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Synthesis and photophysical properties of fluorescence sensing ester- and amidoamine-functionalized 1,8-naphthalimides

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Abstract

Novel ester- and amidoamine-functionalized 1,8-naphthalimides have been synthesized based on a convergent approach. Their basic photophysical properties in both protic and aprotic organic solvents of different polarity have been determined and discussed. Depending on the solvent polarity the fluorescence maxima are in the spectral range 480–550 nm, the fluorescence quantum yields vary from 0.23 to 0.46, the fluorescence lifetimes are long, in order of 9 ns. Absorption and fluorescence characteristics of the dyes as a function of pH were investigated in water/ethanol (4:1, v/v) solution. The starting 1,8-naphthalimide, containing primary amino receptor at the 1,8-naphthalimide 4-amino moiety, did not show significant changes in the emission properties as a function of pH. On the contrary the ester- and amidoamine-functionalized 1,8-naphthalimides were found to display sensitive fluorescence signal amplification over a wide pH scale, which has been ascribed to a photoinduced electron transfer from the tertiary amine receptor to the fluorophore 4-amino donor. From the changes in the fluorescence intensity pK_a values of 4.42 and 4.86 for ester- and amidoamine-functionalized 1,8-naphthalimides, respectively were determined, making the synthesized compounds of potential use as pH chemosensing materials.

Keywords: 1,8-Naphthalimide; Fluorescence; pH sensing; Photoinduced electron transfer (PET)

1. Introduction

Environment-sensitive fluorophores are a special class of chromophores [1]. Particularly useful 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 colouration of polymers [2], laser active media [3], potential photosensitive biologically units [4], fluorescent markers in biology [5], analgesics in medicine [6], light emitting diodes [7], photoinduced electron transfer sensors [8], fluorescence switchers [9], electroluminescent materials [10], liquid crystal displays [11] and ion probes [12].

Branched molecules are well defined and exhibit a three-dimensional structure that is roughly spherical or globular. A characteristic of branched molecules is the presence of numerous peripheral chain ends that all surround a single core. The globular shape of branched molecules provides a large surface area that can be decorated with the chromophores. In this context, labelling of branched architectures with fluorophore units is one of the viable routes of generating suitable luminescent molecules [13] having well-defined branched and compartmentalized structures.

Molecular systems in which fluorescence switches between "on" and "off" states are currently of great interest as these can be modulated, or tuned, by employing external sources such as ions, molecules, light, etc. [14,15]. They can be designed according to a few principles with emphasis on the mechanism of photoinduced electron transfer (PET). PET systems using the "fluorophore-spacer-receptor" format, developed by de Silva [16], are one of the most popular approaches to the design of fluorescent sensors and switchers [17]. In this model the excited state of the fluorophore can be quenched by intermolecular electron transfer from the receptor to the fluorophore (or *vice versa*) prior recognition. Upon recognition of species such as cations, the oxidation potential of the receptor is increased and this causes

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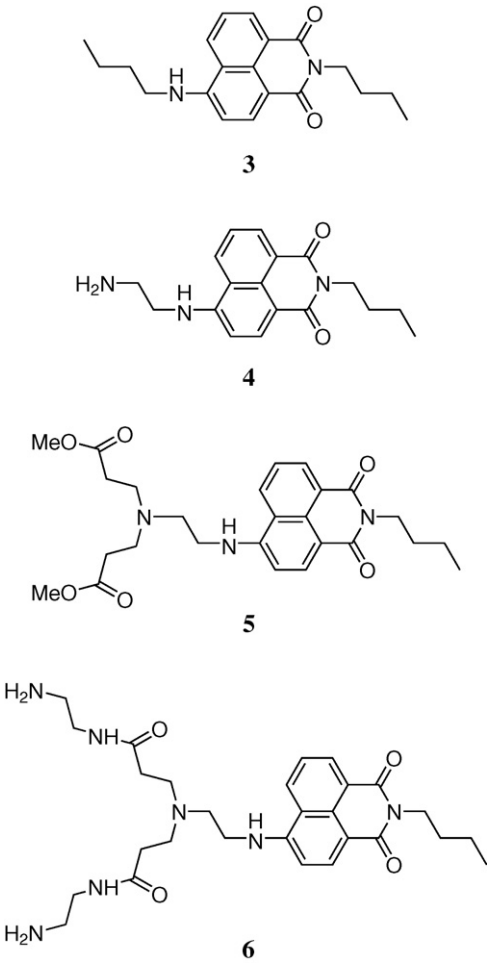
the electron transfer to be "switched off" and in turn the emission to be "switched on" [18].

Considerable interest in branched molecules has arisen because of their novel structural properties and wide range of potential applications [19]. Our first investigations on the synthesis and photophysical properties of some new polyamidoamine derivatives comprising 1,8-naphthalimide units in their periphery were published previously [20]. We have studied their fluorescence properties in the presence of different "guest" molecules and we have observed enhancement of the fluorescence intensity, making them of potential use as chemosensing materials. Constructing ester- and amidoamine branches around a luminescent group could profitably alter the luminescence signals in the macromolecular structure and amplify the signals for sensing purposes. In this paper, we report the convergent construction of novel ester- and amidoamine-branched fluorophores core-functionalized with 1,8-naphthalimide units together with their photophysical properties and fluorescence signalling as a function of pH. This issue takes on added significance given the growing body of sensors and other optical devices which employ 1,8-naphthalimide fluorophores [1,18]. Hence, synthesized compounds **4**–**6** (Scheme 1) were investigated by electronic absorption and emission spectroscopy.



Scheme 1.

In order to receive a more complete comparative picture for the influence of both the branched and peripheral nitrogen donor (amine receptor) to the 4-amino-1,8-naphthalimide fluorophore through the ethylene spacer (compounds **4**–**6**), 4-*n*-butylamino-*N*-*n*-butyl-1,8-naphthalimide **3** [21], not containing amine receptor in its molecule, was involved in the present study (Scheme 1).

