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Design, Synthesis and pH Sensing Properties of Novel PAMAM Light-Harvesting Dendrons Based on Rhodamine 6G and 1,8-naphthalimide

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Abstract Herein we report on the design, divergent synthesis and photophysical behavior of novel PAMAM light-harvesting dendrons from first and second generation. The surface of novel compounds is labeled with 4-alkylamino-1,8-naphthalimide yellow-green emitting "donor" fluorophores capable of absorbing light and efficiently transferring the energy to a single rhodamine "acceptor" dye. Due to the pH dependent rhodamine absorption the novel systems show "off-on" switching energy transfer mechanism from alkaline to acid media. The results obtained illustrate the high potential of the synthesized wavelength-shifting fluorophores as efficient pH chemosensing materials.

Abbreviation

PAMAM	Polyamidoamine
FRET	Fluorescence Resonance Energy Transfer
PET	Photoinduced Electron Transfer
ICT	Internal Charge Transfer
ET	Energy Transfer
FE	Fluorescence Enhancement

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Introduction

Fluorescent sensors are currently of great interest due to the increasing need of fast and reliable sensing of chemical species in many areas of human activity. With their intense "naked eye detectable" fluorescent signal and high sensitivity, they allow immediate detection of protons [1–3], anions [4–6] and cations [7–9] in vivo or in the environment [10, 11], as well as detection of potentially dangerous substances like alkylation agents [12], organophosphorous compounds [13], chemical warfare [14], etc. Different design strategies are being employed in the development of fluorescent sensors and variety of sensor systems which differ in their operation principle, for instance PET (photoinduced electron transfer) based sensors [15, 16], CT (charge transfer) sensor [17, 18], ET (energy transfer) sensors [19, 20], ring-opening sensors [21, 22].

The most reported fluorescent sensors display an increase or decrease in the emission intensity upon binding to species of interest. As the change in fluorescence intensity is the only detection signal, factors such as instrumental efficiency, environmental conditions, and the probe concentration can be interfered with the signal output. To eliminate those effects, a ratiometric fluorescent measurement is desirable. This technique uses the ratio of the fluorescent intensities at two different wavelengths, and provides a built-in correction for environmental effects, and stability under illumination, allowing precise and quantitative analysis and imaging even in complicated systems [23].

Fluorescence resonance energy transfer (FRET) is a distance-dependent interaction between the electronic excited states of two different dye molecules in which excitation

is transferred from a donor molecule to an acceptor molecule without emission of a photon [24, 25]. It would be possible to fabricate a ratiometric probe based on the FRET mechanism if a molecule could generate a suitable fluorescent energy acceptor by the interaction with target analyte. In addition, because the pseudo-Stokes shifts of FRET based probes are larger than the Stokes shifts of either the donor or acceptor dyes, thus, the possible self-quenching as well as fluorescence detection errors due to backscattering effects from the excitation source will be efficiently avoided [23].

Among the different fluorescent probes, we were interested in developing new wavelength-shifting bichromophores with fluorescence sensing properties, based on Rhodamine 6G and 1,8-naphthalimide. Because of their excellent fluorescence properties and good photostability, 1,8-naphthalimide dyes were used extensively in a number of areas, including chemosensing materials [26–29]. On the basis of the spirolactam (non-fluorescent) to ring-open amide (fluorescent) equilibrium of rhodamine, series of rhodamine-based dyes with excellent "off-on" switching of fluorescence upon encountering the correct target have been synthesized [30–32].

Recently, our group has synthesized FRET based wavelength-shifting bichromophoric systems using a 1,8-naphthalimide donor fluorophore and a Rhodamine 6G acceptor dye [33]. The results obtained showed the high potential of the synthesized wavelength-shifting chromophores as efficient pH chemosensing materials. However these systems exhibit lower ability to capturing photons with donor units in comparison with the acceptor Rhodamine 6G due to the lower extinction coefficient of the 1,8-naphthalimide donor. This fact encouraged us towards the design and synthesis of light-harvesting systems containing more 1,8-naphthalimide donor fluorophores around a single Rhodamine 6G unit.

The most attractive light-harvesting systems are the dendritic assemblies because of their unique structures, reminiscent of the architecture of natural light-harvesting complexes [34–39]. 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 [40]. 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 [41–44].

In this paper, we report on the design, synthesis and pH sensing properties of novel PAMAM light-harvesting dendrons 9 and 11 (Scheme 1).

Experimental

Materials

The starting 4-nitro-1,8-naphthalic anhydride 7 was prepared according to the reported procedure [45]. Commercially available Rhodamine 6G 1, ethylenediamine, allyl amine and methylacrylate (Aldrich, Merck) were used without purification. All solvents (Fluka, Merck) were pure or of spectroscopy grade.
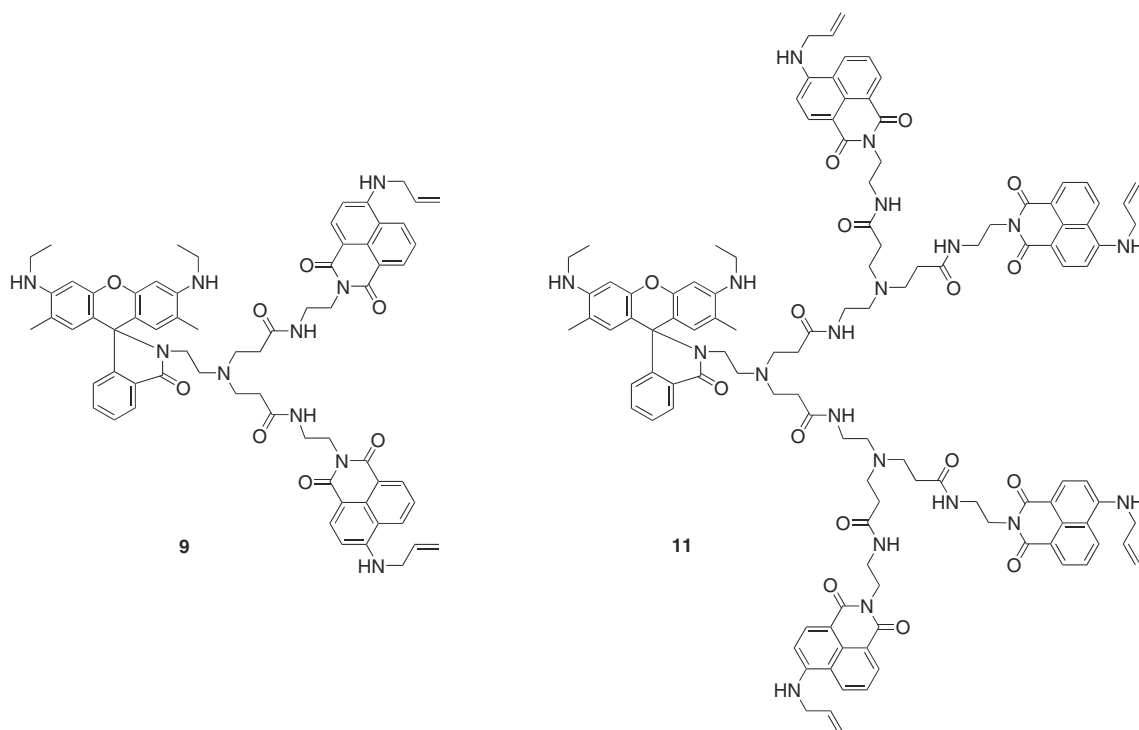
Methods

FT-IR spectra were recorded on a Varian Scimitar 1000 spectrometer. The ^{1}H 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 Hewlett Packard 8452A. The fluorescence spectra were taken on a Scinco FS-2 spectrofluorimeter. The fluorescence quantum yields (Φ_F) were measured relatively to Rhodamine 6G ($\Phi_F = 0.95$ in ethanol [46]) or Coumarin 6 ($\Phi_F = 0.78$ in ethanol [47]) as standards. All the experiments were performed at room temperature (25.0 °C). A 1×1 cm quartz cuvette was used for all spectroscopic analysis. To adjust the pH, very small volumes of hydrochloric acid and sodium hydroxide were used.

