 1H, J = 8.6 Hz, naphthalimide H-7); 8.39 (d, 1H, J = 8.2 Hz, naphthalimide H-2); 7.81 (dd, 1H, J = 8.5 Hz, J = 7.4 Hz, naphthalimide H-6); 7.35 (d, 1H, J = 8.1 Hz, naphthalimide H-3); 4.07 (t, 2H, J = 6.8 Hz, $(CO)_2N\underline{CH_2}$); 3.39 (s, 6H, 2 × $O\underline{CH_3}$); 3.24 (t, 4H, J = 6.4 Hz, 2 × $ArN\underline{CH_2}$-piperazine); 2.74 (t, 4H, J = 6.8 Hz, 2 × $\underline{CH_2}COOCH_3$); 2.65 (m, 6H, 3 × $N\underline{CH_2}$); 2.37 (t, 4H, J = 6.8 Hz, 2 × $CH_3N\underline{CH_2}$-piperazine); 2.31 (s, 3H, $N\underline{CH_3}$). Elemental analysis: Calculated for $C_{27}H_{34}N_4O_6$ (MW 510.6) C 63.51, H 6.71, N 10.97%; Found C 63.79, H 6.80, N 11.07%.

2.3.3. Amidoamine-functionalized 1,8-naphthalimide(5)

To a solution of ethylenediamine (3.6 g, 60 mmol) in 5 ml of methanol, a solution of 1,8-naphthalimide **4** (0.5 g, 1 mmol) in 10 ml of methanol was added dropwise at 5 °C for a period of 30 min. The reaction mixture was stirred for a week at room temperature. Then 80 ml of toluene was added and the methanol was distilled under vacuum along with the part of the toluene. The amino-functionalized dendron **5** was obtained as yellow-brown oil (0.53 g, 95%) after decantation of the excess of ethylenediamine together with the toluene.

IR (oil) cm^{-1}: 3316, 3210 (νNH and $νNH_2$); 2920 and 2854 (νCH); 1682 ($ν^{as}$N–C═O); 1630 (νNH–C═O). ^{1}H NMR (DMSOl-d_6, 250.13 MHz) ppm: 8.44 (m, 2H, naphthalimide H-5 and H-7); 8.38 (d, 1H, J = 8.7 Hz, naphthalimide H-2); 7.85 (br.s, 2H, 2 × NHCO); 7.78 (t, 1H, J = 7.8 Hz, naphthalimide H-6); 7.29 (d, 1H, J = 8.2 Hz, naphthalimide H-3); 4.06 (m, 2H, $(CO)_2NCH_2$); 3.72 (m, 4H, 2 × NH_2); 3.15 (m, 8H, 2 × $NHCH_2CH_2NH_2$ and 2 × ArNCH_2-piperazine); 2.73 (m, 6H, 3 × NCH_2); 2.60 (m, 8H, 2 × $NHCH_2CH_2NH_2$ and 2 × CH_3NCH_2-piperazine); 2.28 (m, 7H, 2 × CH_2CONH and NCH_3). Elemental analysis: Calculated for $C_{29}H_{42}N_8O_4$ (MW 566.7) C 61.46, H 7.47, N 19.77%; Found C 61.77, H 7.39, N 19.62%.

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

To a solution of 4-bromo-1,8-naphthalic anhydride **1** (0.5 g, 1.8 mmol) in 30 ml of boiling methanol, a solution of amino-terminated 1,8-naphthalimide dendron **5** (0.51 g, 0.9 mmol) in 20 ml of methanol was added dropwise under stirring over a period of 2 h. The resulting solution was refluxed for 6 h. After cooling the orange precipitate was filtered off and treated with 50 ml of 5% aqueous sodium hydroxide to give after filtration and drying 0.51 g (52%) of peripherally functionalized with 4-bromo-1,8-naphthalimide units dendron **6**. The solid was suspended in solution of 0.056 g KOH (1 mmol) in 25 ml of allyl alcohol and the reaction mixture was refluxed under stirring for a period of 16 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 0.12 g (25%) of peripherally functionalized with 4-allyloxy-1,8-naphthalimide units dendron **7** as yellow crystals (m.p. 159–162 °C).