2. Experimental

2.1. Materials

The starting 4-bromo-1,8-naphthalic anhydride **1** was prepared according to the reported procedure [22]. 4-*n*-Butylamino-*N*-*n*-butyl-1,8-naphthalimide **3** and 4-(2-aminoethyl)amino-*N*-*n*-butyl-1,8-naphthalimide **4** were prepared by analogy with the previously reported procedures [21,23]. Butylamine, ethylenediamine and methyl acrylate (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 ^1H NMR spectra (chemical shifts are given as δ in ppm) were recorded on a Bruker DRX-250 spectrometer, operating at 250.13 MHz. TLC was performed on silica gel, Fluka F60 254, 20 × 20, 0.2 mm. The melting points were determined by means of a Kofler melting point microscope. The UV–vis absorption spectra were recorded on a spectrophotometer Lambda 25 (Perkin Elmer). The corrected excitation and fluorescence spectra were taken on a Perkin Elmer LS55 spectrofluorimeter. The fluorescence quantum yields (Q_F) were measured relatively to Coumarin 6 ($Q_F = 0.78$ in ethanol) [24]. The fluorescence decay curves were measured in solution at room temperature (25 °C) with a nanosecond Single Photon Counting Spectrofluorimeter System PRA 2000, using a nitrogen filling flash lamp with FWHM about 2.5 ns, excitation wavelength 337 nm, emission wavelength 540 nm, time-resolution 0.1 ns/channel. All collected decay curves have 10,000 counts in the maximum. The fluorescence lifetimes τ_f were calculated from the decay curves using the method of non-linear least-squares curve fitting. The goodness of the fit was assessed by the weighted residuals and the reduced chi-square values χ^2.

2.3. Synthesis of 1,8-naphthalimides

2.3.1. 4-Bromo-N-n-butyl-1,8-naphthalimide (2)

A suspension of 4-bromo-1,8-naphthalic anhydride **1** (2.5 g, 9.0 mmol) and *n*-butylamine (0.9 ml, 9.0 mmol) in 25 ml of ethanol was refluxed with stirring for 6 h. The crude product that precipitated on cooling was filtered off and treated with 25 ml of 5% aqueous sodium carbonate. The solid phase was filtered off, washed with water and dried to give 2.1 g (70%) of pure 4-bromo-*N*-*n*-butyl-1,8-naphthalimide **2** as yellow-brown crystals, m.p. 108–110 °C (lit. [23] 109–110 °C).

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

To a solution of *n*-butylamine (0.3 ml, 3.0 mmol) and 4-bromo-*N*-*n*-butyl-1,8-naphthalimide **2** (1.0 g, 3.0 mmol) in 10 ml of DMF, 0.1 g of $CuSO_4 \cdot 5H_2O$ were added. The resulting mixture was heated to reflux for 5 h with stirring. After cooling to room temperature, the solution was poured into 100 ml of water, and the precipitate was collected by filtration, washed with water and dried. Recrystallization from ethanol afforded 0.79 g (81%) of 4-*n*-butylamino-*N*-*n*-butyl-1,8-naphthalimide **3** as yellow-orange crystals, m.p. 124–125 °C (lit. [21b] 126–127 °C, lit. [21c] 127–128 °C).

*2.3.3. 4-(2-Aminoethyl)amino-N-n-butyl-1,8-naphthalimide (**4**)*

To a solution of ethylenediamine (6.0 ml, 90 mmol) and 4-bromo-*N*-*n*-butyl-1,8-naphthalimide **2** (1.0 g, 3.0 mmol) in 15 ml of DMF, 0.1 g of $CuSO_4 \cdot 5H_2O$ were added. The resulting mixture was heated to reflux for 5 h with stirring. After cooling to room temperature, the solution was poured into 100 ml of water, and the precipitate was collected by filtration, washed with water and dried. Recrystallization from toluene afforded 0.55 g (59%) of 4-(2-aminoethyl)amino-*N*-*n*-butyl-1,8-naphthalimide **4** as yellow-orange crystals, m.p. 131–133 °C (lit. [23] 128–131 °C).

IR (KBr) cm^{-1}: 3362 and 3288 (νNH_2); 2946 and 2910 (νCH); 1694 ($\nu^{as}N–C{=}O$); 1660 ($\nu^{s}N–C{=}O$).

^1H NMR ($CHCl_3$-*d* + MeOH-d_4, 250 MHz) ppm: 8.45 (dd, 1H, *J* = 7.3 Hz, *J* = 0.9 Hz, naphthalimide H-5); 8.31 (dd, 1H, *J* = 8.3 Hz, *J* = 0.9 Hz, naphthalimide H-7); 8.29 (d, 1H, *J* = 8.3 Hz, naphthalimide H-2); 7.52 (dd, 1H, *J* = 8.3 Hz, *J* = 7.3 Hz, naphthalimide H-6); 6.61 (d, 1H, *J* = 8.5 Hz, naphthalimide H-3); 4.04 (t, 2H, *J* = 7.5 Hz, $(CO)_2NCH_2$); 3.72 (br.s, 2H, NH_2); 3.61 (m, 1H, NH); 3.40 (dd, 2H, *J* = 5.9 Hz, *J* = 5.6 Hz, ArNH$CH_2CH_2NH_2$); 2.99 (dd, 2H, *J* = 6.1 Hz, *J* = 5.4 Hz, ArNHCH$_2CH_2$NH$_2$); 1.59 (m, 2H, $CH_2CH_2CH_2CH_3$); 1.33 (m, 2H, $CH_2CH_2CH_2CH_3$); 0.86 (t, 3H, *J* = 7.2 Hz, $CH_2CH_2CH_2CH_3$).

