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# Design and synthesis of core and peripherally functionalized with 1,8-naphthalimide units fluorescent PAMAM dendron as light harvesting antenna

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**Abstract**

This paper reports on the design, synthesis and spectral characteristics of a novel PAMAM dendron (**7**), core and peripherally functionalized with 1,8-naphthalimide fluorophores. The novel compound **7** was configured as light harvesting antenna where the system surface is functionalized with "donor" dyes (blue emitting 1,8-naphthalimides) that are capable of absorbing light and efficiently transferring the energy to a single "acceptor" dye (yellow-green emitting 1,8-naphthalimide) in the focal point of the dendron. The overlap between the emission of the donor and the absorbance of the acceptor was more than 95%. As a result of the energy transfer, the blue emission intensity of the periphery in the donor–acceptor system was decreased with 93%, while the yellow-green core fluorescence enhancement ($\lambda_{ex} = 360$ nm) of the system was more than 26 times with respect to the fluorescence intensity of the comparative yellow-green emitting 1,8-naphthalimide. This indicates efficient energy transfer between the donor and acceptor dye fragments and that the novel compound **7** would be able to act as a highly efficient light harvesting antenna.

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

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## 1. Introduction

Molecular systems capable of light harvesting and energy transfer are currently of great interest [1]. Progress in the study of natural photosynthetic systems has provided the impetus to design artificial light harvesting assemblies based on a variety of architectures. For instance, numerous reports on organic [2], organometallic [3], supramolecular [4], and polymeric [5] chromophore assemblies capable of acting as light harvesting antennae have appeared in the literature. More recently, dendritic light harvesting assemblies have also attracted much attention [6].

Dendrimers are well-defined macromolecules exhibiting a three-dimensional structure that is roughly spherical or globular. A characteristic of dendritic macromolecules is the presence of numerous peripheral chain ends that all surround a single core. The globular shape of dendrimers provides a large surface area that can be decorated with the chromophores. In this context, labeling of dendritic macromolecular architectures with fluorophore units is one of the viable routes of generating suitable luminescent dendritic macromolecules having well-defined branched and compartmentalized structures [7]. Particularly useful for this purpose are solvatochromic fluorophores such as 1,8-naphthalimide derivatives. Because of their strong fluorescence and good photostability, the 1,8-naphthalimide derivatives have found application in a number of areas including coloration of polymers [8], laser active media [9], potential photosensitive biologically units [10], fluorescent markers in biology [11], analgesics in medicine [12], light emitting diodes [13], photoinduced electron transfer sensors [14], fluorescence switchers [15], electroluminescent materials [16], liquid crystal displays [17] and ion probes [18].

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. Our first investigations on the synthesis and photophysical properties of polyamidoamine (PAMAM) derivatives comprising 1,8-naphthalimide

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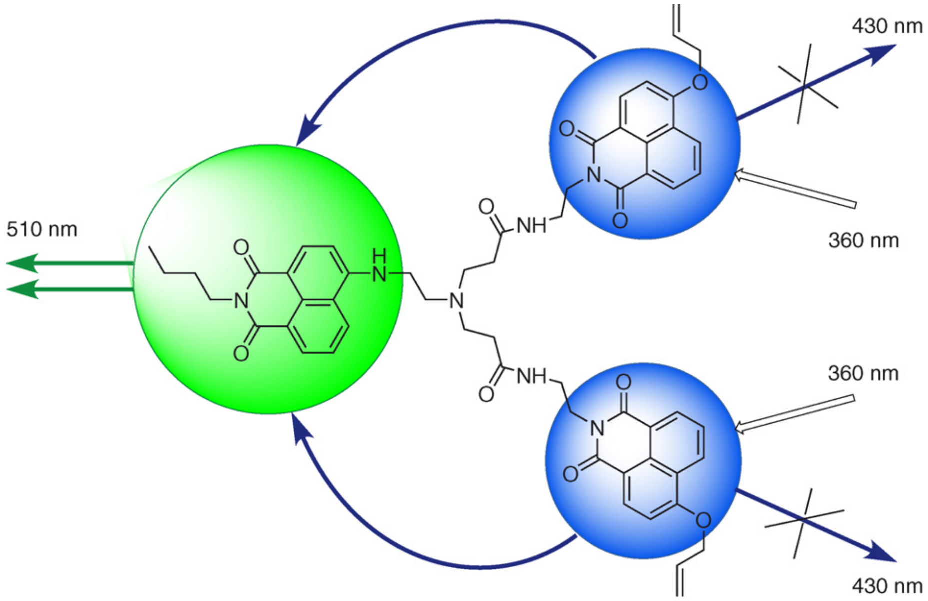


**7**

Scheme 1.

units in their periphery were published before [19]. In this paper, we report the synthesis of a novel light harvesting antenna (**7**) by both core and peripherally fluorescent functionalization of a PAMAM dendron together with the photophysical and fluorescence signaling properties of the system (Scheme 1).

In this system (Scheme 1), the dendron surface is functionalized with “donor” dyes (blue emitting 4-allyloxy-1,8-naphthalimide fluorophores) that are capable of absorbing light and efficiently transferring the energy to a single “acceptor” dye (yellow-green emitting 1,8-naphthalimide) in the focal point of the dendron, that is, dendron branches act as the “molecular lens”.

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 yellow-green emitting amidoamine-dendronized 1,8-naphthalimide **5** [20] and the blue emitting 4-allyloxy-*N*-*n*-butyl-1,8-naphthalimide **8** [21] were involved in the present study as reference compounds (Scheme 2).

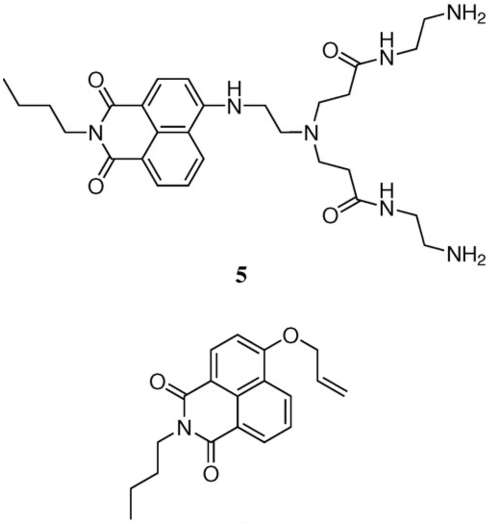
## 2. Experimental

### 2.1. Materials

The starting 4-bromo-1,8-naphthalic anhydride **1** was prepared according to the reported procedure [22]. Amidoamine-functionalized 1,8-naphthalimide **5** [20] and 4-allyloxy-*N*-*n*-butyl-1,8-naphthalimide **8** [21] were prepared as described before. Butylamine, ethylenediamine, allyl alcohol and methyl acrylate (Fluka, Merck), p.a. grade, were used without purification. All solvents (Fluka, Merck) were pure or of spectroscopy grade.