IR (KBr) cm^{-1}: 3344 (νNH); 2922 and 2840 (νCH); 1684 ($ν^{as}$N–C═O); 1642 ($ν^{s}$N–C═O). ^{1}H NMR ($CDCl_3$-*d*, 250.13 MHz) ppm: 8.58 (d, 2H, J = 8.7 Hz, 2 × peripheral naphthalimide H-5); 8.44 (m, 2H, focal naphthalimide H-5 and H-7), 8.33 (d, 2H, J = 8.4 Hz, 2 × peripheral naphthalimide H-2); 8.26 (d, 2H, J = 8.3, 2 × peripheral naphthalimide H-7); 8.18 (d, 1H, J = 7.7 Hz, focal naphthalimide H-2); 7.63 (m, 4H, 2 × NHCO and 2 × peripheral naphthalimide H-6); 7.42 (t, 1H, J = 7.9 Hz, focal naphthalimide H-6); 6.97 (d, 1H, J = 8.1 Hz, focal naphthalimide H-3); 6.77 (d, 2H, J = 8.4 Hz, 2 × peripheral naphthalimide H-3); 6.10 (m, 2H, 2 × OCH_2CH═CH_2); 5.53 (dd, 2H, J_{trans} = 16.4 Hz, J = 1.4 Hz, 2 × allyl HCH═); 5.45 (d, 2H, J_{cis} = 10.0 Hz, 2 × allyl HCH═); 4.83 (m, 2H, $(CO)_2NCH_2$); 4.66 (m, 4H, 2 × OCH_2CH═CH_2); 4.22 (m, 4H, 2 × $(CO)_2NCH_2$); 3.57 (m, 4H, 2 × $CONHCH_2$); 3.28 (m, 4H, 2 × CH_2CONH); 2.80 (m, 10H, 3 × NCH_2 and 2 × piperazine ArNCH_2); 2.46 (s, 3H, NCH_3); 2.39 (m, 4H, 2 × piperazine CH_3NCH_2). Elemental analysis: Calculated for $C_{59}H_{58}N_8O_{10}$ (MW 1039.1) C 68.19, H 5.63, N 10.78%; Found C 67.81, H 5.70, N 10.91%.

2.3.5. Synthesis of reference dendron(11)

To a solution of methyl acrylate (3.6 g, 40 mmol) in 20 ml of methanol, a solution of *n*-butylamine (0.29 g, 4 mmol) in 5 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 derivative **8** was obtained as colourless oil (0.96 g, 97%). Further a solution of **8** (0.96 g, 3.9 mmol) in 30 ml of methanol was added dropwise to a solution of ethylenediamine (13.8 g, 230 mmol) in 10 ml of methanol at 5 °C for a period of 30 min. The reaction mixture was stirred for a week at room temperature. Then the bulk of solvent and the excess of ethylenediamine were distilled under vacuum. Finally the traces of ethylenediamine were removed by an azeotropic distillation using a 9:1 toluene/methanol (v/v) solution to give a colourless oil of dendron **9**.

To a solution of 4-bromo-1,8-naphthalic anhydride **1** (0.9 g, 3.23 mmol) in 50 ml of boiling methanol, a solution of dendron **9** (0.48 g, 0.9 mmol) in 25 ml of methanol was added dropwise under stirring over a period of 2 h. The resulting solution was refluxed for 6 h. After cooling the brown precipitate was filtered off and treated with 30 ml of 5% aqueous sodium hydroxide to give after filtration and drying 1.02 g (52%) of peripherally functionalized with 4-bromo-1,8-naphthalimide units dendron **10**. The solid was suspended in solution of 0.07 g KOH (1.25 mmol) in 20 ml of allyl alcohol and the reaction mixture was refluxed under stirring for a period of 10 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 was collected by filtration and dried. Silica gel chromatography (*n*-propanol:ammonium hydroxide = 1:1) afforded 0.20 g (52%) of peripherally functionalized with 4-allyloxy-1,8-naphthalimide units reference dendron **11** as yellow-white crystals (m.p. 89–93 °C).