Synthesis of Amino-Functional Rhodamine 6G Core (2)

To a solution of Rhodamine 6G 1 (2.3 g, 4.6 mmol) in 90 ml of absolute ethanol, 1.8 ml of ethylenediamine (28 mmol) was added dropwise at room temperature. The resulting solution was stirred at reflux for 5 h. After cooling to room temperature the solid precipitated was filtered off, washed with water and dried to give 1.9 g (88 %) of 2 as pale pink crystals (m.p.>250 °C, R_f=0.45 in a solvent system chloroform / ethylacetate / ethanol=1:1:1).

IR (KBr) cm^{-1}: 3220 (νNH and νNH$_2$); 2942, 2848 (νCH); 1678 (νC=O); 1634, 1528 and 1484 (νAr=CH). ^{1}H NMR (CDCl$_3$-d, 250.13 MHz) ppm: 7.96-7.90 (m, 1H, 9-Ph H-3); 7.52-7.43 (m, 2H, 9-Ph H-4 and 9-Ph H-5); 7.09-7.02 (m, 1H, 9-Ph H-6); 6.34 (s, 2H, Rhodamine H-4 and H-5); 6.22 (s, 2H, Rhodamine H-1 and H-8); 3.51 (br.s, 2H, 2× Ar$\underline{NH}$); 3.27-3.18 (m, 6H, 2×$\underline{CH_2}$CH$_3$ and $\underline{CH_2}$NCO); 2.35 (t, 2H, J=6.8 Hz, $\underline{CH_2}$NH$_2$); 1.90 (s, 6H, 2×Ar$\underline{CH_3}$); 1.38-1.26 (m, 8H, 2×CH$_2$$\underline{CH_3}$ and NH$_2$). Elemental analysis: Calculated for C$_{28}$H$_{32}$N$_4$O$_2$ (MW 456.58) C 73.66, H 7.06, N 12.27 %; Found C 74.19, H 7.08, N 12.36 %.

Scheme 1 Light-harvesting dendrons **9** and **11**

General Preparation Procedure for Ester-Functionalized
Rhodamines 6G (3) and (5)

A suspension of amino-functional Rhodamine 6G core **2** or
amino-terminated Dendron **4** in methanol was added
dropwaise over a period of 20-30 min to a solution of
methylacrylate (10 equiv. per reactive amine group) in
cooled to 0 °C methanol. The reaction mixture was allowed
to warm slowly to room temperature and then stirred for
3 days. The final product was obtained after evaporation of
methylacrylate and methanol under vacuum.

Ester-Functionalized Rhodamine 6G (3) General procedure
described above was used. To a solution of methylacrylate
(3.6 ml, 40 mmol) in 4 ml of methanol, a suspension of **2**
(1.82 g, 4 mmol) in 40 ml of methanol was added. The final
compound was obtained as white crystals (yield - 2.46 g
(98 %), m.p. 134-136 °C, R_f=0.66 in a solvent system
toluene/ethanol=2:1).

   IR (KBr) cm^{-1}: 3324 (νNH); 2942, 2896 (νCH);
1728(νCOOMe); 1670 (νC=O); 1622, 1518 and 1450
(νArCH). ^{1}H NMR (CDCl$_3$-*d*, 250.13 MHz) ppm: 7.94-
787 (m, 1H, 9-Ph H-3); 7.48-739 (m, 2H, 9-Ph H-4 and 9-
Ph H-5); 7.08-7.01 (m, 1H, 9-Ph H-6); 6.35 (s, 2H, Rhoda-
mine H-4 and H-5); 6.20 (s, 2H, Rhodamine H-1 and H-8);
3.59 (s, 6H, 2×O$\underline{CH_3}$); 3.48 (br.s, 2H, , 2×Ar$\underline{NH}$); 3.21 (q,
4H, *J*= 7.1 Hz, 2×ArNH$\underline{CH_2}$); 2.58 (t, 4H, *J*=7.2 Hz,
2×$\underline{CH_2}$COOCH$_3$); 2.22 (t, 2H, *J*=7.2 Hz, $\underline{CH_2}$NCOAr);

2.25-2.15 (m, 6H, N($\underline{CH_2}$)$_3$); 1.89 (s, 6H, 2×Ar$\underline{CH_3}$); 1.32
(t, 6H, *J*=7.1 Hz, 2×CH$_2$$\underline{CH_3}$). Elemental analysis: Calcu-
lated for C$_{36}$H$_{44}$N$_4$O$_6$ (MW 628.76) C 68.77, H 7.05, N
8.91 %; Found C 68.96, H 6.99, N 8.96 %.

Ester-Functionalized Rhodamine 6G (5) General procedure
described above was used. To a solution of methylacrylate
(5 ml, 58 mmol) in 4 ml of methanol, a suspension of **4**
(1.98 g, 2.9 mmol) in 20 ml of methanol was added. The
final compound was obtained as yellow-brown oil (yield -
2.94 g (99 %), R_f=0.70 in methanol).

   IR (oil) cm^{-1}: 3328 (νNH); 2938 (νCH); 1724
(νCOOMe); 1670 (νC=O); 1622, 1518 and 1450
(νAr=CH). ^{1}H NMR (CDCl$_3$-*d*, 250.13 MHz) ppm:
7.91-7.85 (m, 1H, 9-Ph H-3); 7.48-7.40 (m, 2H, 9-Ph
H-4 and 9-Ph H-5); 7.10 (t, 2H, *J*=5.5, 2×$\underline{NH}$CO);
7.06-7.02 (m, 1H, 9-Ph H-6); 6.35 (s, 2H, Rhodamine
H-4 and H-5); 6.18 (s, 2H, Rhodamine H-1 and H-8);
3.64 (s, 12H, 4×O$\underline{CH_3}$); 3.23-3.18 (m, 6H, 2×
ArNH$\underline{CH_2}$ and 2×Ar$\underline{NH}$); 3.06-3.01 (m, 4H, 2×
CONH$\underline{CH_2}$CH$_2$NH$_2$); 2.75 (t, 8H, *J*=6.9 Hz,
4×$\underline{CH_2}$COOCH$_3$); 2.58 (t, 4H, *J*=6.1 Hz, 2×
CH$_2$$\underline{CH_2}$CONH); 2.52-2.38 (m, 18H, 3×N($\underline{CH_2}$)$_3$);
2.16 (t, 2H, *J*=6.7 Hz, $\underline{CH_2}$NCOAr); 1.89 (s, 6H, 2×
Ar$\underline{CH_3}$); 1.32 (t, 6H, *J*=7.2 Hz, 2×CH$_2$$\underline{CH_3}$). Elemental
analysis: Calculated for C$_{54}$H$_{76}$N$_8$O$_{12}$ (MW 1029.23) C
63.02, H 7.44, N 10.89 %; Found C 63.39, H 7.32, N
10.96 %.

General Preparation Procedure for Amino-Functional Rhodamine 6G Dendrons (4) and (6)

A suspension of ester-terminated compound (**3** or **5**) in methanol was added dropwise to a cooled (0 °C) solution of ethylenediamine (30 equiv. per reactive ester group) in methanol over a period of 20-30 min. The reaction mixture was stirred for 7 days at room temperature. Then the solvent and the ethylenediamine excess were distilled under vacuum. Final traces of excess ethylenediamine were removed azeotropically using a 9:1 toluene/methanol (v/v) solution.

Rhodamine 6G dendron (4) General procedure described above was used. To a solution of ethylenediamine (12.5 ml, 18 mmol) in 10 ml of methanol, a suspension of ester-functionalized rhodamine **3** (1.88 g, 3 mmol) in 15 ml of methanol was added. The final compound was obtained as white crystals (yield - 2 g (99 %), m.p. 88-90 °C).