### 2.2. Methods

FT-IR spectra were recorded on a Varian Scimitar 1000 spectrometer at 2 cm$^{-1}$ resolution. The $^{1}$H NMR spectra (chemical shifts are given as $\delta$ 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 in a solvent system ethanol:chloroform = 9:1. The melting points



**5**

**8**

Scheme 2.

were determined by means of a Kofler melting point microscope. The UV–vis absorption spectra were recorded on a spectrophotometer Lambda 25 (PerkinElmer). The corrected excitation and fluorescence spectra were taken on a PerkinElmer LS55 spectrofluorimeter. The fluorescence quantum yields ($\Phi_F$) were measured relatively to *p*-methoxybenzylidenephthalide ($\Phi_F = 0.14$ in ethanol) [23].

### 2.3. Synthesis of light harvesting 1,8-naphthalimide dendron

To a solution of 4-bromonaphthalic-1,8-anhydride (1.00 g, 3.6 mmol) **1** in 30 ml of boiling methanol, a solution of amino-terminated 1,8-naphthalimide dendron **5** (1.94 g, 3.6 mmol) in 15 ml of methanol was added dropwise under stirring over a period of 2 h. The resulting solution was refluxed for 5 h. After cooling the yellow–orange precipitate was filtered off, washed with fresh methanol and dried in vacuum to afford 1.83 g of 4-bromo-1,8-naphthalimide peripherally functionalized dendron **6** (48%). The solid was suspended in 50 ml of allyl alcohol and the reaction mixture was refluxed under stirring for a period of 16 h. The crude product that precipitated after cooling was filtered off, washed with water and dried. Silica gel chromatography (ethanol:chloroform = 9:1) afforded 0.4 g (23%) of 4-allyloxy-1,8-naphthalimide peripherally functionalized dendron **7** (m.p. 138–144 °C, TLC $R_f$ value 0.67).

IR (KBr) cm$^{-1}$: 3350 ($\nu$NH); 2924 and 2904 ($\nu$CH); 1696 ($\nu^{as}$N–*C*=*O*); 1654 ($\nu^{s}$N–*C*=*O*); 1633 ($\nu$NH–*C*=*O*).

$^1$H NMR (DMSO-$d_6$, 250 MHz) ppm: 8.58 (d, 1H, $J = 8.3$ Hz, focal naphthalimide H-2); 8.35 (m, 6H, 3× naphthalimide H-5 and H-7); 8.13 (d, 2H, $J = 7.9$ Hz, 2× peripheral naphthalimide H-2); 8.02 (br.s, 2H, 2× NHCO); 7.68 (m, 3H, 3× naphthalimide H-6); 7.35 (br.s, 1H, ArNH); 7.09 (d, 2H, $J = 7.9$ Hz, 2× peripheral naphthalimide H-3); 6.57 (d, 1H, $J = 8.3$ Hz, focal naphthalimide H-3); 6.15 (m, 2H, 2× $OCH_2\mathit{CH}{=}CH_2$); 5.52 (d, 2H, $J_{trans} = 17.1$ Hz, 2× allyl H*CH*=); 5.35 (d, 2H, $J_{cis} = 9.5$ Hz, 2× allyl H*CH*=); 4.78 (s, 4H, 2× $O\mathit{CH_2}CH{=}CH_2$); 4.03 (m, 10H, 2× $CONH\mathit{CH_2}$ and 3× $(CO)_2NCH_2$); 3.26 (m, 2H, $ArNH\mathit{CH_2}$); 2.63 (br.s, 6H, 3× $NCH_2$); 2.13 (br.s, 4H, 2× $\mathit{CH_2}CONH$); 1.55 (m, 2H, $CH_2\mathit{CH_2}CH_2CH_3$); 1.33 (m, 2H, $CH_2CH_2\mathit{CH_2}CH_3$); 0.91 (t, 3H, $J = 7.3$ Hz, $CH_2CH_2CH_2\mathit{CH_3}$).

$^{13}$C NMR (62.90 MHz, DMSO-$d_6$) $\delta$ (ppm): 171.2 (2× NH–CO); 161.4 (focal naphthalimide 2× N–C=O); 159.8 (peripheral naphthalimide 4× N–C=O); 158.1 (peripheral naphthalimide 2× Ar–C–O); 150.2 (focal naphthalimide Ar–C–NH); 134.1, 133.4, 132.9, 130.6, 130.1, 128.7, 127.1, 126.7, 124.3, 123.2, 122.9, 120.6, 119.7, 116.8, 112.3 and 107.2 (Ar CH and Ar C); 133.7 (2× allyl CH=); 116.5 (2× allyl $CH_2$=); 70.8 (2× allyl $OCH_2$); 51.9 ($ArNHCH_2\mathit{CH_2}N$); 50.6 (2× $N\mathit{CH_2}CH_2CONH$); 49.4 (2× $CONHCH_2\mathit{CH_2}N(CO)_2$); 45.5 (2× $CONH\mathit{CH_2}CH_2N(CO)_2$); 43.4 ($ArNH\mathit{CH_2}CH_2N$); 40.4 $(CO)_2N\mathit{CH_2}CH_2CH_2CH_3$); 32.9 (2× $NCH_2\mathit{CH_2}CONH$); 29.9 ($NCH_2\mathit{CH_2}CH_2CH_3$); 20.2 ($NCH_2CH_2\mathit{CH_2}CH_3$); 13.8 ($CH_3$).

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 69.18, H 5.59, N 9.83%.