Elemental analysis: calculated for $C_{18}H_{21}N_3O_2$ (MW 311.38) C 69.43, H 6.80, N 13.49%; found C 69.71, H 6.69, N 13.65%.

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

To a solution of methyl acrylate (0.55 g, 6.4 mmol) in 5 ml of methanol, a solution of 4-(2-aminoethyl)amino-*N*-*n*-butyl-1,8-naphthalimide **4** (0.2 g, 0.64 mmol) in 10 ml of methanol was added dropwise for a period of 30 min. The reaction mixture was stirred for 3 days at room temperature and the excess of methyl acrylate was removed under vacuum, whereupon the ester-functionalized derivative **5** was obtained as yellow-brown oil (0.3 g, 98%).

IR (oil) cm^{-1}: 3348 (νNH); 2950 and 2915 (νCH); 2833 (νOCH_3); 1730 ($\nu COOCH_3$); 1682 ($\nu^{as}N–C{=}O$); 1642 ($\nu^{s}N–C{=}O$).

^1H NMR ($CHCl_3$-*d*, 250 MHz) ppm: 8.57 (d, 1H, *J* = 7.3 Hz, naphthalimide H-5); 8.45 (d, 1H, *J* = 8.6 Hz, naphthalimide H-2); 8.38 (dd, 1H, *J* = 8.3 Hz, *J* = 1.0 Hz, naphthalimide H-7); 7.60 (dd, 1H, *J* = 8.3 Hz, *J* = 7.3 Hz, naphthalimide H-6); 6.67 (d, 1H, *J* = 8.6 Hz, naphthalimide H-3); 6.28 (m, 1H, NH); 4.16 (t, 2H, *J* = 7.6 Hz, $(CO)_2NCH_2$); 3.55 (s, 6H, 2× OCH_3); 3.44 (m, 2H, ArNHCH_2); 2.83 (m, 6H, 3× NCH_2); 2.49 (t, 4H, *J* = 6.4 Hz, 2× CH_2COOCH_3); 1.57 (m, 2H, $CH_2CH_2CH_2CH_3$); 1.32 (m, 2H, $CH_2CH_2CH_2CH_3$); 0.96 (t, 3H, *J* = 7.2 Hz, $CH_2CH_2CH_2CH_3$).

Elemental analysis: calculated for $C_{26}H_{33}N_3O_6$ (MW 483.56) C 64.58, H 6.88, N 8.69%; found C 64.27, H 6.97, N 8.58%.

*2.3.5. Amidoamine-functionalized 1,8-naphthalimide (**6**)*

To a solution of ethylenediamine (1.51 ml, 22.55 mmol) in 2 ml of methanol, a solution of 1,8-naphthalimide **5** (0.2 g, 0.41 mmol) in 10 ml of methanol was added dropwise at 5 °C for a period of 30 min. The reaction mixture was stirred for 168 h at room temperature. Then 10 ml of toluene were added and the methanol was distilled under vacuum. The amidoamine-functionalized 1,8-naphthalimide **6** was obtained as yellow-brown oil (0.22 g, 99%) after the ethylenediamine excess decantation together with the toluene.

IR (oil) cm^{-1}: 3342, 3274 and 3260 (νNH_2 and νNH); 2924 and 2904 (νCH); 1696 ($\nu^{as}N–C{=}O$); 1654 ($\nu^{s}N–C{=}O$); 1633 ($\nu NH–C{=}O$).

^1H NMR (DMSOl-d_6, 250 MHz) ppm: 8.71 (d, 1H, *J* = 8.5 Hz, naphthalimide H-5); 8.42 (d, 1H, *J* = 7.1 Hz, naphthalimide H-7); 8.26 (d, 1H, *J* = 8.6 Hz, naphthalimide H-2); 8.09 (br.s, 1H, NHCO); 8.00 (br.s, 4H, 2× NH_2); 7.67 (t, 1H, *J* = 7.7 Hz, naphthalimide H-6); 6.78 (d, 1H, *J* = 8.6 Hz, naphthalimide H-3); 7.51 (br.s, 1H, NHCO); 4.00 (t, 2H, *J* = 7.3 Hz, $(CO)_2NCH_2$); 3.45 (m, 2H, ArNHCH_2); 3.35 (br.s, 1H, ArNH); 3.06 (m, 4H, CONH$CH_2CH_2NH_2$); 2.73 (m, 6H, 3× NCH_2); 2.56 (m, 4H, CONHCH$_2CH_2$NH$_2$); 2.26 (m, 4H, 2× CH_2CONH); 1.58 (m, 2H, $CH_2CH_2CH_2CH_3$); 1.32 (m, 2H, $CH_2CH_2CH_2CH_3$); 0.91 (t, 3H, *J* = 7.3 Hz, $CH_2CH_2CH_2CH_3$).