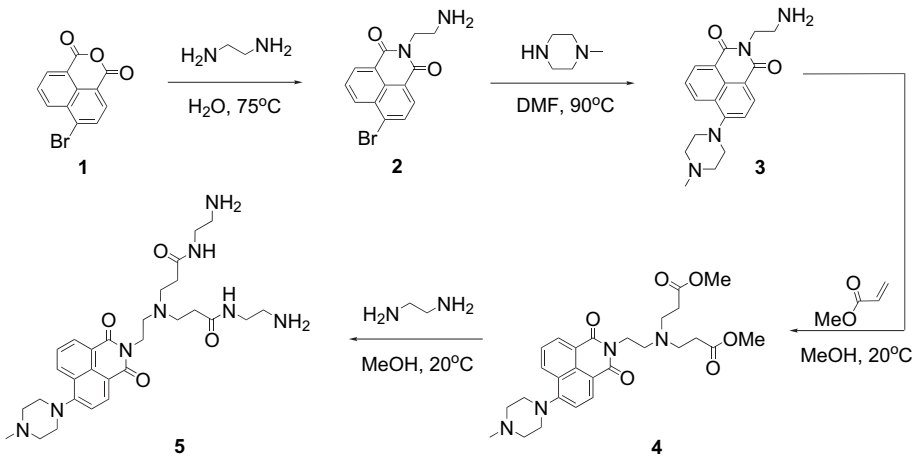
IR (KBr) cm^{-1}: 3208 and 3066 (νNH); 2904 and 2812 (νCH); 1688 ($ν^{as}$N–C═O); 1664 ($ν^{s}$N–C═O); 1632 (νNH–C═O). ^{1}H NMR ($CDCl_3$-*d*, 250.13 MHz) ppm: 8.26 (dd, 1H, J = 7.3 Hz, J = 1 Hz, naphthalimide H-5); 8.20 (dd, 1H, J = 8.4 Hz, J = 1.1 Hz, naphthalimide H-7); 8.18 (d, 1H, J = 7.3 Hz, naphthalimide H-2) 7.9 (t, 2H, CONH); 7.42 (dd, 2H, J = 8.3 Hz, J = 7.3 Hz, naphthalimide H-6); 6.76 (d, 2H, J = 8.4 Hz, naphthalimide H-3); 6.14 (m, 2H, 2 × OCH_2CH═CH_2); 5.54 (d, 2H, J_{trans} = 17.2 Hz, 2 × allyl HCH═); 5.44 (d, 2H, J_{cis} = 10.5 Hz, 2 × allyl HCH═); 4.71 (d, 4H, J = 5.3 Hz, 2 × OCH_2CH═CH_2); 4.19 (t, 4H, J = 5.3 Hz, 2 × $(CO)_2NCH_2$); 3.64 (m, 4H, 2 × $CONHCH_2$); 2.63 (t, 4H, 2 × CH_2CONH); 2.32 (m, 6H, $N(CH_2)_3$); 1.26 (m, 4H, $CH_2CH_2CH_2CH_3$); 0.87 (t, 3H, J = 7.6 Hz, $CH_2CH_2CH_2CH_3$). Elemental analysis: Calculated for $C_{44}H_{47}N_5O_8$ (MW 773.9) C 68.29, H 6.12, N 9.05%; Found C 68.62, H 6.05, N 8.94%.

3. Results and discussion

3.1. Design and synthesis of light harvesting 1,8-naphthalimide PAMAM dendron with PET based chemosensing core

The PAMAM dendron **7**, core and peripherally labelled with 1,8-naphthalimide units, was designed as fluorescent light harvesting antenna that core fluorescence can be switched between "off" and "on" state. Recently we have reported on the synthesis of two PAMAM based light harvesting dendrons, core and peripherally decorated with 1,8-naphthalimide units [53,54]. The high efficiency of the energy transfer in both dendrons clearly showed that the 4-alkoxy- and 4-alkylamino-1,8-naphthalimides are suitable fluorescence donor-acceptor pair for light harvesting systems. With a view to obtain a similar light harvesting antenna, but with "off-on" PET based chemosensing core, we used 4-(*N*-methylpiperazinyl)-1,8-naphthalimide as a "focal" (acceptor) dye. The 4-(*N*-methylpiperazinyl)-1,8-naphthalimides are well known PET chemosensors based on the "fluorophore-spacer-receptor" format, which display highly sensitive fluorescence signalling in the presence of various guests cations [58–60].

The synthesis of amino-terminated 1,8-naphthalimide dendron **5** was performed in four steps following Scheme 2. First, the



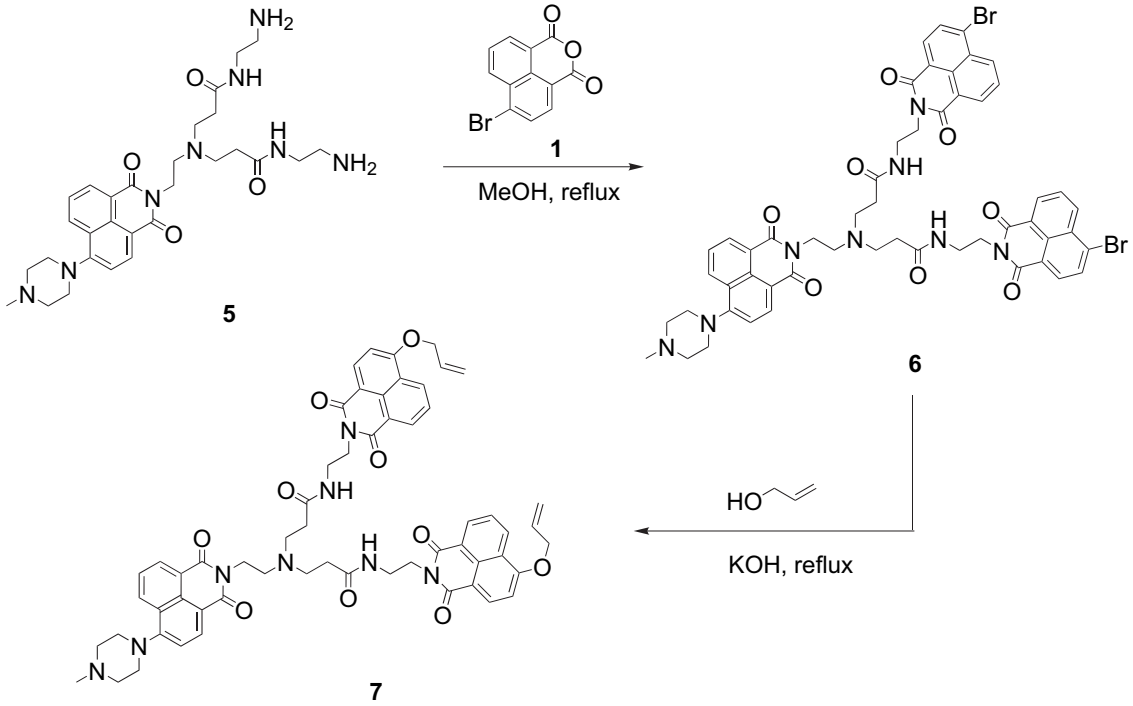
Scheme 2.