## 3. Results and discussion

### 3.1. Design and synthesis of light harvesting antenna

The core and peripherally functionalized PAMAM dendron (**7**) was designed as fluorescent light harvesting antenna. It is well known that absorption and fluorescence characteristics of the 1,8-naphthalimide derivatives depend on the nature of the substituent at C-4 position of the 1,8-naphthalimide ring. 4-Alkylamino-1,8-naphthalimides are yellow-green fluorophores with maximal absorption in the blue region at about $\lambda_A = 430$–$440$ nm [12,17c,20,24c,24d]. In contrast, 4-alkoxy-1,8-naphthalimides act as an additional light source by transporting the absorbed UV light of terrestrial solar irradiation, below about 400 nm, re-emitting the light as a violet-blue fluorescence in the visible region [21,24a,24b,25a]. This, together with their chemical stability and high fluorescent efficiency, was the reason to chose 1,8-naphthalimide chromophores as both a fluorescent core and a periphery end fluorophores for the synthesized compound (**7**), constructed by amidoamine branches with a specific functional periphery.

When selecting a light harvesting donor–acceptor pair, it is important to maximize the spectral overlap between the emission of the peripheral donor dyes and the absorbance of the acceptor focal dye to enhance the probability of energy transfer [26]. Recently, our group has synthesized a yellow-green emitting amidoamine-dendronized 1,8-naphthalimide with maximum absorption wavelength at about $\lambda_A = 440$ nm [20], hence a 4-allyoxy-1,8-naphthalimide is a suitable donor because it has a maximum emission in the same region. This can be seen from Fig. 1, where are depicted the absorbance of amidoamine-dendronized 1,8-naphthalimide **5** and the emission of the reference compound 4-allyloxy-*N*-*n*-butyl-1,8-naphthalimide **8**. The overlap between the emission of the peripheral donor dyes and the absorbance of the acceptor focal 1,8-naphthalimide was more than 95%.

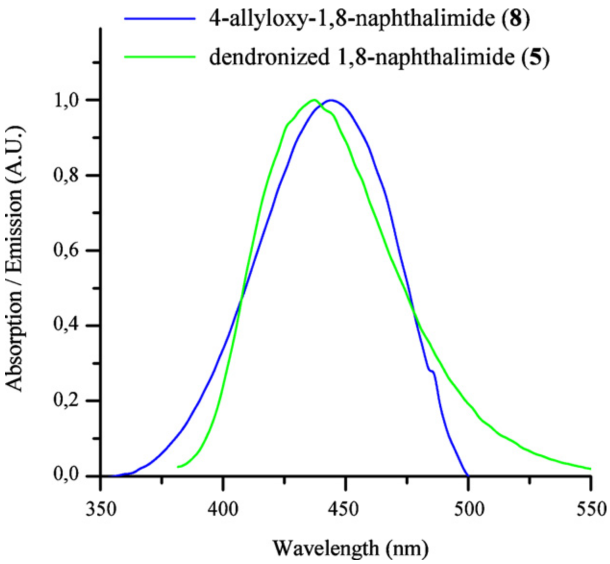
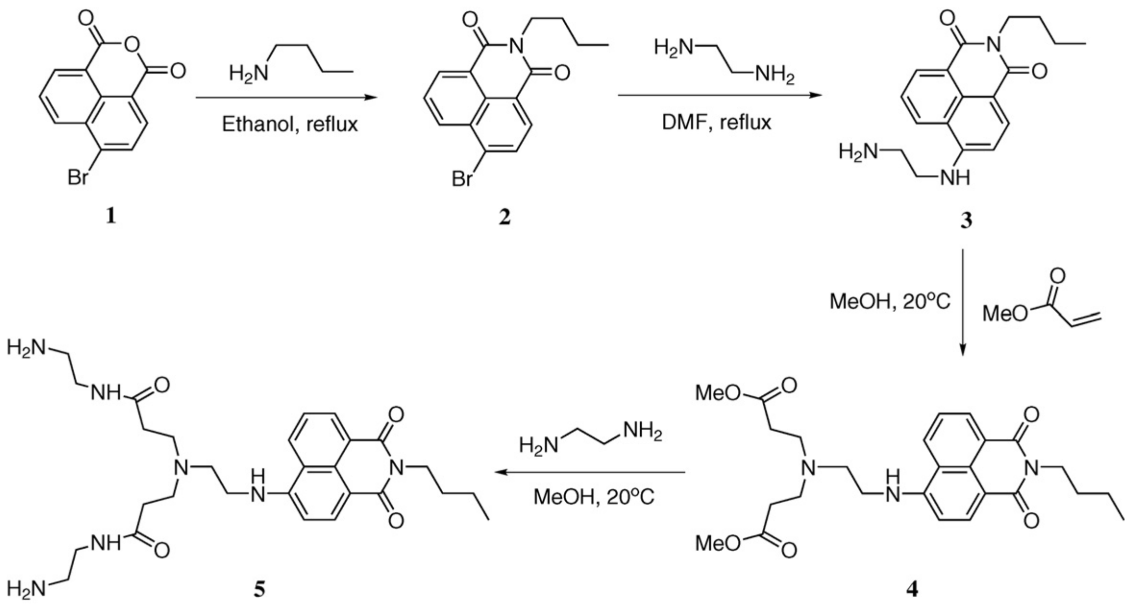


Fig. 1. Normalized core absorption (compound **5**, green line) and peripheral emission at $\lambda_{ex} = 360$ nm (compound **8**, blue line) of antenna **7**.



Scheme 3.

The amino-terminated 1,8-naphthalimide **5** (Scheme 3) was synthesized as we described before [20] by convergent strategy involves initial Michael addition of 4-(2-aminoethyl)amino-*N*-*n*-butyl-1,8-naphthalimide **3** [27,28] with methyl acrylate followed by exhaustive amidation of the resulting ester **4** with a large excess of ethylenediamine to afford the amidoamine-functionalized 1,8-naphthalimide (**5**) with reactive amine groups of its periphery [29].

The synthesis of light harvesting antenna **7** was achieved in two steps following Scheme 4.