IR (KBr) cm^{-1}: 3314 and 3204 (νNH and νNH$_2$); 2922, 2878 (νCH); 1644 (νC=O); 1636 and 1490 (νAr=CH). ^{1}H NMR (CDCl$_3$-d, 250.13 MHz) ppm: 7.91-7.85 (m, 1H, 9-Ph H-3); 7.49-7.41 (m, 2H, 9-Ph H-4 and 9-Ph H-5); 7.34 (t, 2H, J=5.7, 2×_NH_CO); 7.07-7.03 (m, 1H, 9-Ph H-6); 6.36 (s, 2H, Rhodamine H-4 and H-5); 6.16 (s, 2H, Rhodamine H-1 and H-8); 3.68-3.62 (m, 4H, 2×CONH_CH_2CH$_2$NH$_2$); 3.55 (br.s, 2H, 2×Ar_NH_); 3.24-3.18 (m, 8H, 2×_NH_2 and 2× ArNH_CH_2); 3.15-3.09 (m, 2H, _CH_2NCOAr); 2.76-2.70 (m, 4H, 2×_CH_2NH$_2$); 2.55 (t, 4H, J=6.1 Hz, 2× CH$_2$_CH_2CONH); 2.20-2.10 (m, 6H, N(_CH_2)$_3$); 1.90 (s, 6H, 2×Ar_CH_3); 0.93 (t, 6H, J=7.2 Hz, 2×CH$_2$_CH_3). Elemental analysis: Calculated for C$_{38}$H$_{52}$N$_8$O$_4$ (MW 684.87) C 66.64, H 7.65, N 16.36 %; Found C 66.96, H 7.49, N 16.58 %.

Rhodamine 6G dendron (6) General procedure described above was used. To a solution of ethylenediamine (16.5 ml, 240 mmol) in 15 ml of methanol, a suspension of ester-functionalized rhodamine **5** (2 g, 2 mmol) in 20 ml of methanol was added. The final compound was obtained as yellow-brown oil in yield of 2.26 g (99 %).

IR (oil) cm^{-1}: 3300 and 3200 (νNH and νNH$_2$); 2932, 2884 (νCH); 1648 (νC=O); 1638 and 1510 (νAr=CH). ^{1}H NMR (DMSO-d_6, 250.13 MHz) ppm: 7.87 (br.s, 4H, 4× _NH_CO); 7.80-7.77 (m, 1H, 9-Ph H-3); 7.70 (br.s, 2H, 2× _NH_CO); 7.54-7.48 (m, 2H, 9-Ph H-4 and 9-Ph H-5); 7.00 (m, 1H, 9-Ph H-6); 6.28 (s, 2H, Rhodamine H-4 and H-5); 6.06 (s, 2H, Rhodamine H-1 and H-8); 5.05 (br.s, 2H, 2× Ar_NH_); 3.16 (br.s, 10H, 4× _NH_2 and ArCON_CH_2); 3.10-3.01 (m, 16H, 6×CONH_CH_2CH$_2$NH$_2$ and 2×ArNH_CH_2); 2.69-2.60 (m, 8H, 6×CH$_2$_CH_2CONH); 2.58-2.54 (m, 4H, 2×CH$_2$_CH_2CONH); 2.45-2.38 (m, 8H, 4×_CH_2NH$_2$); 2.23-2.15 (m, 12H, 2×_N(CH_2)$_3$); 2.04-2.00 (m, 6H, N(_CH_2)$_3$);

1.87 (s, 6H, 2×Ar_CH_3); 1.22 (t, 6H, J=7.1 Hz, 2× CH$_2$_CH_3). Elemental analysis: Calculated for C$_{58}$H$_{92}$N$_{16}$O$_8$ (MW 1141.45) C 61.03, H 8.12, N 19.63 %; Found C 61.39, H 8.03, N 19.76 %.

General Preparation Procedure for Light-Harvesting Dendrons (9) and (11)

To a solution of 4-nitro-1,8-naphthalic anhydride **7** (one equiv. per reactive amino group) in boiling methanol, a solution of Rhodamine 6G dendron (**4** or **6**) in 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, treated with 50 ml of 5 % aqueous sodium hydroxide to give after filtration and drying an intermediate **8** or **10**. Then to a solution of the intermediate in DMF, allylamine (four equiv. per reactive nitro group) was added at room temperature. After 48 h the resulting solution was poured into water. The precipitate was filtered off and washed with water. The final products were obtained after purification by column chromatography using silica gel as stationary phase.

Light-Harvesting Dendron (9) General procedure described above was used. To a solution of 0.97 g (4 mmol) 4-nitro-1,8-naphthalic anhydride **7** in 40 ml of methanol, a solution of 1.37 (2 mmol) Rhodamine 6G dendron **4** in 25 methanol was added. Allylamine (0.36 ml, 4.8 mmol) was added to a solution of intermediate **8** (0.68 g, 0.6 mmol) in 12 ml of DMF. The final product was obtained after purification by column chromatography using acetone as mobile phase (yield - 0.58 g (84 %), m.p. 176-179 °C).

IR (KBr) cm^{-1}: 3336 (νNH); 2918 and 2888 (νCH); 1692 (ν^{as}N–C=O); 1646 (ν^sN–_C=O_); 1620, 1516 and 1450 (νAr=CH). ^{1}H NMR (CDCl$_3$-d, 250.13 MHz) ppm: 8.02 (d, 2H, J=7.7 Hz, 2×naphthalimide H-5); 7.92 (d, 2H, J=8.6 Hz, 2×naphthalimide H-2); 7.89-7.85 (m, 3H, 9-Ph H-3 and 2×_NH_CO); 7.51 (d, 2H, J=8.4 Hz, 2×naphthalimide H-7); 7.47-7.42 (m, 2H, 9-Ph H-4 and 9-Ph H-5); 7.09-7.02 (m, 1H, 9-Ph H-6); 6.89 (dd, 2H, J=7.7 Hz, J=8.3 Hz, 2×naphthalimide H-6); 6.38 (s, 2H, Rhodamine H-4 and H-5); 6.21 (s, 2H, Rhodamine H-1 and H-8); 6.21 (d, 2H, J=8.6 Hz, 2×naphthalimide H-3); 5.96-5.88 (m, 4H, 2×NCH$_2$_CH_=CH$_2$ and 2×Ar_NH_); 5.32 (d, 2H, J_{trans}= 17.1 Hz, 2×trans-allyl H_CH_=); 5.24 (d, 2H, J_{cis}=10.3 Hz, 2×cis-allyl H_CH_=); 4.14 (m, 4H, 2×(CO)$_2$N_CH_2); 3.87-3.79 (m, 4H, 2×N_CH_2CH=CH$_2$); 3.65-3.55 (m, 6H, 2× CONH_CH_2 and 2×Ar_NH_); 3.25-3.14 (m, 6H, 2×ArNH_CH_2 and _CH_2NCOAr); 2.53 (t, 4H, J=6.1 Hz, 2× CH$_2$_CH_2CONH); 2.24-2.12 (m, 6H, N(_CH_2)$_3$); 1.90 (s, 6H, 2xAr_CH_3); 1.30 (t, 6H, J=7.1 Hz, 2xCH$_2$_CH_3).

Calculated for $C_{68}H_{70}N_{10}O_8$ (MW 1155.35) C 70.69, H 6.11, N 12.12 %; Found C 71.02, H 5.97, N 11.98 %.

Light-Harvesting Dendron (11) General procedure described above was used. To a solution of 1.5 g (6.3 mmol) 4-nitro-1,8-naphthalic anhydride **7** in of 60 methanol, a solution of 1.8 g (1.6 mmol) Rhodamine 6G dendron **6** in 50 of methanol was added. Allylamine (0.24 ml, 3.2 mmol) was added to a solution of intermediate **10** (0.4 g, 0.2 mmol) in 7 ml of DMF. The final product was obtained after purification by column chromatography using methanol/chloroform (1:2 v/v) mixture as mobile phase (yield - 0.24 g (58 %), m.p. 163-165 °C).