amino-terminated 1,8-naphthalimide **2** was synthesized as we described before [54] by reaction of 4-bromo-1,8-naphthalic anhydride **1** with ethylenediamine in water at 75 °C. The intermediate **2** was subsequently converted into the yellow-green emitting dendron core **3** by reaction with *N*-methylpiperazine in DMF at 90 °C for 4 h in the presence of $CuSO_4 \cdot 5H_2O$.

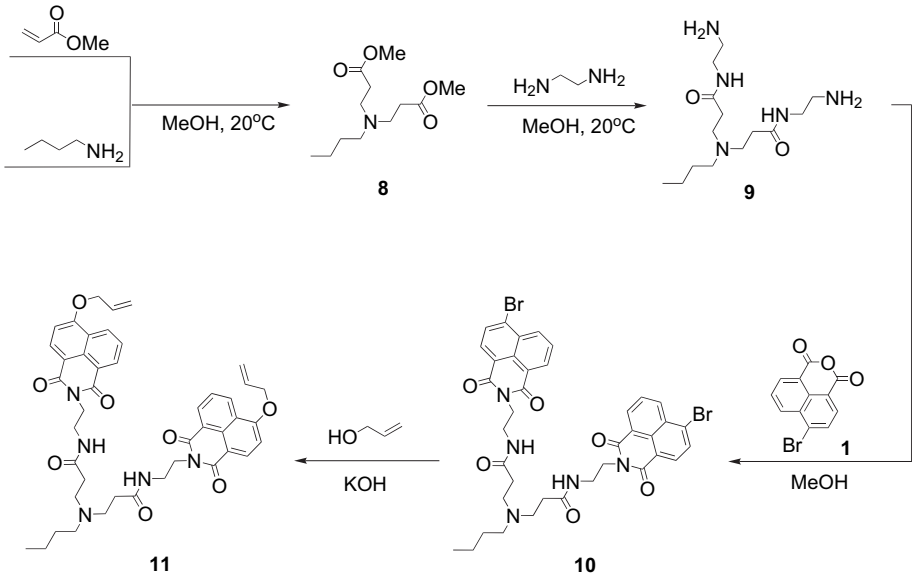
The amino-terminated PAMAM dendron **5** was synthesized via divergent strategy, involving an initial Michael addition of 4-(*N*-methylpiperazinyl)-*N*-(2-aminoethyl)-1,8-naphthalimide **3** to the methyl acrylate followed by exhaustive amidation of the resulting diester **4** with a large excess of ethylenediamine to afford the dendron **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 dendron **6**, peripherally functionalized with 4-bromo-1,8-naphthalimide units, was obtained by reaction of 4-bromo-1,8-naphthalic anhydride **1** with amidoamine-functionalized 1,8-naphthalimide **5** 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 substituted with alkoxy groups under reflux of intermediate **6** in allyl alcohol in the presence of finely ground potassium hydroxide.

The reference blue emitting PAMAM dendron **11**, peripherally functionalized with 4-allyloxy-1,8-naphthalimide units, was obtained by analogy with the synthesis of antenna **7** (Scheme 4). First, PAMAM dendron **9**, containing reactive amine groups in its periphery, was synthesized by an initial Michael addition of *n*-butylamine to the methyl acrylate followed by exhaustive amidation of the resulting diester **8** with ethylenediamine. Dendron **9** was further reacted with 4-bromo-1,8-naphthalic anhydride **1** under reflux in methanol solution to afford an intermediate dendron **10**, peripherally functionalized with 4-bromo-1,8-naphthalimide



Scheme 3.