First, the intermediate 4-bromo-1,8-naphthalimide peripherally functionalized dendron **6** was obtained by reaction of 4-bromo-1,8-naphthalic anhydride **1** under reflux in methanol solution with amidoamine-functionalized 1,8-naphthalimide **5**, possessing two primary terminal amine groups. In order to obtain a blue emitting periphery of the desired antenna **7**, the bromine atoms in the intermediate **6** were subsequently nucleophilic 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 antenna **7** were confirmed by conventional techniques—melting point, TLC ($R_\mathrm{f}$ values), elemental analysis data, UV–vis, fluorescence, FT-IR and $^1$H NMR spectroscopy. For instance, in the $^1$H NMR (250.13 MHz, DMSO-$d_6$) spectrum of compound **7** a resonance at 7.09 ppm was observed. This is characteristic for the proton in position C-3 of the periphery blue emitting1,8-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 (6.57 ppm). Furthermore, the $^1$H NMR spectrum contained peaks in range of 6.15–4.78 ppm, attributed to the protons for the peripheral allyloxy groups.

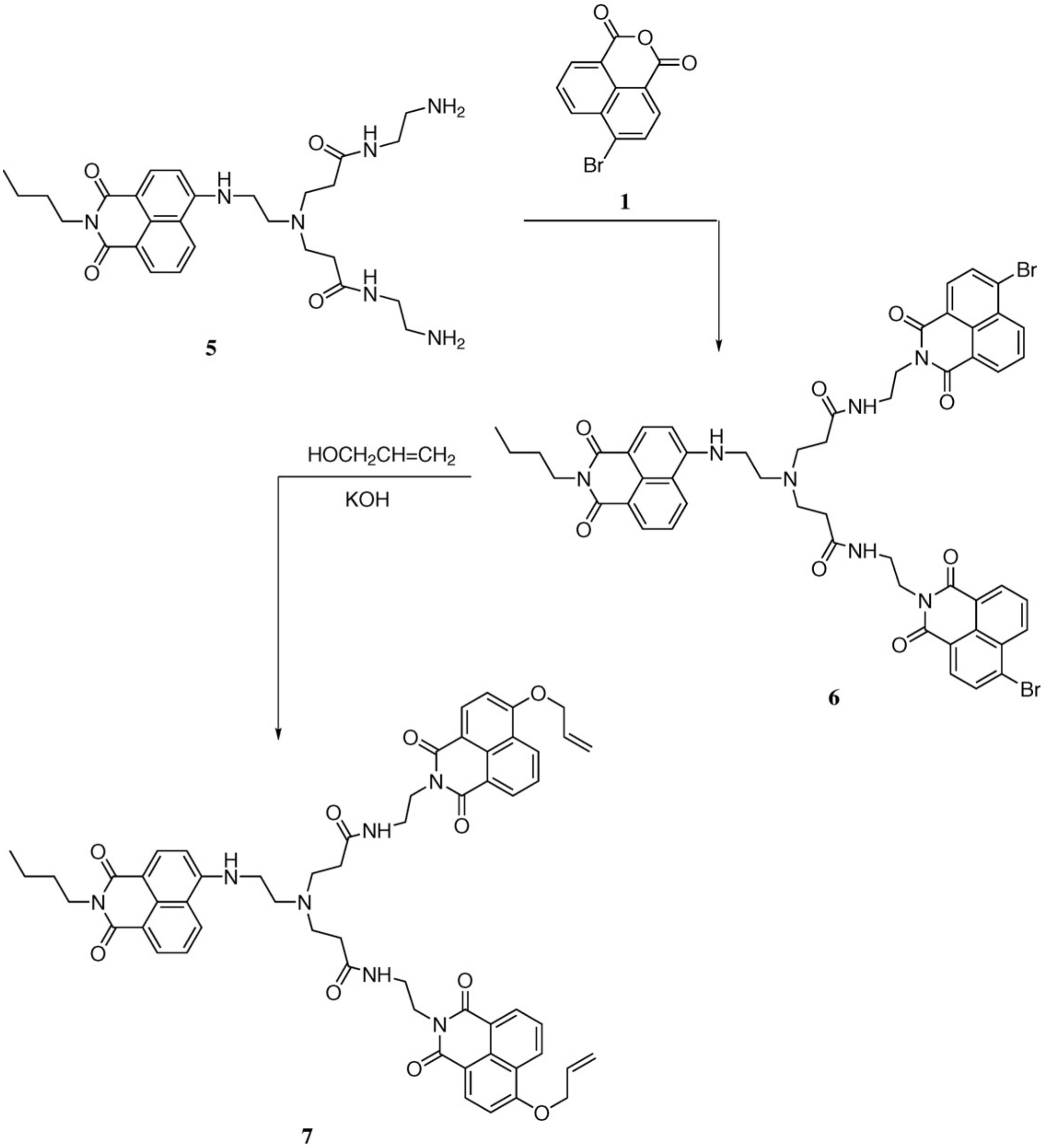
### 3.2. Photophysical investigations

Normalized absorption spectra of the light harvesting antenna **7** and reference compounds (amidoamine-dendronized 1,8-naphthalimide **5** and 4-allyloxy-*N*-*n*-butyl-1,8-naphthalimide **8**) in a chloroform solution are plotted in Fig. 2. As can be seen the spectrum of light harvesting system **7**, as expected, contains two bands corresponding to the individual absorptions of the 4-allyoxy-1,8-naphthalimide donors **8** and the 4-amino-1,8-naphthalimide acceptor **5**.

Photophysical properties of the 4-substituted-1,8-naphthalimides are basically related to the polarization of the 1,8-naphthalimide molecule and may be influenced by the environmental effect of the media.

The absorption spectral data of the examined compounds **5**, **7** and **8**, measured in solvents of different polarity, are listed in Table 1. The absorption peaks at about 358–363 nm are attributed to the absorption of the peripheral blue emitting 1,8-naphthalimide moieties (compound **8**), while the absorption peaks characterized focal yellow-green emitting 1,8-naphthalimide unit (compound **5**) are located at 430–440 nm. The dendron **7** shows very similar absorption characteristics as shown in Fig. 2. A typical bathochromic shift of the longest-wavelength band (compounds **5** and **7**) with increasing the solvent polarity was observed. Any specific effects in protic ethanol were not observed, which indicates lack of intermolecular H-bond formation in the dyes' ground state.

The molar extinction coefficients ($\varepsilon$) of the dyes 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 ($\pi$,$\pi$*) 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



Scheme 4.

blue emitting 1,8-naphthalimide **8**, suggesting no ground state interaction between the peripheral 1,8-naphthalimide units. On the other hand the molar extinction coefficient (ε) of the focal 1,8-naphthalimide chromophore in antenna **7** is approximately the same as that of the reference yellow-green emitting 1, 8-naphthalimide **5**.