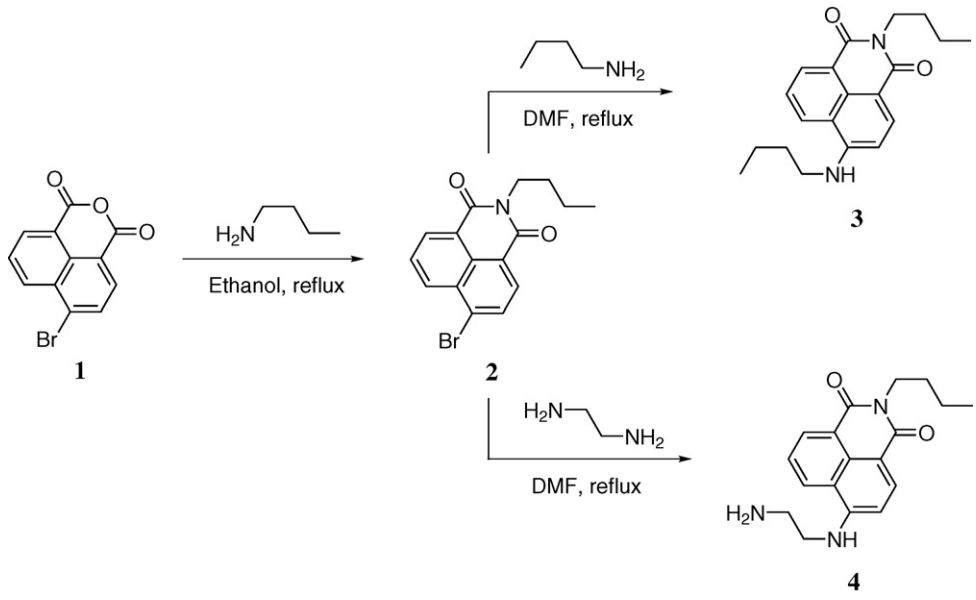
Elemental analysis: calculated for $C_{28}H_{41}N_7O_4$ (MW 539.67) C 62.32, H 7.66, N 18.17%; found C 62.65, H 7.58, N 17.99%.

3. Results and discussion

3.1. Design and synthesis of light-emitting 1,8-naphthalimides

The dyes under study were designed as branched core-functionalized ester- and amino-terminated 1,8-naphthalimide fluorophores for determining pH changes over a wider pH scale. We chose 1,8-naphthalimide chromophore as a fluorescent core of the synthesized compounds, constructed by ester and amidoamine branches with a specific functional periphery, because of its chemical stability and high fluorescent efficiency.

1,8-Naphthalimide **4** and the dendronized dyes (**5**–**6**) are based on the "fluorophore-spacer-receptor" model, where the 4-amino-1,8-naphthalimide moiety is the fluorophore and the ester and amidoamine dendrons are the proton receptors. The ethylene part between fluorophore and the dendrons serves as spacer that covalently separates the two units. In these particular cases, it was predicted that a PET process (an electron trans-



Scheme 2.

fer from the receptor to the excited state of the fluorophore) would quench fluorescence emission of the 1,8-naphthalimide unit. This would represent the "off-state" of the system. The protonation of the amine receptor would increase its oxidation potential, and as such, thermodynamically disallow the electron transfer [25]. Consequently the emission would be "switched on". Thus, we expect the fluorescence to be amplified in acidic media.

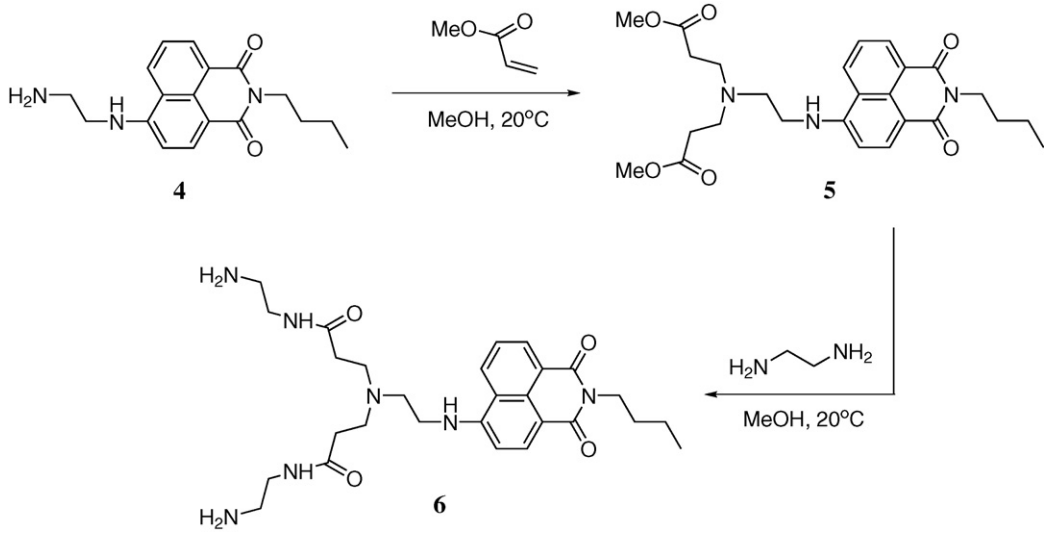
The synthesis of 1,8-naphthalimides **3**–**4** was achieved in two steps as shown in Scheme 2.

4-*n*-Butylamino-*N*-*n*-butyl-1,8-naphthalimide **3**, not containing amine receptor in its molecule, was involved in the present study to receive comparative picture for the influence of the amine receptor to the 4-amino-1,8-naphthalimide fluorophore through the ethylene spacer.

First, intermediate 4-bromo-*N*-*n*-butyl-1,8-naphthalimide **2** was obtained by reacting the 4-bromo-1,8-naphthalic anhydride **1** and *n*-butylamine in anhydrous ethanol at 60 °C by analogy with our previous works [26]. The intermediate **2** was subsequently reacted in DMF under reflux for 5 h with *n*-butylamine or excess of ethylenediamine respectively in the presence of $CuSO_4{\cdot}5H_2O$ as described by Liu and Tian [23] to yield target dyes **3** and **4**. Each target molecule was obtained as yellow-orange solids.

1,8-Naphthalimides **5** and **6** were synthesized as shown in Scheme 3.

The ester-terminated and amino-terminated 1,8-naphthalimides **5** and **6** were synthesized by convergent strategy involves initial Michael addition of 4-(2-aminoethyl)amino-*N*-*n*-butyl-1,8-naphthalimide **4** with methyl acrylate followed by exhaustive amidation of the resulting ester **5** with a large excess of ethylenediamine to afford the amidoamine-functionalized 1,8-naphthalimide (**6**) with reactive amine groups of its periphery.