Scheme 4.

units. Finally, the intermediate dendron **10** was converted into the blue emitting PAMAM dendron **11** under reflux in allyl alcohol in the presence of finely ground potassium hydroxide.

Synthesized compounds were characterized (Table 1) and identified by their melting points, TLC (R_f values), elemental analysis data, UV–VIS, fluorescence, FT-IR and ^{1}H NMR spectroscopy. For instance, in the ^{1}H NMR ($CDCl_3$-*d*, 250.13 MHz) spectrum of antenna **7** a resonance at 6.77 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 (6.97 ppm). Furthermore, the ^{1}H NMR spectrum contained peaks in range of 6.10–4.66 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 derivates are basically related to the polarization of their chromophoric system. Light absorption in this molecule generates a charge transfer interaction between the substituent at C-4 position and the imide carbonyl functions. In general, the derivatives with alkoxy groups are colourless with blue emission, while the amino substituted 1,8-naphthalimides are yellow coloured and emit in the yellow-green region [53,54]. The absorption data of the examined compounds are listed in Table 1. Compounds **3-5** showed typical for the 4-piperazinyl-1,8-naphthalimides absorption band with well pronounced maximum at 404–408 nm in ethanol, while the absorption spectrum of periphery functionalized with 4-allyloxy-1,8-naphthalimide units dendron **11** contains an usual for the 4-alkoxy-1,8-naphthalimides maximum at 368 mn. The absorption spectra of light harvesting dendron **7** as expected corresponded to the sum of the absorption spectra of a core dendronized 1,8-naphthalimide **5** and a periphery functionalized 1,8-naphthalimide dendron **11** (Fig. 1). This indicates that the dendron bone in antenna **7** acts just as a scaffold holding peripheral and core chromophores together and there is no electronic communication between the donor and acceptor units through the dendritic bone. 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}), indicating that this is a charge transfer (CT) band, due to (π,π^*) character of the $S_0 \rightarrow S_1$ transition.

Table 1
Yields, melting points, retention factors and absorption data for 1,8-naphthalimides **3–5**, antenna **7** and dendron **11** in ethanol solution.

Compound	Yield (%)	Mp (°C)	R_f	λ_A (nm)	ε (l mol^{-1} cm^{-1})
3	47	171–173	0.78[a]	408	11 641
4	90	oil	0.28[b]	406	10 955
5	95	oil	0.30[a]	402	10 244
7	25	159–162	0.74[c]	368	25 462
				404	10 025
11	52	89–93	0.44[d]	368	25 139

[a] TLC in a solvent system *n*-propanol:25% ammonium hydroxide = (1:1).
[b] TLC in a solvent system *n*-hexane:acetone = (1:1).
[c] TLC in a solvent system *n*-propanol:25% ammonium hydroxide = (3:1).
[d] TLC in a solvent system chloroform:methanol = (1:9).

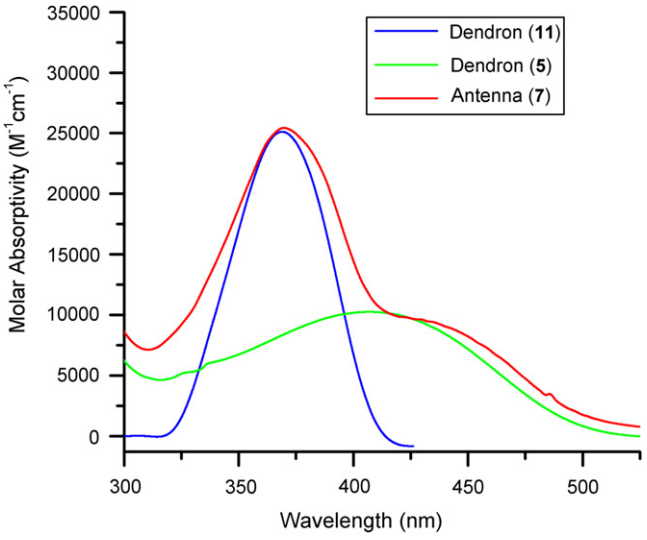


Fig. 1. Absorption spectra of antenna **7**, core functional 1,8-naphthalimide dendron **5** and periphery functional 1,8-naphthalimide dendron **11** in ethanol solution.

Table 2
Fluorescence characteristics of 1,8-naphthalimides **3–5**, antenna **7** and dendron **11** in ethanol solution.

Compound	λ_F (nm)	ν_A–ν_F (cm^{-1})	Φ_F
3	536	5852	0.04[a]
4	538	6044	0.03[a]
5	540	6357	0.03[a]
7	440	4373	0.03[a]
	543	6336	
11	445	4702	0.38[b]

[a] Referred to Coumarin 6 [56].
[b] Referred to p-methoxybenzylidenephthalide [57].