IR (KBr) cm^{-1}: 3354 (νNH); 2924 2828 (νCH); 1694 (ν^{as}N–C=O); 1652 (ν^sN–C=O). 1624, 1518 and 1458 (νAr=CH). ^{1}H NMR (CDCl$_3$-*d*, 250.13 MHz) ppm: 8.04 (d, 4H, *J*=7.8 Hz, 4×naphthalimide H-5); 7.90 (d, 4H, *J*=8.6 Hz, 4×naphthalimide H-2); 7.84 (m, 1H, 9-Ph H-3); 7.50 (d, 4H, *J*=8.4 Hz, 4×naphthalimide H-7); 7.52-7.44 (m, 2H, 9-Ph H-4 and 9-Ph H-5); 7.11-7.05 (m, 1H, 9-Ph H-6); 6.87 (t, 4H, *J*=7.9 Hz, 4×naphthalimide H-6); 6.37 (s, 2H, Rhodamine H-4 and H-5); 6.26 (d, 4H, *J*=8.6 Hz, 2× naphthalimide H-3); 6.19 (s, 2H, Rhodamine H-1 and H-8); 6.04-5.63 (m, 8H, 4×NCH$_2$*CH*=CH$_2$ and 4×Ar*NH*); 5.35-5.19 (m, 8H, 4×CH=*CH$_2$*); 4.26-4.12 (m, 8H, 4×(CO)$_2$N*CH$_2$*); 3.88-3.76 (m, 8H, 4×N*CH$_2$*CH=CH$_2$); 3.14 (br.s, 2H, 2×Ar*NH*CH$_2$); 3.06-3.03 (m, 16H, 6× CONH*CH$_2$* and 2×ArNH*CH$_2$*); 2.71-2.60 (m, 8H, 6× CH$_2$*CH$_2$*CONH); 2.58-2.50 (m, 4H, 2×CH$_2$*CH$_2$*CONH); 2.48-2.39 (m, 8H, 4×*CH$_2$*NH$_2$); 2.19-2.12 (m, 12H, 2× N(*CH$_2$*)$_3$); 2.07-1.98 (m, 6H, N(*CH$_2$*)$_3$); 1.91 (s, 6H, 2× Ar*CH$_3$*); 1.33 (t, 6H, *J*=7.1 Hz, 2×CH$_2$*CH$_3$*). Calculated for $C_{118}H_{128}N_{20}O_{16}$ (MW 2082.40) C 68.06, H 6.20, N 13.45 %; Found C 68.48, H 5.96, N 13.09 %.

Results and Discussion

Design and Synthesis

The target PAMAM dendrons **9** and **11** were designed as bichromophoric light-harvesting systems, based on a modulating FRET process, comprising a 1,8-naphthalimide donor and a rhodamine acceptor. We chose 1,8-naphthalimide for the fluorescence donor in a view of its chemical stability and high fluorescent efficiency [48]. On the basis of the spirolactam (non-fluorescent) to ring-open amide (fluorescent) equilibrium of rhodamine, rhodamine-based dyes are excellent "off-on" fluorescence probes [30–33]. A requirement for efficient energy transfer is that there be a spectral overlap between the emission of the donor dye and the absorbance of the acceptor chromophore. 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 groups. In general, the derivatives with alkoxy groups are colorless and have blue emission, while the amino substituted 1,8-naphthalimides have a yellow color and green fluorescence [42, 43]. Rhodamines are red-orange emitting fluorophores with maximal absorption in the 4-alkylamino-1,8-naphthalimides emission region. Consistent with this requirement, 4-alkylamino-1,8-naphthalimides and rhodamine dyes are suitable fluorescence donor-acceptor pair for dyad systems [23, 33, 49].

Due to the pH sensitive character of Rhodamine 6G acceptor dye, we expect the fluorescence signal of novel systems **9** and **11** to be a function of pH. In alkaline solution (pH>5) the Rhodamine 6G derivatives are in colorless spirolactam closed form and the energy transfer from the peripheral 1,8-naphthalimes to the Rhodamine 6G core in the novel PAMAM light-harvesting antennae is not feasible (Scheme 2). It could be expected that under these conditions the light-harvesting dendrons **9** and **11** will exhibit a typical for 4-amino-1,8-naphthalimides yellow-green fluorescence. In acid media the Rhodamine 6G spirolactam ring is opened, the energy of peripheral 1,8-naphthalimides in antenne **9** and **11** is transferred to the focal Rhodamine and the systems will emit red-orange fluorescence signal.

The novel light-harvesting antennae were prepared in three basic steps: synthesis of amino functional Rhodamine 6G core, PAMAM dendronization of the amino functional core to Rhodamine 6G PAMAM dendrons and peripheral decoration of the latter with yellow-green emitting 4-allylamino-1,8-naphthalimides to the desired antennae.

The synthesis of amino functional Rhodamine 6G core **2** was performed following Scheme 3 by reaction of Rhodamine 6G **1** with ethylenediamine under reflux in absolute ethanol for 5 h.

The Rhodamine 6G core **2** was subsequently converted into the PAMAM dendron **4** with two reactive amine groups of its periphery via convergent strategy, involves initial Michael addition of amino-functionalized core **2** with methylacrylate followed by exhaustive amidation of the resulting ester **3** with a large excess of ethylenediamine. The same strategy was used in the synthesis of PAMAM dendron **6** with four reactive amine groups of its periphery, staring from PAMAM dendron **4** (Scheme 4).

The light harvesting antennae **9** and **11** were synthesized in two steps as shown in Scheme 5. First, the intermediate dendrons **8** and **10** with 4-nitro-1,8-naphthalimide periphery were obtained by reaction of 4-nitro-1,8-naphthalic anhydride **7** and PAMAM dendrons **4** and **6**, possessing primary
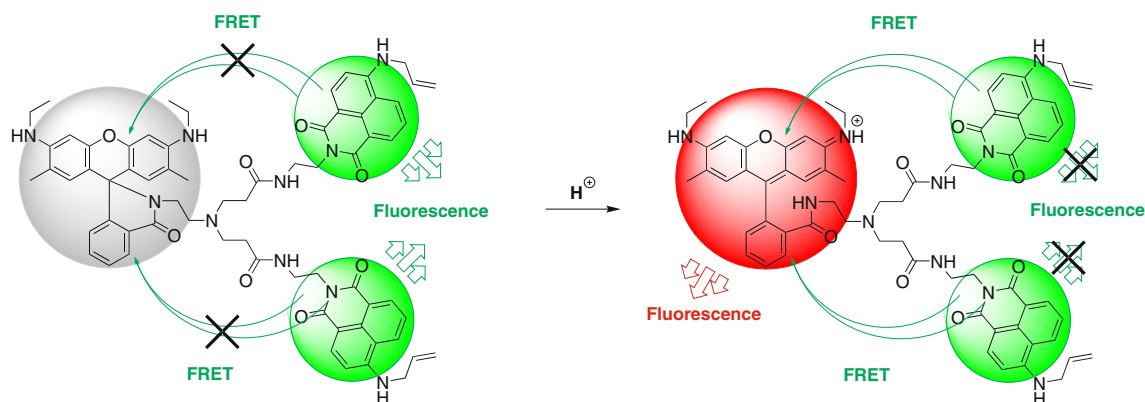
Scheme 2 Energy transfer in light-harvesting antenna **9** as a function of pH

terminal amine groups, under reflux in methanol solution. In order to obtain a yellow-green emitting periphery of the desired antennae **9** and **11**, the nitro groups in the intermediates **8** and **10** were subsequently nucleophilically substituted with allylamino groups by reaction of **8** and **10** with allylamine in DMF at room temperature.