The fluorescence spectrum of the light harvesting antenna **7**, obtained after excitation within the spectral region of maximal absorption of the peripheral fluorophore ($\lambda_{ex} = 360$ nm), showed as expected two emission bands, corresponding to the emission bands of the donor and acceptor 1,8-naphthalimide fragments in the donor–acceptor system **7** (Fig. 3).

Table 1

Absorption maxima $\lambda_A$ and extinction coefficient ε (log ε) of antenna **7**, “yellow-green” amidoamine-functionalized 1,8-naphthalimide **5** and blue emitting 1,8-naphthalimide **8** in solvents of different polarity

| Compound | Chloroform | | Acetonitrile | Ethanol | DMF |
|---|---|---|---|---|---|
| | $\lambda_A$ (nm) | ε, log ε (l mol$^{-1}$ cm$^{-1}$) | $\lambda_A$ (nm) | $\lambda_A$ (nm) | $\lambda_A$ (nm) |
| **5** | 434 | 11 870, 4.074 | 430 | 440 | 440 |
| **7** | 370 | 22 536, 4.353 | 365 | 369 | 365 |
| | 436 | 12 088, 4.082 | 434 | 445 | 441 |
| **8** | 362 | 12 313, 4.090 | 358 | 360 | 361 |

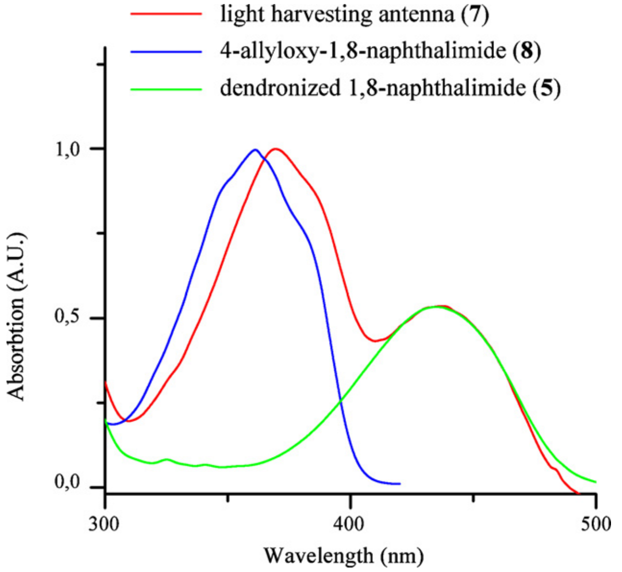


Fig. 2. Normalized absorption spectra of antenna **7** (red line), periphery (compound **8**, blue line) and core (compound **5**, green line) in chloroform at concentration $10^{-5}$ mol l$^{-1}$.

The steady-state fluorescence characteristics of the light harvesting antenna **7** and reference compounds **5** and **8** such as fluorescence ($\lambda_F$) maxima, Stokes shift ($\nu_A - \nu_F$), oscillator strength (*f*), fluorescent both quantum ($\Phi_F$) and energy ($E_F$) yields were measured in a chloroform solution and presented in Table 2.

In a chloroform solution the periphery of antenna **7** and reference 1,8-naphthalimide **8** display blue fluorescence, while the core of dendron **7** and the reference compound **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) substituents at C-4 position to the electron-accepting carbonyl groups. The fluorescence Franck Condon (FC) transitions $\lambda_F$ are in the spectral region 437–443 nm for antenna periphery and reference blue emitting fluorophore **8** and 508–514 nm for antenna core and reference yellow-green emitting fluorophore **5**. In all cases the shape and the maximum of the fluorescence band do not depend of the excitation wavelength and the excitation spectra are identical to the corresponding absorption spectra.

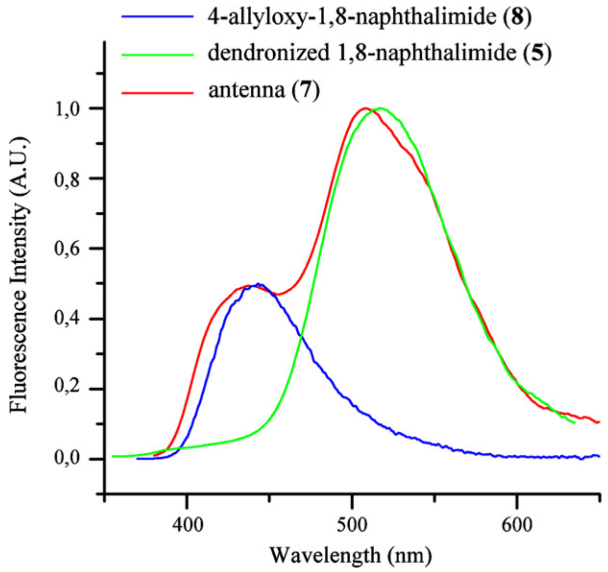


Fig. 3. Normalized emission spectra of periphery at $\lambda_{ex}$ = 360 nm (compound **8**, blue line), core at $\lambda_{ex}$ = 440 nm (compound **5**, green line) and antenna **7** at $\lambda_{ex}$ = 360 nm (red line) in chloroform at concentration $10^{-5}$ mol l$^{-1}$.

Table 2
Fluorescence characteristics of antenna **7** and reference compounds **5** and **8** in a chloroform solution

| Compound | $\lambda_F$ (nm) | $\nu_A - \nu_F$ (cm$^{-1}$) | *f* | $\Phi_F$ | $E_F$ |
|---|---|---|---|---|---|
| **5** | 514 | 3568 | 0.200 | 0.17 | 0.144 |
| **7** | 437 | 4144 | 0.450 | 0.03 | 0.025 |
| | 508 | 3251 | 0.196 | 0.23 | 0.197 |
| **8** | 443 | 5051 | 0.248 | 0.98 | 0.801 |

The Stokes shift ($\nu_A - \nu_F$) and oscillator strength (*f*) are important characteristics for the fluorescent compounds. The Stokes shift is a parameter 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 Stokes shifts (cm$^{-1}$) were calculated by Eq. (1).

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

The Stock's shift values of the compounds under study between 3251 and 3568 cm$^{-1}$ for the blue emitting dendron periphery **7** and blue emitting reference compound **8** as well as between 4144 and 5051 cm$^{-1}$ for the yellow-green focal chromophore **7** and yellow-green emitting reference compound **5** correspond to the results for other 1,8-naphthalimide derivatives [25] and these values do not indicate remarkable changes in the geometry of the first singlet excited state due to the excitation.