Scheme 3.

Table 1
Yields, melting points, retention factors and absorption data for 1,8-naphthalimides **2**–**6** in ethanol solution

Compound	Yield (%)	Melting point (°C)	R_f	λ_A (nm)	log ε (l mol^{-1} cm^{-1})
2	70	108–110	0.68[a]	340	4.45
3	81	124–125	0.49[a]	444	4.18
4	59	131–133	0.79[b]	438	4.17
5	98	Oil	0.84[a]	438	4.05
6	99	Oil	0.66[b]	440	4.01

[a] TLC in a solvent system *n*-hexane: acetone = (2:1).
[b] TLC in a solvent system *n*-propanol: 25% ammonium hydroxide = (1:1).

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.

The structures and purities of the desired products were confirmed by conventional techniques. For instance, in the ^{1}H NMR (250.13 MHz, $CDCl_3$) spectra of compounds **4**–**6** a resonance at 6.61–6.78 ppm was observed. This is characteristic for the proton in position C-3 of the 1,8-naphthalimide ring, substituted in position C-4 with an electron-donating amine group. Furthermore, the ^{1}H NMR spectra contained peaks, attributed to the protons for the ester- or amino-terminated compounds **5**–**6** as well as for a *n*-butyl group.

3.2. Photophysical characterization of the dyes

3.2.1. UV–vis absorption properties

The absorption spectrum of compound **2**, containing electron-withdrawing bromine atom at 1,8-naphthalimide C-4 position, in ethanol solution at room temperature shows longest-wavelength absorption maximum in the UV region at $\lambda_A = 340$ nm. Substitution of the bromine atom in compound **2** with electron-donating alkylamino group (compounds **3**–**6**) results in a large bathochromic shift of the longest-wavelength absorption maximum to visible region at $\lambda_A = 438$–444 nm (Fig. 1), which is a typical effect for the conjugated organic compounds. The molar absorptivities of the longest-wavelength absorption maximum in ethanol solution, presented in Table 1, are common for the 1,8-naphthalimide derivatives [2,8d,11c,22,25e].

Absorption spectra of dyes **3**–**6** were recorded in both protic and aprotic solvents of different polarity (Table 2). Data presented in Table 2 and Fig. 1 show that the different alkylamino substituents at the 1,8-naphthalimide C-4 position (compounds **3**–**6**) have a small effect on the energy and the shape of the dyes' absorption bands.

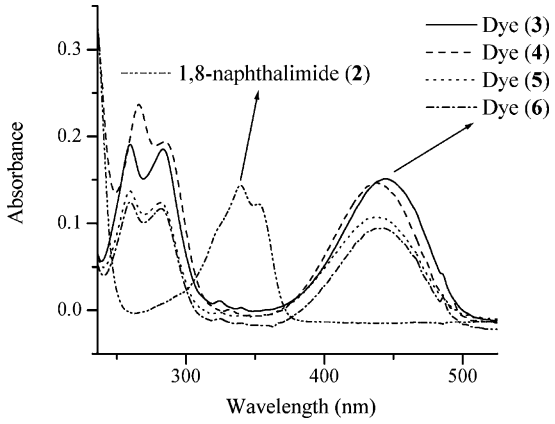


Fig. 1. Absorption spectra of 1,8-naphthalimides **2**–**6** in ethanol at concentration 10^{-5} mol l^{-1}.

Table 2
Absorption maxima (nm) of 1,8-naphthalimides **3**–**6** in solvents of different polarity

Compound	*n*-Hexane	Chloroform	Acetonitrile	Ethanol	Methanol
3	408	427	433	444	444
4	–	426	427	438	436
5	410	428	427	438	438
6	–	430	430	440	438

Also a typical bathochromic shift of the longest-wavelength band with increasing the solvent polarity was observed. Any specific effects in protic solvents (ethanol, methanol) were not observed, which indicates lack of intermolecular H-bond formation in the dyes' ground state.

3.2.2. Steady-state fluorescence measurements in solution at room temperature

The steady-state fluorescence characteristics of 1,8-naphthalimides **3**–**6** in protic and aprotic solvents of different polarity are presented in Table 3. The fluorescence Franck Condon (FC) transitions λ_F are in the spectral region 480–550 nm and shift bathochromically with increasing the solvent polarity. Fig. 2 illustrates the changes in the fluorescence band for compound **5** in solvents of different polarity.

The effect of the C-4 alkylamino substituent on the energy of the dyes' fluorescence maximum is negligible, no more than 350 cm^{-1} in chloroform solution, while in more polar solvents it is even less.

Table 3
Fluorescence characteristics of 1,8-naphthalimides **3**–**6** in solvents of different polarity

Compound	Methanol		Ethanol		Acetonitrile		Chloroform	*n*-Hexane
	λ_F (nm)	Q_F	λ_F (nm)	Q_F	λ_F (nm)	Q_F	λ_F (nm)	λ_F (nm)
3	549	0.56	543	0.7	539	0.75	507	*455* (474 s)
4	549	0.31	543	0.51	539	0.57	509	–
5	549	0.23	543	0.32	539	0.46	509	480
6	550	0.25	545	0.35	540	0.43	514	–

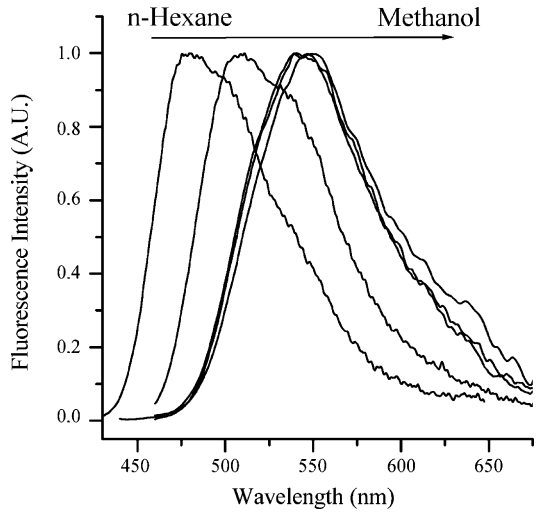


Fig. 2. Normalized fluorescence spectra of 1,8-naphthalimide **5** in solvents of increasing polarity: *n*-hexane, chloroform, acetonitrile, ethanol, methanol at concentration 10^{-5} mol l^{-1}.