The synthesized compounds were characterized and confirmed by conventional techniques - elemental analysis data, UV-vis, fluorescence, FT-IR and ^{1}H NMR spectroscopy. For instance, in the ^{1}H NMR (CDCl3-*d*, 250.13 MHz) spectrum of antennae **9** and **11**, a resonance at 6.21 ppm and 6.25 ppm, respectively, was observed. These are characteristic for the proton in position C-3 of the donor yellow-green emitting 1,8-naphthalimide moiety, substituted in position C-4 with an electron-donating alkylamino group. These values are rather different from the corresponding values for a non-substituted 4-nitro-1,8-naphthalimide moiety (8.35-8.70 ppm) [33, 50]. Furthermore, the ^{1}H NMR spectra contain all requisite peaks for rhodamine and 1,8-naphthalimide moieties as well as peaks in the range of 3-6 ppm, attributed respectively to the protons in the peripheral allylamine.

Photophysical Characterization of the Compounds

Photophysical properties of the examined compounds **2-6**, **9** and **11** were determined in water/DMF (4:1, v/v) solution. Under these conditions the rhodamine moiety adopts a
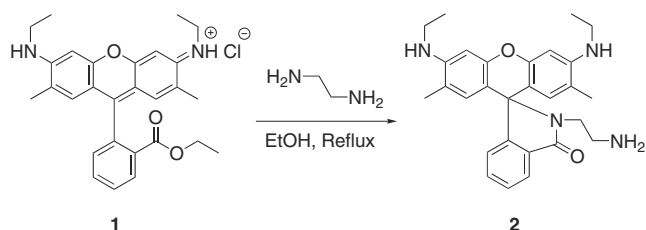

Scheme 3 Synthesis of amino functional Rhodamine 6G core **2**

closed, non-fluorescent spirolactam form. At *ca.* pH 2 the spirolactam ring of rhodamine is opened, which results in a new absorption (rhodamine) band between 450 and 575 nm with maxima at 530-534 nm. The listed in Table 1 absorption data for compounds **2**-**6** are common for Rhodamine 6G derivates [51, 52]. The presented data shows that the different alkylamino substituents in the 9-phenyl amide of Rhodamine 6G (compounds **2**-**6**) have a small effect on the energy and the shape of the dyes' absorption bands.

In water/DMF (4:1, v/v) at pH 7 (spirolactam closed form) light-harvesting dendrons **9** and **11** show absorption band in range 380-530 nm, which is attributed to an internal charge transfer process in the 1,8-naphthalimide chromophores. After acidification to pH 2 where the spirolactam is in opened form, as expected the absorption spectrum of light harvesting systems **9** and **11** show two bands (Fig. 1) corresponding to the absorption location of the peripheral 4-allylamino-1,8-naphthalimide donors (λ_A=456 nm for **9** and λ_A=452 nm for **11**) and the focal rhodamine acceptor unit (λ_A=534 nm for the both antennae). The molar extinction coefficient values of the peripheral absorption of light-harvesting antenna **11** containing four donor fragments is about two times higher than those of light-harvesting antenna **9** with two donors, suggesting no ground state interaction between the peripheral 1,8-naphthalimide units. This fact clearly shows the greater ability of periphery in light-harvesting system **11** to capturing photons form the environment in comparison to the antenna **9**.

In water/DMF (4:1, v/v) at pH 2 and excitation at 510 nm, compounds **2-6**, **9** and **11** show typical for Rhodamine 6G fluorescence spectra with maxima at about 560 nm [51, 52], suggesting that the substituents at 9-phenyl amide do not affect the energy of the dyes' fluorescence maximum.

The fluorescence spectra of light-harvesting antennae **9** and **11** in water/DMF (4:1, v/v) solution at pH 7, obtained after excitation within the spectral region of maximal absorption of the donor fluorophore (λ_{ex}=430 nm), showed
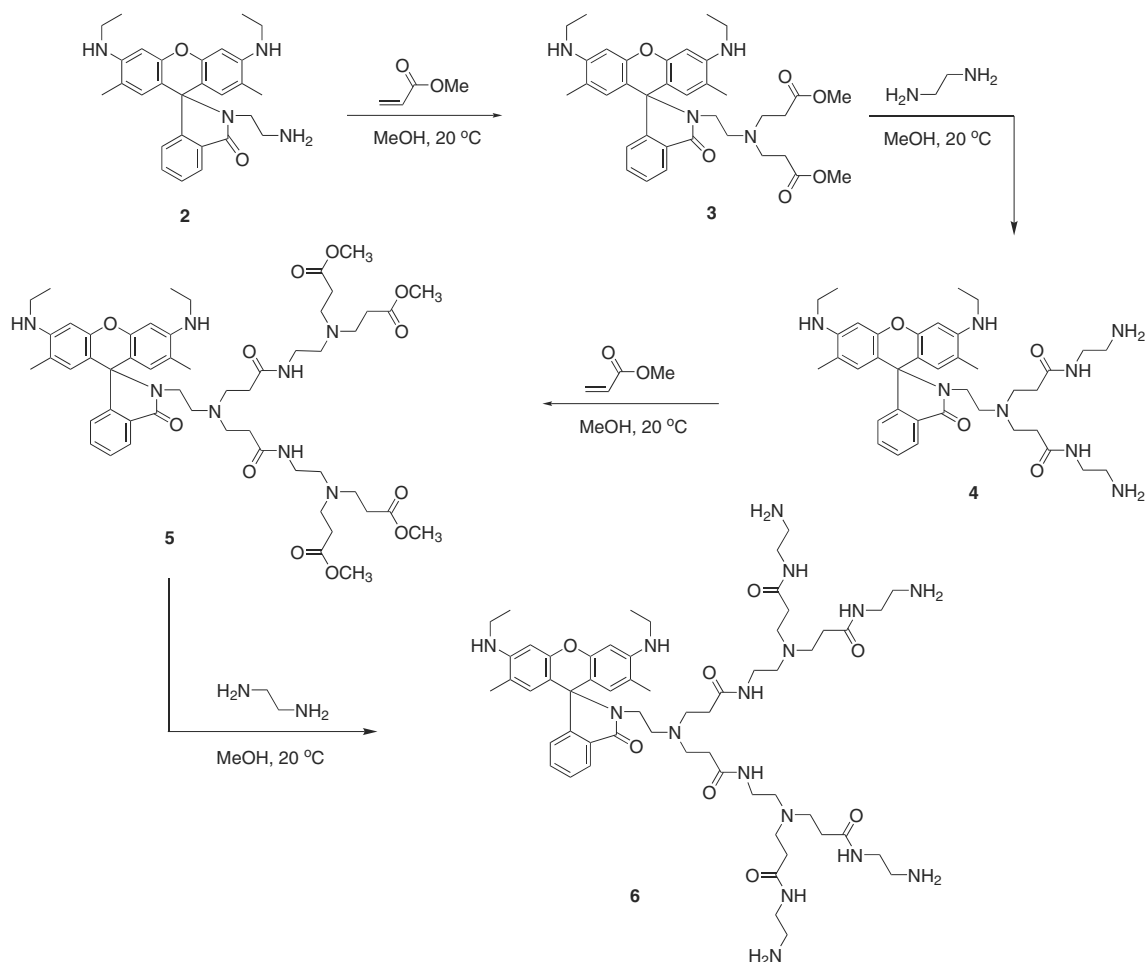
Scheme 4 Synthesis of amino-terminated Rhodamine 6G dendrons **4** and **6**

emission band at 540 nm, corresponding to the emission band of the donor 1,8-naphthalimide fragments in the donor-acceptor systems. In contrast, when the fluorescence spectra was recorded at pH2 (λ_{ex}=430 nm), the observed emission was shifted to 560 nm, which can be attributed to the energy transfer from the donor 1,8-naphthalimide to the ring-opened form of the rhodamine 6G acceptor under these conditions.

The Stoke's shift ($\nu_A - \nu_F$) is an 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 shifts (cm^{-1}) were calculated by Eq. (1).

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

The Stoke's shift values for compounds under study observed after excitation at 510 nm and pH 2 are between 806 cm^{-1} and 947 cm^{-1} that is typical for Rhodamine 6G [51, 52] and do not indicate remarkable changes in the fluorophore excited state due to incorporation in the dendritic

systems. Also after excitation at 430 nm (1,8-naphthalimide absorption region) and pH7 (spirolactam closed form) the light-harvesting systems **9** and **11** show usual for the 1,8-naphthalimide fluorophores Stoke's shift values between 3 411 cm^{-1} and 3 605 cm^{-1}.