The oscillator strength (*f*) shows the effective number of electrons whose transition from ground to excited state gives the absorption area in the electron spectrum. Values of the oscillator strength were calculated using Eq. (2) where $\Delta\nu_{1/2}$ is the width of the absorption band (cm$^{-1}$) at 1/2 ($\varepsilon_{max}$).

$$f = 4.32 \times 10^{-9} \Delta\nu_{1/2}\varepsilon_{max} \tag{2}$$

The values of the oscillator strength for the 1,8-naphthalimides **5**, **7** and **8** are 0.196–0.450, which is in agreement with previous investigations where 1,8-naphthalimide derivatives have oscillator strength values in the range 0.15–0.45 depending on the experimental conditions [24].

The ability of the molecules to emit the absorbed light energy is characterized quantitatively by the fluorescence quantum yield ($\Phi_F$). The quantum yields of fluorescence were calculated using *p*-methoxybenzylidenephthalide ($\Phi_F$ = 0.14 in ethanol) 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.

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

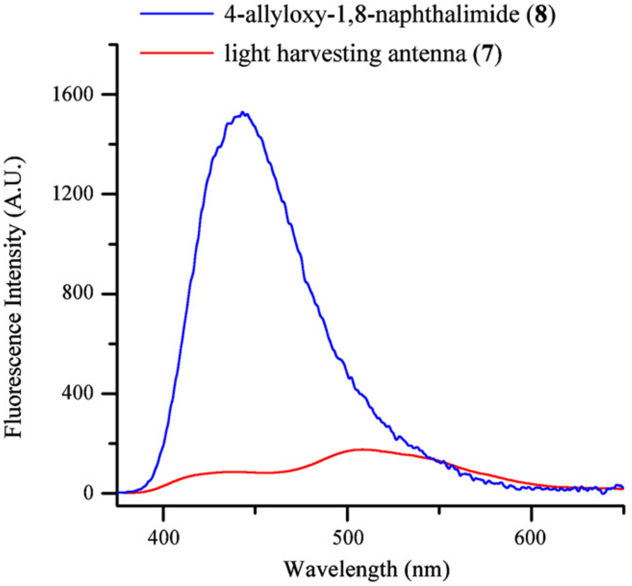


Fig. 4. Fluorescence spectra at $\lambda_{ex} = 360$ nm of blue emitting 1,8-naphthalimide **8** (blue line) and donor–acceptor system **7** (red line) in chloroform, recorded at the same optical density.

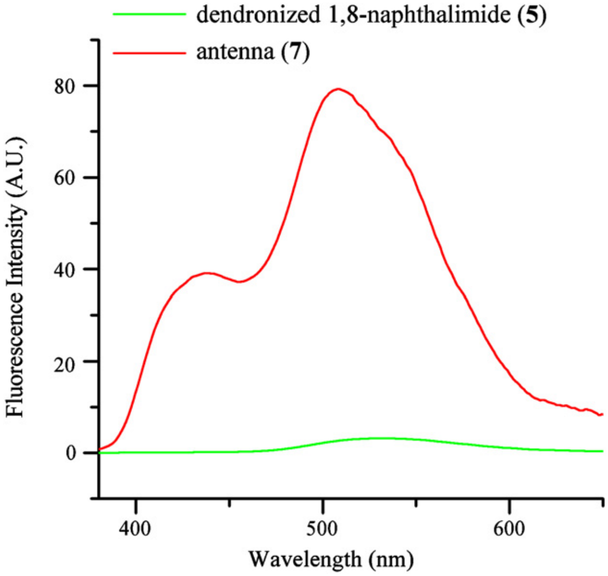


Fig. 5. Fluorescence spectra ($\lambda_{ex} = 360$ nm) of yellow-green emitting 1,8-naphthalimide **5** (green line) and donor–acceptor system **7** (red line) in chloroform at concentration $10^{-5}$ mol $l^{-1}$.

The energy yield of fluorescence $E_F$ (Table 1), calculated by Eq. (4), could also be used instead of $\Phi_F$.

$$E_F = \Phi_F \frac{\lambda_A}{\lambda_F} \qquad (4)$$

As can be seen (Table 2) the quantum yield of fluorescence of the blue emitting dendron periphery is much lower than that of reference compound **8**. This phenomenon is due to the periphery fluorescence quenching in donor–acceptor system **7** caused by the energy transfer from the terminal dye fragments to the focal chromophore. This is apparently from the graphics plotted in Fig. 4 where are presented the fluorescence spectra of the light harvesting system **7** and the comparative 1,8-naphthalimide **8**, recorded at the same optical density.

As a result of the energy transfer, the emission intensity of the periphery (blue emitting donor 1,8-naphthalimide fragments) in the light harvesting system was decreased more than 93% in comparison with the reference blue emitting 4-allyoxy-*N*-*n*-butyl-1,8-naphthalimide **8** (Fig. 4). At the same time, under excitation at 360 nm (within the maximal absorption of the peripheral fluorophore) the amidoamine-dendronized 1,8-naphthalimide **5** showed a scarcely perceptible emission in the yellow-green spectral region, while the core fluorescence intensity of the donor–acceptor system **7** in the yellow-green spectral region, due to the energy transfer from the periphery, is considerably higher (Fig. 5).

The core fluorescence intensity enhancement of the donor–acceptor system **7** is more than 26 times in respect to the fluorescence intensity of amidoamine-dendronized 1,8-naphthalimide **5**, which indicates efficient energy transfer between the donor and acceptor 1,8-naphthalimide fragments.

It should be also pointed out that the results obtained are in agreement with the photophysical properties of other similar systems capable of directional energy transfer between different chromophores. For example, Fréchet et al. [30] and Tian at al. [31] reported several donor/acceptor couples (coumarin 2/coumarin 343, coumarin 2/1,8-naphthalimide, 1,8-naphthalimide/perylene, carbazole/1,8-naphthalimide, oxadiazole/1,8-napthalimide) based on poly(aryl ether) dendrimers, in which peripheral donor emission quenching efficiency is 84–98% and core luminescence enhancing ratio is between 3 and 16, depending the dendrimer generation number. This shows that the novel polyamidoamine based cascade system **7** would be able to act as highly efficient light harvesting antenna.