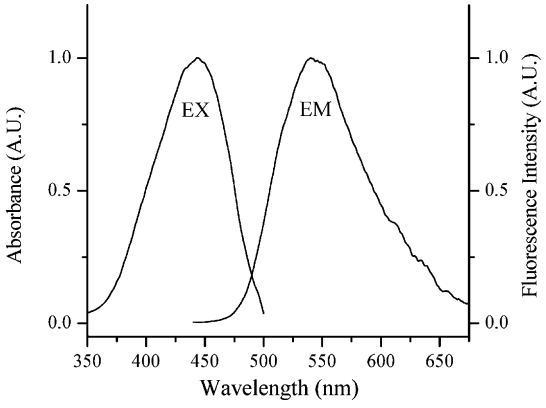


Fig. 3. Normalized excitation (λ_{em} = 550 nm) and emission (λ_{ex} = 450 nm) spectra of 1,8-naphthalimide **6** in ethanol at concentration 10^{-5} mol l^{-1}.

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 presents the normalized excitation and emission spectra of 1,8-naphthalimide **6** in ethanol solution as a typical example for the spectra of all compounds under study. The fluorescence band is the mirror image of the longest-wavelength absorption one and no concentration effects on the shape of the fluorescence bands were observed for $C < 10^{-5}$ mol l^{-1}.

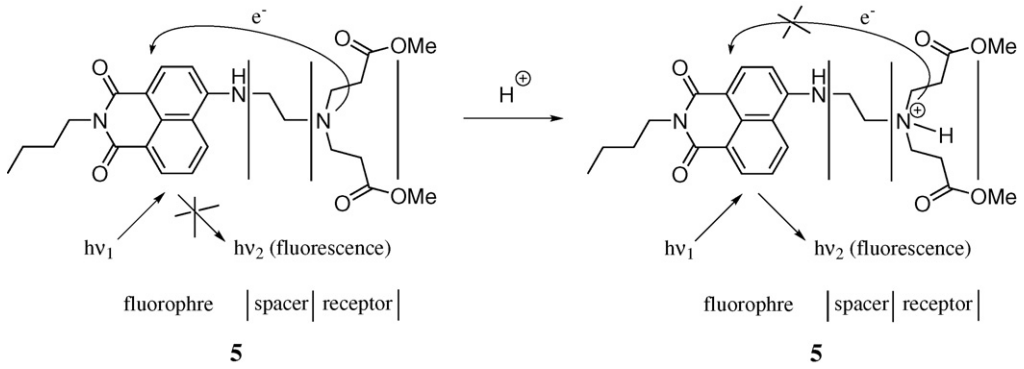
The Stock's shift values are about 4000 cm^{-1}, which corresponds to the results for other 1,8-naphthalimide derivatives [27] and these values do not indicate remarkable changes in the geometry of the first singlet excited state due to the excitation.

On the contrary to the negligible effect on the energy of the fluorescence FC transitions, the fluorescence ability of compounds **3**–**6** is clearly influenced by the nature of the substituent at C-4 position in the 1,8-naphthalimide molecule. As can be seen from the data in Table 3 the quantum yield of fluorescence of 1,8-naphthalimides **4**–**6** are lower in comparison with the data for compound **3**, not containing amine receptor. On the other hand the quantum yield of fluorescence of dendronized 1,8-naphthalimides **5** and **6**, containing tertiary amine receptor, is higher than that of compound **4**, containing primary amine receptor. This phenomenon might be caused by the possible PET process from the amine receptor to the 4-amino-1,8-naphthalimide fluorophore through the ethylene spacer [16,17]. Thus, the fluorescence of the 4-amono-1,8-naphthalimide fluorophore is quenched (Scheme 4). Furthermore, as demonstrated experimentally by de Silva et al. [25a] only the receptor that is directly attached to the 4-amino moiety is capable of quenching the fluorophores excited state (compounds **4**–**6**).

3.2.3. Low temperature measurements

Freezing the ethanol solutions at 77 K for all compounds leads to the typical for many organic luminophores [28] batochromical shift of the fluorescence FC transitions with about 40 nm in comparison to the results in liquid phase at 300 K. Along with that increasing of the fluorescence intensity in frozen matrix was observed.

The polarization degree P_0 [29] was calculated from the polarized excitation spectra for compounds **3** and **6**. In both cases the P_0 values remain constant in the frame of the two pronounced absorption bands 250–350 nm and 350–500 nm, which gives reason to assign them as $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$ transitions, respectively. The P_0 values for compound **3** are 0.11 and 0.31 and for compound **6** are 0.26 and 0.43, respectively. According to Ref. [30] the calculated angle between the $S_0 \rightarrow S_1$ absorption and the emission transient moment β is 32° for compound **3** and 18° for compound **6**.



Scheme 4.

Table 4
Fluorescence decay parameters of compounds **3–6** in ethanol, $\lambda_{ex} = 337$ nm, $\lambda_F = 540$ nm

Compound	τ_1(ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	χ^2
3			9.2	100	1.01
4	2.0	7	8.9	93	1.00
5	2.2	25	8.2	75	1.01
6	2.4	28	8.7	72	1.09

No phosphorescence was detected in the frozen ethanol matrix for all compounds, which is in line with the effective fluorescence observed under these conditions.