The fluorescence characteristics of the 1,8-haphthalimides **3-5**, dendron **11** and light harvesting antenna **7** such as fluorescence (λ_F) maxima, Stokes shift (ν_A–ν_F) and quantum yield of fluorescence (Φ_F) were measured in ethanol and presented in Table 2.

In ethanol solution the periphery functionalized with 1,8-naphthalimide units dendron **11** displays blue fluorescence, while 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 spectrum of the light harvesting antenna **7** in ethanol solution, obtained after excitation within the spectral region of maximal absorption of the peripheral fluorophore (λ_{ex} = 360 nm), showed two emission bands, corresponding to the emission bands of the donor and acceptor 1,8-naphthalimide fragments. As a result of the energy transfer, the blue emission intensity of the periphery in the light harvesting system **7** was strongly decreased in comparison with the emission intensity of the reference dendron **11** (Fig. 2).

The efficiency of the energy transfer (E) in light harvesting dendron **7** was calculated equal to 96% using Eq. (1) [50], where F_D is the normalized fluorescence intensity of the donor without acceptor (model compound **11**) and F_{DA} is the normalized fluorescence intensity of the donor chromophore in the presence of acceptor (light harvesting dendron **7**).

$$E = 1 - F_{DA}/F_D \quad (1)$$

The Stoke's shift (ν_A–ν_F) is important parameter for the fluorescent compounds that indicates the differences in the properties and structure of the fluorophores between the ground state S_0 and the first excited state S_1. The Stoke's shift values (cm^{-1}) were calculated by Eq. (2).

$$(\nu_A - \nu_F) = \left(\frac{1}{\lambda_A} - \frac{1}{\lambda_F}\right) \times 10^7 \quad (2)$$

The Stoke's shift values of the compounds under study between 4373 cm^{-1} and 6357 cm^{-1} correspond to the results for other

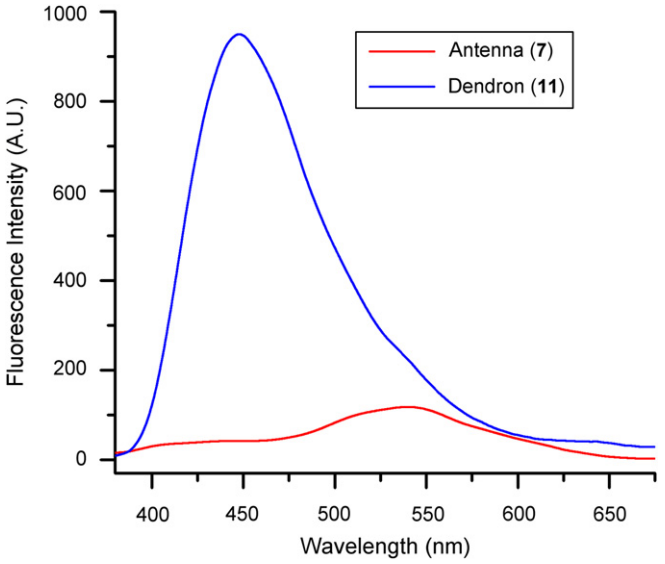


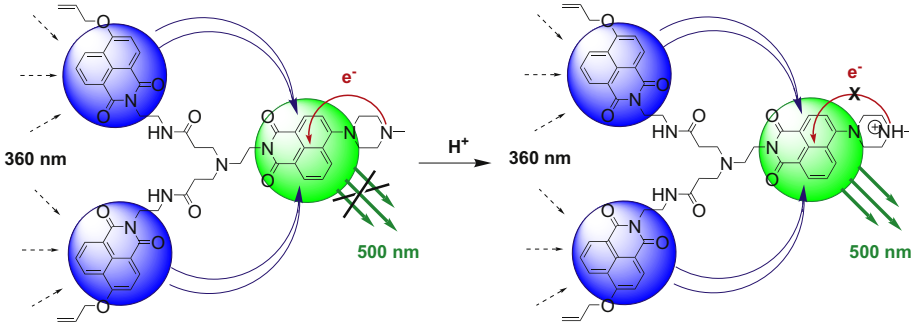
Fig. 2. Fluorescence spectra of antenna **7** and periphery functionalized dendron **11** in ethanol solution (λ_{ex} = 360 nm), recorded at the same optical density.