## 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 convergent 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 emission of the peripheral donor dyes and the absorbance of the acceptor 1,8-naphthalimide was more than 95%. After excitation within the spectral region of maximal absorption of the peripheral fluorophores ($\lambda_{ex} = 360$ nm), as a result of the energy transfer, the blue emission intensity of the periphery was decreased with 93%, while the yellow-green core fluorescence enhancement of the system was more than 26 times with respect to the fluorescence intensity of the comparative yellow-green emitting 1,8-naphthalimide **5**. This indicates efficient energy transfer between the donor and acceptor 1,8-naphthalimide fragments in the donor–acceptor system. Data obtained clearly showed that the novel compound

**7** would be able to act as highly efficient light harvesting antenna.

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## References

[1] (a) G. Mc Dermott, S. Prince, A. Freer, A. Hawthornthwaite-Lawless, M. Papiz, R. Cogdell, N. Isaacs, Nature 374 (1995) 517;
(b) W. Kühlbrandt, D. Wang, Nature 350 (1991) 130;
(c) W. Kühlbrandt, Nature 374 (1995) 497.

[2] (a) G. Stewart, M. Fox, J. Am. Chem. Soc. 118 (1996) 4354;
(b) D. Gust, T. Moore, A. Moore, Acc. Chem. Res. 26 (1993) 198;
(c) G. Steinberg-Yfrach, P. Liddell, S. Hung, A. Moore, D. Gust, T. Moore, Nature 385 (1997) 239.

[3] (a) J.-S. Hsiao, B. Krueger, R. Wagner, T. Johnson, J. Delaney, D. Mauzerall, G. Fleming, J. Lindsey, D. Bocian, R. Donohoe, J. Am. Chem. Soc. 118 (1996) 11181;
(b) F. Li, S. Yang, Y. Ciringh, J. Seth, C. Martin, D. Singh, D. Kim, R. Birge, D. Bocian, D. Holten, J. Lindsey, J. Am. Chem. Soc. 120 (1998) 10001;
(c) A. Nakano, A. Osuka, I. Yamazaki, T. Yamazaki, Y. Nishimura, Angew. Chem. Int. Ed. 37 (1998) 3023.

[4] (a) G. Denti, S. Campagna, S. Serroni, M. Ciano, V. Balzani, J. Am. Chem. Soc. 114 (1992) 2944;
(b) P. Belser, A. von Zelewsky, M. Frank, C. Seel, F. Vögtle, L. De Cola, F. Barigelletti, V. Balzani, J. Am. Chem. Soc. 115 (1993) 4076;
(c) C.-C. You, C. Hippius, M. Grüne, F. Würthner, Chem. Eur. J. 12 (2006) 7510.

[5] (a) D. Ng, J. Guillet, Macromolecules 15 (1982) 724;
(b) D. Ng, J. Guillet, Macromolecules 15 (1982) 728;
(c) D. Watkins, M. Fox, J. Am. Chem. Soc. 116 (1994) 6441;
(d) J. Serin, X. Schultze, A. Adronov, J. Fréchet, Macromolecules 35 (2002) 5396.

[6] (a) C. Devadoss, P. Bharathi, J. Moore, J. Am. Chem. Soc. 118 (1996) 9635;
(b) M. Shortreed, S. Swallen, Z.-Y. Shi, W. Tan, Z. Xu, C. Devadoss, J. Moore, R. Kopelman, J. Phys. Chem. B 101 (1997) 6318;
(c) A. Adronov, P. Malenfant, J. Fréchet, Chem. Mater. 12 (2000) 1463;
(d) A. Adronov, S. Gilat, J. Fréchet, K. Ohta, F. Neuwahl, G. Fleming, J. Am. Chem. Soc. 122 (2000) 1175;
(e) T. Weil, E. Reuter, K. Müllen, Chem. Eur. J. 10 (2004) 1398;
(f) W.R. Dichtel, S. Hecht, M.J. Fréchet, Org. Lett. 7 (2005) 4451.

[7] (a) D. Tomalia, A. Naylor, W. Goddard, Angew. Chem. Int. Ed. 29 (1990) 138;
(b) S. Gilat, A. Adronov, J. Fréchet, J. Org. Chem. 64 (1999) 7474;
(c) V. Balzani, P. Ceroni, S. Gestermann, C. Kauffmann, M. Gorka, F. Vögtle, Chem. Commun. (2000) 853;
(d) C. Cardona, J. Alvarez, A. Kaifer, T. McCarley, S. Pandey, G. Baker, N. Bonzagni, F. Bright, J. Am. Chem. Soc. 122 (2000) 6139;
(e) V. Balzani, P. Ceroni, S. Gestermann, M. Gorka, C. Kauffmann, F. Vögtle, Tetrahedron 58 (2002) 629;
(f) S. Ghosh, A. Banthia, Tetrahedron Lett. 43 (2002) 6459;
(g) S. Ghosh, A. Banthia, Supramol. Chem. 16 (2004) 487.

[8] (a) L. Patrick, A. Whiting, Dyes Pigments 52 (2002) 137;
(b) I. Grabchev, R. Betcheva, J. Photochem. Photobiol. A: Chem. 142 (2001) 73;
(c) I. Grabchev, T. Konstantinova, S. Guittonneau, P. Mealier, Dyes Pigments 35 (1997) 361;
(d) L. Patrick, A. Whiting, Dyes Pigments 55 (2002) 123;
(e) T. Konstantinova, R. Lazarova, J. Univ. Chem. Technol. Met. (Sofia) 38 (2003) 69.

[9] (a) E. Martin, R. Weigand, A. Pardo, J. Lumin. 68 (1996) 157;
(b) V. Gruzinskii, A. Kukhta, G. Shakkah, J. Appl. Spectrosc. 65 (1998) 444.

[10] Z.-F. Tao, X. Qian, Dyes Pigments 43 (1999) 139.

[11] W. Stewart, J. Am. Chem. Soc. 103 (1981) 7615.

[12] M.M. de Souza, R. Correa, V.C. Filho, I. Grabchev, V. Bojinov, Pharmazie 56 (2002) 430.