3.2.4. Time-resolved fluorescence measurements

The fluorescence decay of compounds **3–6** in ethanol were recorded upon excitation at 337 nm and emission at 540 nm. The deconvoluted from the lamp profile decay function was fitted by mono- and bi-exponential decay function. The theoretical fluorescence intensity at time t is given by the Eq. (1), where A_1 and A_2 are amplitudes in %.

$$I^F(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (1)$$

The value of the parameter χ^2 was less than 1.1 (Table 4). The residuals between the theoretical and experimental decay curves were flat and random, which demonstrates a good quality of the fit. The calculated lifetimes, the relative amplitudes and the χ^2-values are shown in Table 4.

Fig. 4 illustrates the fluorescence decay of compound **6** and the result from the fitting procedure.

The analysis of the data from the fluorescence decays shows a clear difference in the kinetics of the deactivation processes for compound **3** and all the rest compounds **4–6**. While the fluorescence decay for **3** is mono-exponential (bi-exponential analysis gives much worse results) with lifetime 9.2 ns, the decay of receptor containing compounds **4–6** is fairly reproduced by bi-exponential function. But also in these cases (compounds **4–6**) the decay function is strongly dominated by long-lived component with similar value—τ_2 is close to 9 ns (Table 4). These results indicate, that in spite of the similar energies of the FC fluorescence transitions for all compounds investigated, the processes of deactivation of the first singlet excited state for compound **3** and compounds **4–6** are not identical, which is in line with the conclusions, based on the results for the fluorescence quantum yields (see Section 3.2.2). The constants for the radiative K_F and nonradiative K_{NF} transitions for compound **3** in ethanol, calculated from τ and Q_F, are 0.076 and 0.033 ns^{-1}, respectively.

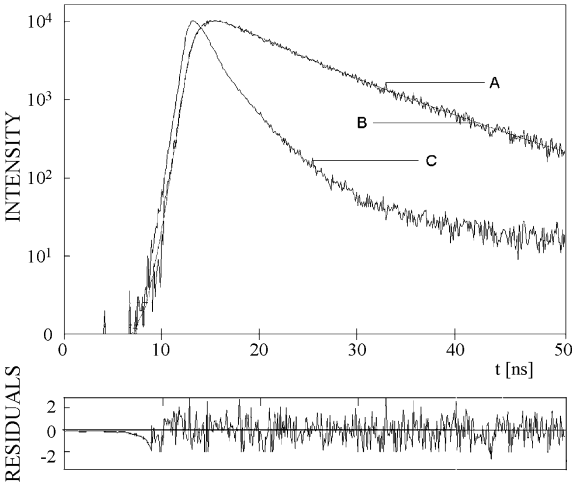


Fig. 4. Fluorescence decay of compound **6** in ethanol, $\lambda_{ex} = 337$ nm, $\lambda_F = 540$ nm. A: Experimental data for the fluorescence decay; B: convoluted results with bi-exponential decay function; C: instrumental response function.

3.3. Influence of pH on the absorption and fluorescence characteristics of the dyes

The above results suppose PET pH sensor properties of 1,8-naphthalimides **4–6**. This was the reason to investigate the photophysical behaviour of compounds **3–6** 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 nitrogen donor (amine receptor) to the 4-amino-1,8-naphthalimide fluorophore, 4-*n*-butylamino-*N*-*n*-butyl-1,8-naphthalimide **3**, not containing amine receptor in its molecule, was involved in the present study.

As a typical example for all compounds under study, when the UV–vis spectra of **5** was recorded in alkaline solution at pH 11, an absorption band was observed between 350 and 510 nm due to the internal charge transfer (ICT) state, with λ_A maximum at 448 nm (Fig. 5). Upon acidification the band was blue shifted with small reductions in its maximum intensity at pH 6.7. However, upon further acidification (pH 2.3) the λ_A became further blue shifted with small intensity enhancements. These changes can however, be considered to be only minor in comparison to the changes in the fluorescence spectra (see later). As Gunnlaugsson et al. comment for the 1,8-naphthalimide fluorophores [9a] the reason for the blue shift is twofold. First, the protonation of the amine receptor (compounds **4–6**) will exert some weak charge repulsion on the 4-amino moiety of the fluorophores.

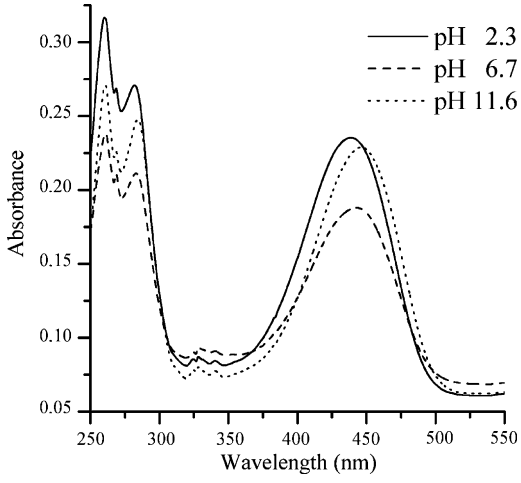


Fig. 5. UV/VIS spectra of 1,8-naphthalimide **5** in water/ethanol (4:1, v/v) solution at three different pHs.

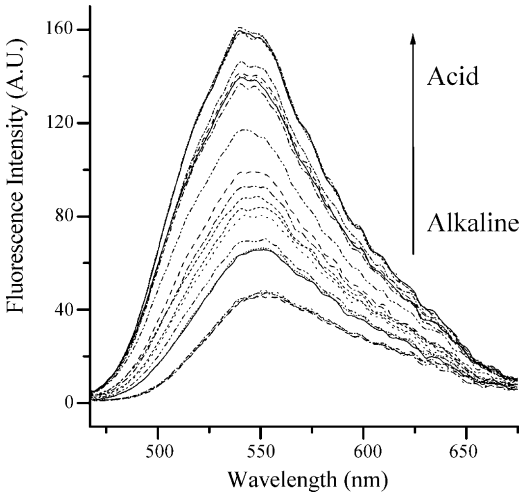


Fig. 6. Changes in the fluorescence intensity of 1,8-naphthalimide **5** as a function of pH in water/ethanol (4:1, v/v). The pH range was from 9.9 to 1.9.