1,8-naphthalimide derivatives [53,60] 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 or p-methoxybenzylidenephthalide as a standard according to Eq. (3), where A_{ref}, S_{ref}, n_{ref} and A_{sample}, S_{sample}, n_{sample} represent the absorbance at the exited wavelength, the integrated emission band area and the solvent refractive index of the standard and the sample, respectively.

$$\Phi_F = \Phi_{ref}\left(\frac{S_{sample}}{S_{ref}}\right)\left(\frac{A_{ref}}{A_{sample}}\right)\left(\frac{n^2_{sample}}{n^2_{ref}}\right) \quad (3)$$

As can be seen from the data presented in Table 2, the quantum yield of fluorescence of 1,8-naphthalimides **3–5** and light harvesting antenna **7**, possessing *N*-methylpiperazine unit at C-4 position, are extremely low. This phenomenon might be caused by the possible photoinduced electron transfer from the *N*-methylpiperazine amine donor (receptor) to the 4-amino-1,8-naphthalimide fluorophore through the saturated piperazinyl ring. Thus the fluorescence of the 4-amino-1,8-naphthalimide fluorophore is quenched (Scheme 5). Furthermore only the receptor that is directly attached to the 4-amino moiety is capable of quenching the fluorophores excited state [31]. The protonation of the tertiary



Scheme 5.

amine in *N*-methylpiperazine would increase the oxidation potential of the receptor, and as such, thermodynamically disallow the electron transfer and the emission would be "switched on" [60]. Thus, we expect the fluorescence signal of the light system **7** to be a function of pH.

3.3. Influence of pH on the fluorescence characteristics of antenna 7

The above results suppose PET pH sensor activity of light harvesting dendron **7**. This was the reason to investigate the photophysical behaviour of antenna **7** in water/ethanol (4:1, v/v) solution at different pH values. In order to receive a more complete comparative picture for the influence of the PAMAM bone nitrogen donor (amine receptor) to pH sensing properties of the antenna, blue emitting dendron **11** was involved in the present study.

After careful titration from pH *ca.* 10 to pH *ca.* 2 the core emission intensity of antenna **7**, excited within the spectral region of maximal absorption of the focal 1,8-naphthalimide ($\lambda_{ex} = 420$ nm), had enhanced more than four times (FE = 4.41) (Fig. 3). These changes are of such magnitude that they can be considered as representing two different "states", where the fluorescence emission of the focal 1,8-naphthalimide in antenna **7** is "switched off" in alkaline and "switched on" in acidic medium.

The emission intensity of the core, excited by energy transfer from peripheral units ($\lambda_{ex} = 360$ nm) is approximately two times higher than that of the core emission intensity, excited within the maximal absorption of the focal fluorophore ($\lambda_{ex} = 420$ nm) at the same pH value (Fig. 4). This fact is due to the greater ability of periphery to capturing photons form environment in comparison to the single core, which is very well correlated with the difference in extinction coefficients of the peripheral and core fluorophores of antenna 7 (Fig. 1, Table 1).

On the other hand, as can be seen from Fig. 4, the core fluorescence enhancement of antenna **7**, excited within periphery ($\lambda_{ex} = 360$ nm) in acid media, is FE = 5.22 which is 1.18 times higher than that of the core fluorescence enhancement of the antenna, excited within focal 1,8-naphthalimide ($\lambda_{ex} = 420$ nm). Such behaviour of antenna **7** can be explained, as we reported before [54], with a possible PET effect from PAMAM tertiary amine to the peripheral 1,8-naphthalimides that affect the energy transfer efficiency. This was the reason to investigate the fluorescent properties

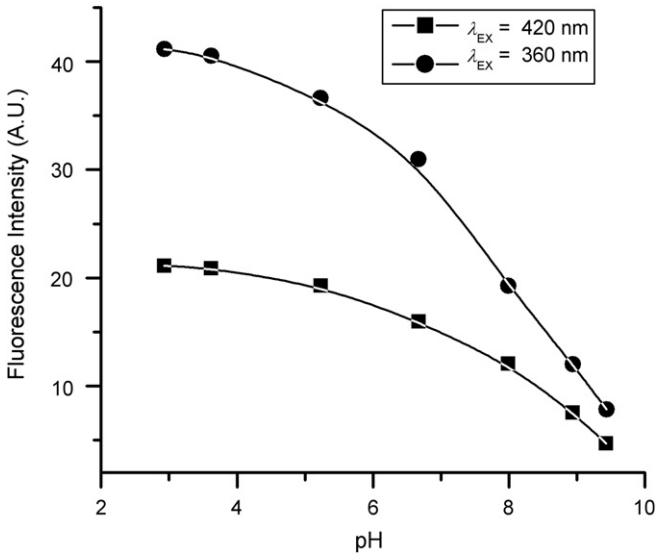


Fig. 4. Effect of pH on the core fluorescence intensity of antenna **7** in water/ethanol (4:1, v/v) excited at 360 nm and 420 nm.

of blue emitting dendron **11** in water/ethanol (4:1, v/v) solution as a function of pH. After protonation of tertiary amine in the PAMAM bone emission intensity of dendron **11** had enhanced about 3 times (FE = 2.70, Fig. 5).