[13] (a) H. Facoetti, P. Robin, P. Le Barny, M. Schott, C.-M. Bouche, P. Berdague, Synth. Met. 81 (1996) 191;
(b) J. Morgado, J. Gruner, S.P. Walcott, T.M. Yong, R. Cervini, S.C. Moratti, A.B. Holmes, R.H. Friend, Synth. Met. 95 (1998) 113;
(c) W. Zhu, C. Hu, K. Chen, H. Tian, Synth. Met. 96 (1998) 151.

[14] (a) H. Tian, J. Gan, K. Chen, J. He, Q. Song, X. Hou, J. Mater. Chem. 12 (2002) 1262;
(b) I. Grabchev, J.-M. Chovelon, X. Qian, J. Photochem. Photobiol. A: Chem. 158 (2003) 37;
(c) I. Grabchev, J.-M. Chovelon, X. Qian, New J. Chem. 27 (2003) 337;
(d) I. Grabchev, X. Qian, Y. Xiao, W. Zhang, New J. Chem. 26 (2002) 920;
(e) H. Tian, T. Xu, Y. Zhao, K. Chen, J. Chem. Soc. Perkin Trans. 2 (1999) 545.

[15] (a) T. Gunnlaugsson, C. McCoy, R. Morrow, C. Phelan, F. Stomeo, ARKIVOC 7 (2003) 216;
(b) X. Poteau, A. Brown, R. Brown, C. Holmes, D. Matthew, Dyes Pigments 47 (2000) 91;
(c) L. Jia, Y. Zhang, X. Guo, X. Qian, Tetrahedron Lett. 45 (2004) 3969.

[16] (a) W. Zhu, M. Hu, R. Yao, H. Tian, J. Photochem. Photobiol. A: Chem. 154 (2003) 169;
(b) T. Hassheider, S. Benning, H.-S. Kitzerow, M.-F. Achard, H. Bock, Angew. Chem. Int. Ed. 40 (2001) 2060;
(c) F. Cacialli, R. Friend, C. Bouche, P. Le Barny, H. Facoetti, F. Soyer, P. Robin, J. Appl. Phys. 83 (1998) 2343;
(e) W. Zhu, N. Minami, S. Kazaoui, Y. Kim, J. Mater. Chem. 13 (2003) 2196.

[17] (a) I. Grabchev, I. Moneva, E. Wolarz, D. Bauman, Z. Naturforsch. 51a (1996) 1185;
(b) I. Grabchev, J.-M. Chovelon, Polym. Adv. Technol. 14 (2003) 601;
(c) I. Grabchev, I. Moneva, V. Bojinov, S. Guittonneau, J. Mater. Chem. 10 (2000) 1291;
(d) G. Scherovsky, Makromol. Chem. Macromol. Symp. 69 (1993) 87;
(e) I. Grabchev, I. Moneva, J. Appl. Polym. Sci. 74 (1999) 151.

[18] F. Cosnard, V. Wintgens, Tetrahedron Lett. 39 (1998) 2751.

[19] (a) I. Grabchev, X. Qian, V. Bojinov, Y. Xiao, W. Zhang, Polymer 43 (2002) 5731;
(b) I. Grabchev, V. Bojinov, J.-M. Chovelon, Polymer 44 (2003) 4421;
(c) I. Grabchev, J.-M. Chovelon, V. Bojinov, G. Ivanova, Tetrahedron 59 (2003) 9591;
(d) I. Grabchev, R. Betcheva, V. Bojinov, D. Staneva, Eur. Polym. J. 40 (2004) 1249;
(e) I. Grabchev, C. Petkov, V. Bojinov, Dyes Pigments 62 (2004) 229.

[20] V. Bojinov, N. Georgiev, P. Nikolov, J. Photochem. Photobiol. A: Chem. 193 (2007) 129.

[21] V. Bojinov, I. Grabchev, Dyes Pigments 51 (2001) 57.

[22] T. Konstantinova, P. Meallier, I. Grabchev, Dyes Pigments 22 (1993) 191.

[23] P. Nikolov, F. Fratov, S. Minchev, Z. Naturforsch. 38a (1983) 200.

[24] (a) V. Bojinov, G. Ivanova, D. Simeonov, Macromol. Chem. Phys. 205 (2004) 1259;
(b) I. Grabchev, C. Petkov, V. Bojinov, Macromol. Mater. Eng. 287 (2002) 904;
(c) V. Bojinov, I. Panova, Dyes Pigments 74 (2007) 551;
(d) V. Bojinov, T. Konstantinova, Sens. Actuators B Chem. 23 (2007) 869;
(e) I. Grabchev, V. Bojinov, H. Petkov, Dyes Pigments 51 (2001) 1;
(f) S. Yang, F. Meng, H. Tian, K. Chen, Eur. Polym. J. 38 (2002) 911.

[25] (a) V. Bojinov, D. Simeonov, N. Georgiev, Dyes Pigments 76 (2008) 41;
(b) J. Mata, Adv. Colour. Sci. Technol. 2 (1999) 162.

[26] (a) T. Förster, Ann. Phys. 2 (1948) 55;
(b) T. Förster, Z. Naturforsch. A 4 (1949) 321.
[27] (a) S.-C. Chang, R. Utecht, D. Lewis, Dyes Pigments 43 (1999) 83;
(b) S. Ghorbanian, J. Tyman, V. Tychopoulos, J. Chem. Technol. Biotechnol. 75 (2000) 1127;
(c) M. Alexiou, J. Tyman, I. Wilson, Tetrahedron Lett. 22 (1981) 2303.
[28] B. Liu, H. Tian, Chem. Commun. (2005) 3156.
[29] R. Esfand, D. Tomalia, in: J. Fréchet, D. Tomalia (Eds.), Dendrimers and Other Dendritic Polymers, John Wiley & Sons, Chichester, 2001, pp. 587–604.
[30] (a) S. Gilat, A. Adronov, J. Fréchet, Angew. Chem. Int. Ed. 38 (1999) 1422;
(b) J. Serin, D. Brousmiche, J. Fréchet, Chem. Commun. (2002) 2605;
(c) P. Furuta, J. Fréchet, J. Am. Chem. Soc. 125 (2003) 13173.
[31] P. Du, W.-H. Zhu, Y.-Q. Xie, F. Zhao, C.-F. Ku, Y. Cao, C.-P. Chang, H. Tian, Macromolecules 37 (2004) 4387.