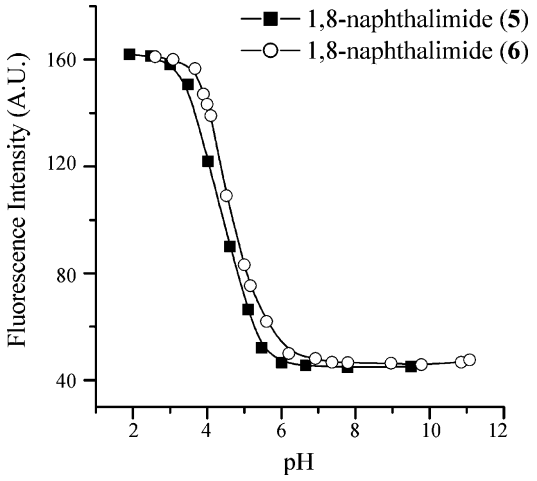


Fig. 7. Effect of pH on the fluorescence intensity (λ_{ex} = 450 nm) of 1,8-naphthalimides **5** and **6** in water/ethanol (4:1, v/v).

However, the major reason is that in very acidic conditions the push–pull character of the ICT state is partially reduced due to the protonation of the 4-amino moiety itself (compounds **3–6**).

The fluorescence spectra of compounds **3–6** were also recorded in water/ethanol (4:1, v/v) solution at different pH values. 4-*n*-Butylamino-*N*-*n*-butyl-1,8-naphthalimide **3**, which lacks the amine receptor, did not show any changes in emission properties as a function of pH except at very low pH where the 4-amino moiety was protonated. Compound **4**, containing primary amine receptor in its molecule, did not show any remarkable changes in the emission properties as a function of pH. The fluorescent enhancement (FE) is less than two times (FE = 1.36).

In contrast to the above results, in alkaline solution for compounds **5** and **6** only a weak emission was observed between 450 and 650 nm, with λ_F at 555 nm. However, upon acidification the emission was gradually increased as demonstrated in Fig. 6. After careful titration to pH *ca*. 2.0, the emission maximal had shifted to 540 nm, and the emission intensity had enhanced more than three times (FE = 3.43 for compound **5** and FE = 3.31 for compound **6**). These changes are of such magnitude that they can be considered as representing two different "states", where the fluorescence emission is "switched off" in alkaline solution and "switched on" in acidic solution.

The changes in the fluorescence intensity as a function of pH for compounds **4–6** should be related to the protonation of their amine receptors. In alkaline solution this moiety is engaged in PET quenching of the 1,8-naphthalimide excited state, and upon protonation of this amine the quenching process in substantially removed.

Obviously, the oxidation potential of the primary amine receptor (compound **4**) increases less than that of the tertiary amine receptor (compound **5**) after the protonation of the amino moieties, and as such, thermodynamically weaker disallows the electron transfer to a lower extent. In contrast to compound **6**, containing both primary and tertiary amine receptors, compound **5** lacks the primary amine receptor. Nevertheless, comparison the fluorescent enhancement of compounds **5** and **6** as a function of pH shows approximately the same values. That is why the fluorescence enhancement of compounds **5** and **6** can be attributed to protonation of the tertiary amine receptor in acidic medium, which disallows PET (Scheme 4). Dendronized 1,8-naphthalimides **5** and **6** are thus efficient "off–on" switcher for pH. This switching process was also found to be reversible.

The changes in the fluorescence intensity of **5** and **6** as a function of pH are presented in Fig. 7. The data clearly show that the emission is "switched off–on" between *ca*. pH 3 and 6.

Taking the part of the graphs located between pH 2.5 and 7, the pK_a values of compounds **5** and **6** have been calculated by the Eq. (2) [25b].

$$\log\left[\frac{I_{Fmax} - I_F}{I_F - I_{Fmin}}\right] = pH - pK_a \quad (2)$$

The calculated pK_a values of 4.42 for compound **5** and 4.86 for compound **6** are consistent with the data for compounds of similar nature that were developed before [25a,31].

4. Conclusions

Four yellow-green emitting 1,8-naphthalimides **3–6** have been synthesized and their photophysical properties were studied in both protic and aprotic solvents of different polarity. Compounds **5** and **6** were designed as branched core-functionalized ester- and amino-terminated 1,8-naphthalimide fluorophores for determining pH changes over a wider pH scale. In water/ethanol (4:1, v/v) solution 1,8-naphthalimide **3**, which lacks the amine receptor at the 1,8-naphthalimide 4-amino moiety, and compound **4**, containing primary amine receptor at the 1,8-naphthalimide 4-amino moiety, did not show any remarkable changes in the emission properties as a function of pH. Conversely, the emission intensity of compounds **5** and **6** had enhanced more than three times (FE = 3.43 for compound **5** and FE = 3.31 for compound **6**) in the pH range 2–11. We attribute this effect to the protonation of the polyamidoamine tertiary amine receptors, which disallow the photoinduced electron transfer in their molecules. The changes were of such magnitude that they can be considered as representing two different

"states", where the fluorescence emission is "switched off" in alkaline solution and "switched on" in acidic solution. The determined pK_a values of 4.42 for **5** and 4.86 for **6** indicate that the dendronized 1,8-naphthalimides would be able to act as efficient "off–on" switchers for pH.

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