The above experiment clearly showed that the higher core fluorescence enhancement of novel light harvesting dendron **7** in acid media, excited at 360 nm in respect to the excitation at 420 nm is due to disallowing the both simultaneous PET effects – one from *N*-methylpiperazine to the core fluorophore and other from PAMAM bone to the peripheral 1,8-naphthalimides.

Taking the part of the graphs plotted in Figs. 4 and 5, the pK_a values of antenna **7** and dendron **11** were calculated by Eq. (4) [61]. The calculated pK_a values were 7.40 for antenna **7** and 7.27 for blue emitting dendron **11.**

$$\log[(I_{Fmax} - I_F)/(I_F - I_{Fmin})] = pH - pK_a \quad (4)$$

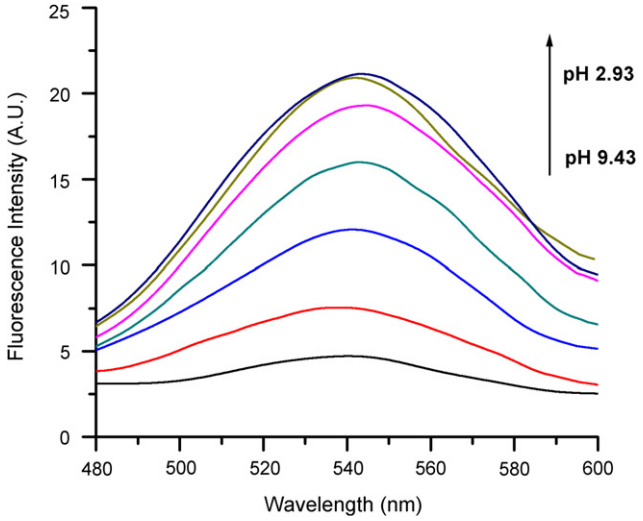


Fig. 3. Effect of pH on the core fluorescence intensity of antenna **7** in water/ethanol (4:1, v/v), after directly excitation within focal 1,8-naphthalimide ($\lambda_{ex} = 420$ nm).

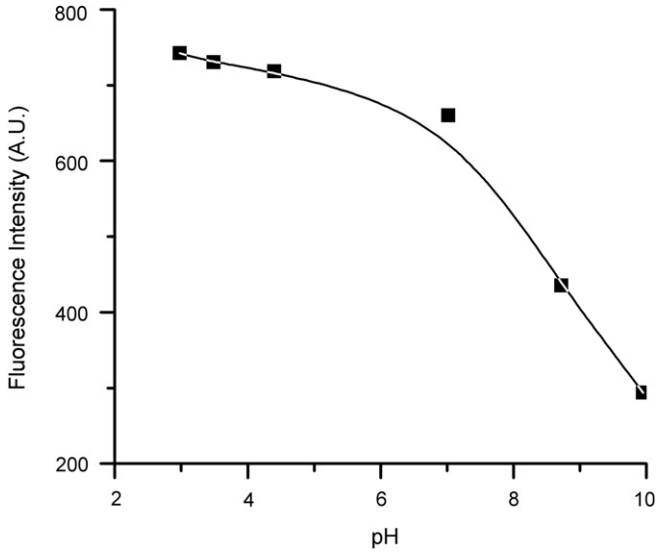


Fig. 5. Effect of pH on the fluorescence intensity of blue emitting dendron **11** in water/ethanol (4:1, v/v).

4. Conclusions

A novel amidoamine 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 a 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 efficiency of energy transfer was calculated to be 96%. This indicates that the selected 1,8-naphthalimide units are suitable donor–acceptor pair for constructing light harvesting materials. Also the 1,8-naphthalimide core of the system was designed on the "fluorophore-spacer-receptor" format, able to act as a fluorescence PET based pH sensor. Core emission intensity of the novel antenna had enhanced more than four times in the pH range *ca.* 2–10. At the same time the core fluorescence enhancement in antenna **7**, excited within the periphery ($\lambda_{ex} = 360$ nm) was higher than the fluorescence enhancement, obtained under directly excitation of focal 1.8-naphthalimide ($\lambda_{ex} = 420$ nm). This is due to the more efficient energy transfer after disallowing both simultaneous PET effects in acidic medium – one from *N*-methylpiperazine to the core fluorophore and other from PAMAM bone to the peripheral 1,8-naphthalimides. The calculated pK_a value of 7.40 indicates that the novel light harvesting dendron **7** would be well suited to monitor changes in the physiological pH range.

Acknowledgements

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