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 Rhodamine 6G (Φ_F=0.95 in ethanol [46]) or Coumarin 6 (Φ_F=0.78 in ethanol [47]) as standards according to Eq. (2), 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.

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

As can be seen from the data in Table 1, the quantum yield of fluorescence of rhodamines **2-6** are decreasing with the increase of their molecular weight. A similar effect was
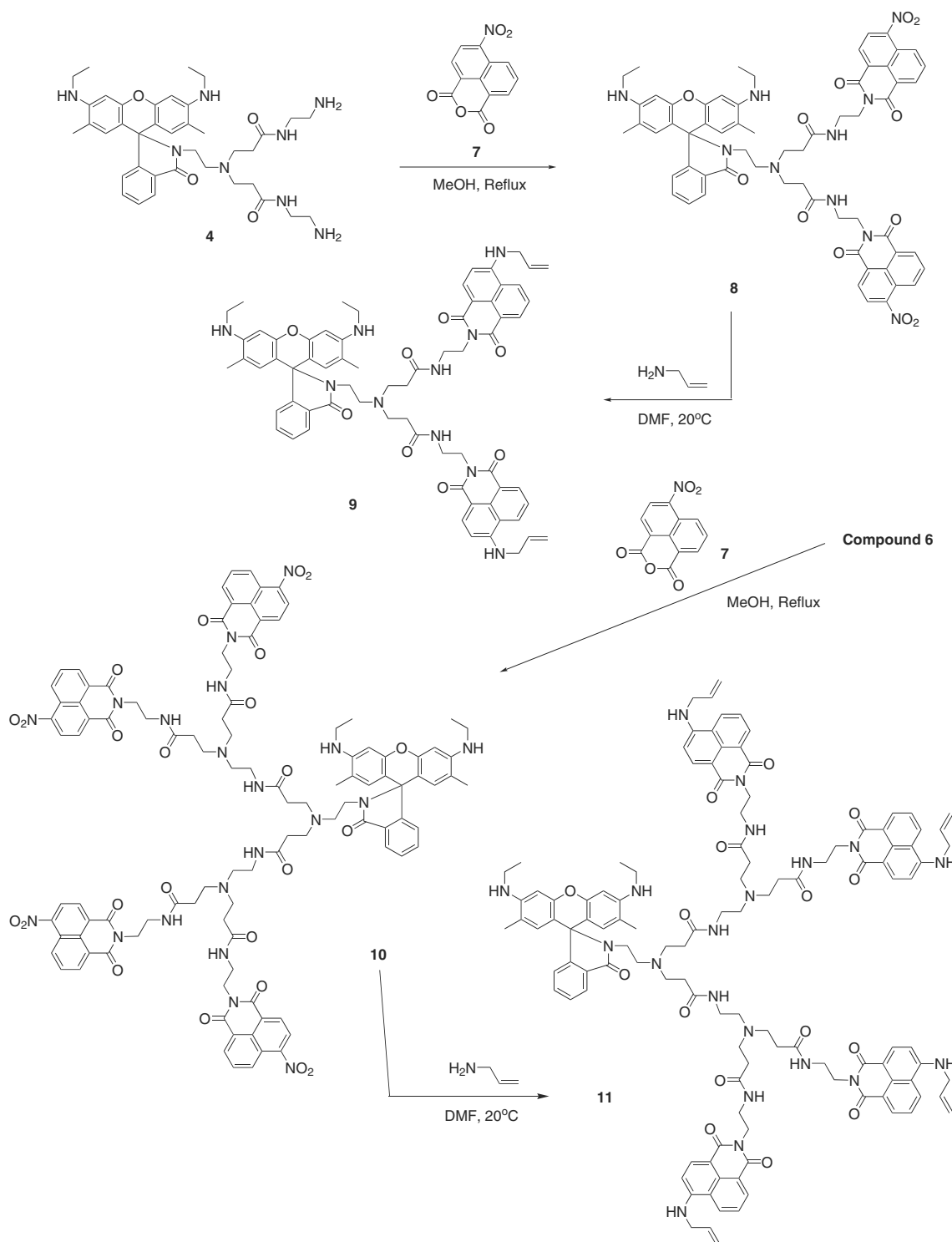
Scheme 5 Synthesis of light harvesting antennae **9** and **11**

reported before for the core functional PAMAM dendrons using 1,8-naphthalimide and perylene-3,4,9,10-tetracarboxylic diimide units [53, 54]. This is probably due to the more flexible PAMAM scaffold in the larger dendron's generations, which are able to induce energy loses reducing the quantum yield of fluorescence. Also, the data in Table 1

reveals that the quantum yield of the peripheral 1,8-naphthalimide donors in antennae **9** and **11** is lower in respect to other simple 1,8-naphthalimides [33] suggesting for the presence of quenching effect in the peripheral 1,8-naphthalimide units that is stronger in **9** than those in **11**. The nature of this quenching effect can be attributed to the PET from

Table 1 Photophysical characteristics of compounds **2-6**, **9** and **11** in water/DMF (4:1, v/v)

Compound	λ_A (nm)	ε (lmol^{-1}cm^{-1})	λ_F (nm)	$\nu_A - \nu_F$ (cm^{-1})	Φ_F
2	530[a]	56 308[a]	558[a]	947[a]	0.92[a]
3	532[a]	46 738[a]	558[a]	876[a]	0.72[a]
4	532[a]	42 988[a]	560[a]	940[a]	0.55[a]
5	532[a]	42 764[a]	560[a]	940[a]	0.52[a]
6	534[a]	42 486[a]	560[a]	820[a]	0.48[a]
9	456[b]	17 564[b]	540[b]	3 411[b]	0.20[b]
	534[a]	42 735[a]	560[a]	820[a]	0.22[a]
11	452[b]	41 839[b]	540[b]	3 605[b]	0.32[b]
	534[a]	42 372[a]	558[a]	806[a]	0.16[a]

[a] Photophysical data recorded at *ca.* pH 2 and λ_{ex}=510 nm

[b] Photophysical data recorded at pH 7 and λ_{ex}=430 nm to avoid rhodamine spirolactam closed (non-fluorescent) form

PAMAM scaffold to the 1,8-naphthalimide units [42] or to the self quenching of the peripheral fluorophores [55].

Influence of pH on the Photophysical Properties of the Compounds

The light-harvesting systems under study were designed as long-wavelength shifting fluorescence sensors for determining pH changes over a wider pH scale. This was the reason to investigate their photophysical behavior in water/DMF (4:1, v/v) solution at different pH values. In order to receive a more complete comparative picture for the influence of the dendritic bone to the focal rhodamine unit at different pHs, compounds **2-6** were involved in the present study. Figure 2a presents the changes of absorption spectra of **3** at different pH values as a typical example for the influence of pH on the absorption spectra of the examined compounds **2-6**. As can be seen, the decrease of pH results in increase of the absorbance at about 530 nm due to the ring opening reaction of rhodamine core.

The changes of the absorption intensity at 532 nm of compounds **2-6** as a function of pH in water/DMF (4:1 v/v) are plotted in Fig. 2b. Taking the part of the graphs located between pH2 and 6, the pK_a values of **2-6** have been calculated by the Eq. (3) [56].
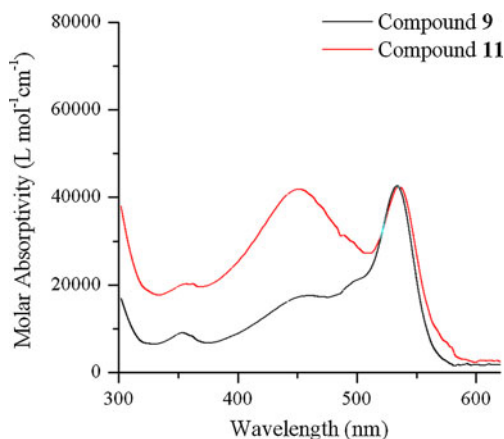
$$\log[(A_{max} - A)/(A - A_{min})] = pH - pK_a \tag{3}$$

The calculated pK_a value for amino-functional rhodamine **2** was 4.0, 3.9 for the branching compounds **3-5** and 3.7 for

Fig. 1 Absorption spectra of antennae **9** and **11** in water/DMF (4:1, v/v) at pH 2
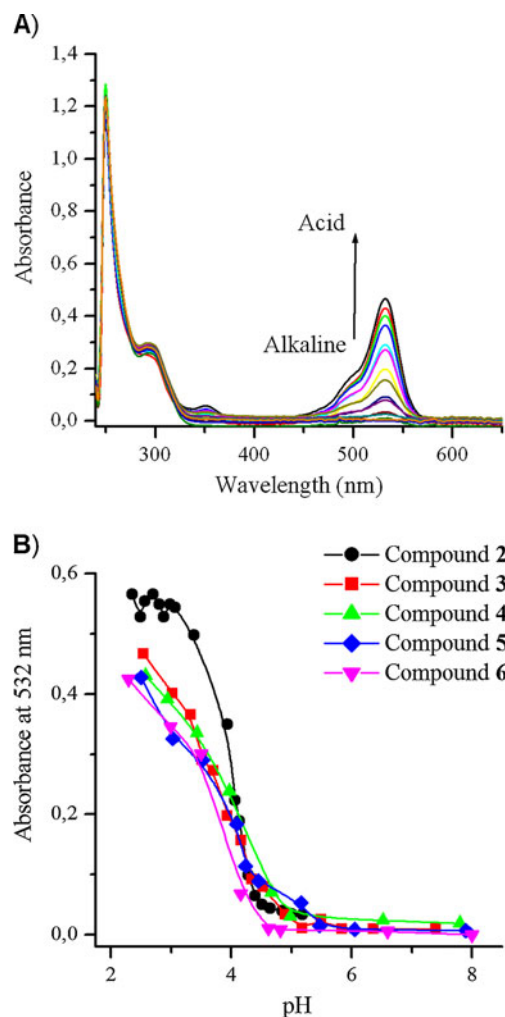

Fig. 2 **a** Absorption changes of **3** in water/DMF (4:1, v/v) at different pHs. **b** Titration curves of compounds **2-6** in water/DMF (4:1, v/v) at different pHs

the PAMAM dendron of second generation **6**. Probably the decrease of pK_a values is a result of the core protective role of the PAMAM scaffold. It is well known that the protonation of PAMAM dendrimers starts from the peripheral groups and continues to the focal ones [57, 58]. As a result, the cores of the dendrimers of high generation are being protonated in a stronger acidic environment in comparison with the cores of the lower generation dendrimers.

The absorption spectra of light-harvesting antennae **9** and **11** do not show significant pH-dependent changes in pH window 5-8, since the 1,8-naphthalimide fluorophore does not affect ICT excited states (Fig. 3). Further acidification of the media from 5 to 2 results in a novel band in the spectra of the examined antennae corresponding to the focal rhodamine absorption. Titration curves of the novel antennae were obtained from the absorption changes at 534 nm (inset of Fig. 3). The calculated using Eq. (3) pK_a values 3.9 for first generation antenna **9** and 3.7 for second generation antenna **11** are identical to the respective pK_a values for PAMAM

dendrons **4** and **6**, from first and second generation, respectively.

The fluorescence spectra of compounds **2-6**, **9** and **11** were also recorded in water/DMF (4:1, v/v) solution at different pH values. In alkaline solution compounds **2-6** are in spirolactam closed form and do not emit light. However, upon acidification an emission signal in range between 500 and 700 nm was gradually increased as is demonstrated in Figs. 4a and b. Analysis of the fluorescence changes at 560 nm (Fig. 4b) according to Eq. (4) [12] gives the pK_a values 4.0 for amino-functional rhodamine **2**, 3.9 for the compounds **3-5** and 3.7 for the PAMAM dendron of second generation **6**. The calculated pK_a values of compound **3-6** using fluorescence changes are similar to the pK_a values calculated according absorption changes and are attributed to the spirolactam opening reaction.

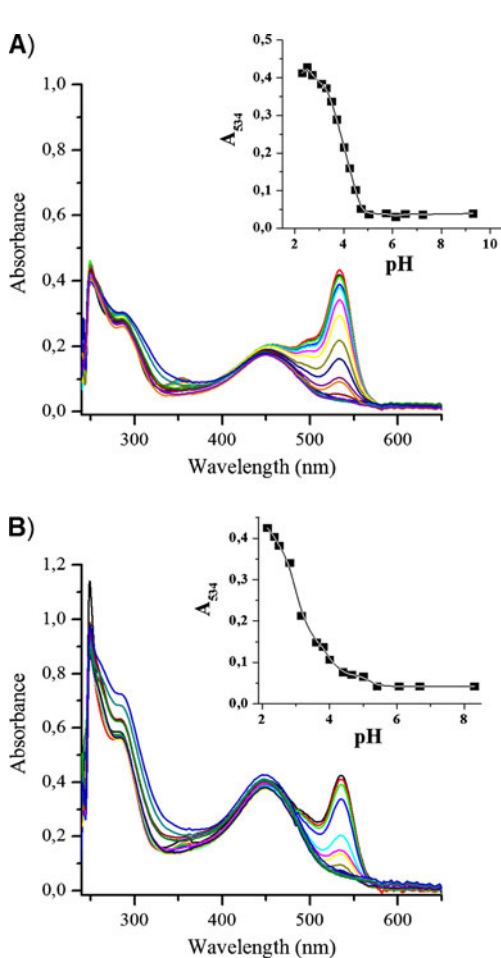$$\log[(I_{F\,max} - I_F)/(I_F - I_{F\,min})] = pH - pK_a \qquad (4)$$

Fig. 3 **a** Absorption changes of antennae **9** in water/DMF (4:1, v/v) at different pHs. **b** Absorption changes of antennae **11** in water/DMF (4:1, v/v) at different pHs
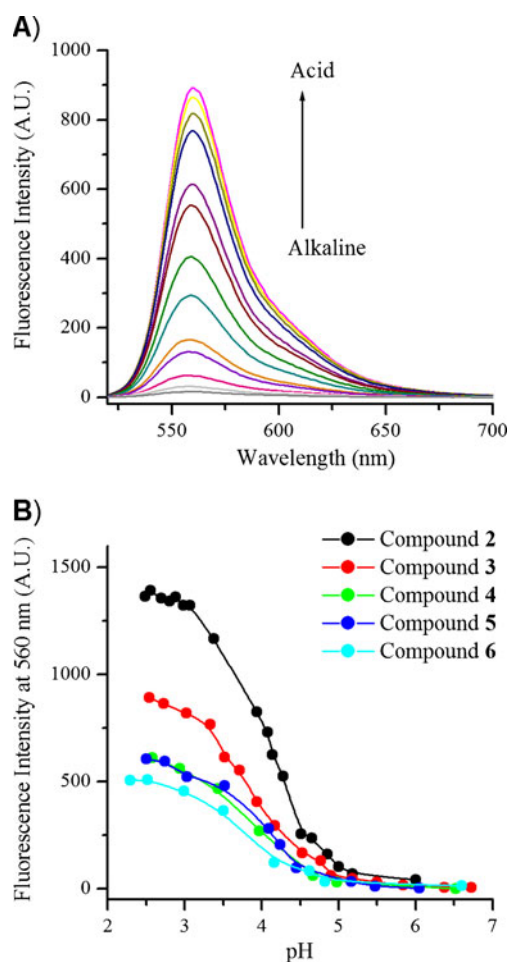

Fig. 4 **a** Fluorescent changes of **3** in water/DMF (4:1, v/v) at different pHs. **b** Titration curves of compounds **2-6** in water/DMF (4:1, v/v) at different pHs

Fig. 5 **a** Fluorescent changes of antenna **9** in water/DMF (4:1, v/v) at different pHs excited at 430 nm. **b** Fluorescent changes of antenna **9** in water/DMF (4:1, v/v) at different pHs excited at 510 nm
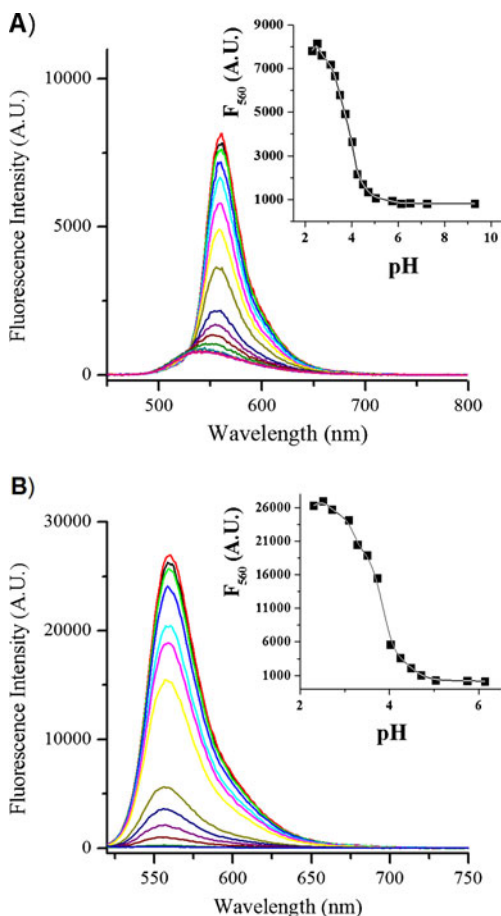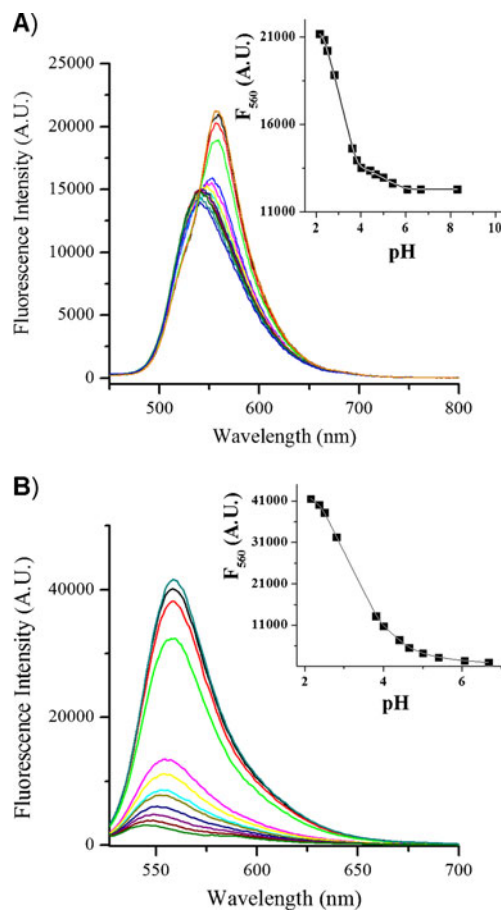

Fig. 6 **a** Fluorescent changes of antenna **11** in water/DMF (4:1, v/v) at different pHs excited at 430 nm. **b** Fluorescent changes of antenna **11** in water/DMF (4:1, v/v) at different pHs excited at 510 nm

In alkaline and neutral media after excitation at 430 nm (within the spectral region of maximal absorption of the donor fluorophores) the novel antennae **9** and **11** show emission band in range 480-700 nm with pronounced maxima at 540 nm (Figs. 5a and 6a). At these conditions the focal acceptor dye is in its closed spirolactam form, energy transfer from the peripheral donor fluorophores to the core is not faceable and the both systems (**9** and **11**) show a typical for 4-amino-1,8-naphthalimdes yellow-green emission.

Upon acidification from pH 6 to pH 2 the spirolactam form became opened, which allows the emission energy transfer from periphery to the acceptor moiety. This results in fluorescence intensity enhancement (FE) in the rhodamine emission region at 560 nm. The FE= I/I_0, calculated using minimal (I_0) and maximal (I) fluorescence intensity recorded in the examined pH interval, was more than 10 times (FE=10.1) for antenna **9** and FE=1.7 for antenna **11**. The remarkable difference in the behavior of both systems could be twofold: (1) the lower quantum yield of focal rhodamine in second generation dendron in comparison to the first generation

(see *section 3.2.*, Table 1); (2) obviously the energy transfer efficiency in antenna **11** is extremely low due to the higher distance between the donor and acceptor units in light-harvesting system from second generation.
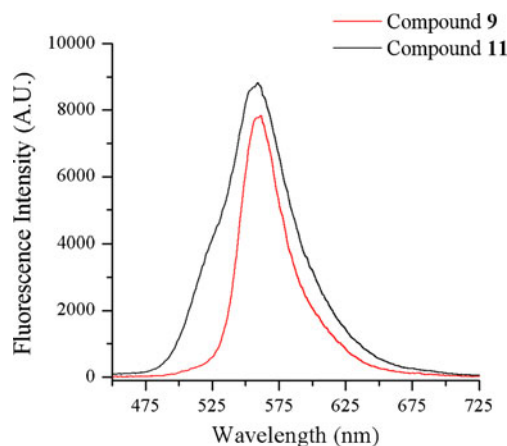

Fig. 7 Normalized to the optical density fluorescent spectra (excited at 430 nm) of antennae **9** and **11** in water/DMF (4:1, v/v) at pH 2

Unfortunately, because of the higher overlap between 1,8-naphthalimide and rhodamine emission in the spectra of the examined compounds the exact energy transfer rate of systems **9** and **11** were not calculated.

In order to illustrate the remarkable difference of the energy transfer efficiency of both systems, the normalized to the optical density fluorescent spectra of antennae **9** and **11** (excited at 430 nm) in water/DMF (4:1, v/v) at pH 2 were presented in Fig. 7. As can be seen, the fluorescence intensity of both systems is approximately the same. However the fluorescence spectrum of antenna **9** contains only the rhodamine acceptor emission while the fluorescence spectrum of antenna **11** shows two well pronounced bands attributed to the emissions of peripheral 1,8-naphthalimide donors and the focal rhodamine. The strong fluorescence of the donor units in antenna **11** clearly illustrates the lower ability of the compound to transfer energy from the peripheral 1,8-naphthalimides to the focal rhodamine acceptor dye.

Analysis of the fluorescence changes at 560 nm after excitation at 430 nm (Figs. 5a-inset and 6a-inset) according to Eq. (4) gives the pK_a values of 3.9 for antenna **9** and 3.6 for **11**. The same results were obtained after direct core excitation at 510 nm (Figs. 5b-inset and 6b-inset) suggesting that only the spirolactam-opening reaction of rhodamine cores in **9** and **11** are responsible for the pH sensing properties of the novel compounds.

Conclusions

In this paper, we have given a comprehensive account of the design and synthesis of two novel light-harvesting dendrons with pH sensing properties. The novel compounds are based on first and second generation PAMAM dendritic scaffolds which surface was labeled with yellow-green emitting 1,8-naphthalimide "donor" dyes capable of absorbing light and efficiently transferring the energy to a single Rhodamine 6G "acceptor" dye. The photophysical properties of all synthesized compounds were studied in water/DMF (4:1, v/v) solution. The core emission intensity of novel systems had enhanced in the pH range 6-2. The determined pK_a values of 3.9 for **9** and 3.6 for **11** indicate that they would be able to act as "off-on" switches for pH. These changes are attributed to the ring-opening reaction of the focal rhodamine in acid media. Thus the distinguishing features of light-harvesting dendrons were successfully combined with the properties of classical ring-opening sensor systems.

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