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Synthesis and sensor activity of photostable blue emitting 1,8-naphthalimides containing *s*-triazine UV absorber and HALS fragments

Vladimir B. Bojinov[a,*], Ionka P. Panova[a], Danail B. Simeonov[b], Nikolai I. Georgiev[a]

[a] *Department of Organic Synthesis, University of Chemical Technology and Metallurgy, 8 Kliment Ohridsky Str., 1756 Sofia, Bulgaria*
[b] *Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

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ABSTRACT

Two novel highly photostable blue emitting 1,8-naphthalimides, containing active fragments of both a hindered amine radical scavenger (HALS) and an *s*-triazine UV absorber were synthesized for the first time. They showed substantially higher photostability in respect to other similar fluorescent brighteners, not containing either UV absorber or HALS component in their molecules. Novel compounds were also configured as "fluorophore–spacer–receptor" systems based on photoinduced electron transfer by incorporation a cation receptor at the C-4 position of the 1,8-naphthalimide fluorophore. The ability of the new compounds to detect cations was evaluated by the changes in their fluorescence intensity in the presence of metal ions and protons. The presence of metal ions and protons was found to disallow a photoinduced electron transfer leading to an enhancement in the 1,8-naphthalimide fluorescence intensity. The results obtained indicate the potential of the novel compounds as highly photostable and efficient "*off–on*" pH switchers and fluorescent detectors for metal ions with pronounced selectivity towards Zn^{2+} and Cu^{2+} ions.

1. Introduction

During the last years, much attention has been paid to the design, synthesis and characterization of photochemical molecular devices. The extension of the concept of a device to the molecular level is of interest, not only for basic research, but also for the growth of nanoscience and the development of nanotechnology [1]. Supramolecular devices that show large changes in their so-called "*off*" and "*on*" states are currently of great interest as these can be modulated, or tuned, by employing external sources such as ions, molecules, light, etc. [1–3]. The "*off*" and "*on*" states of the molecular-level devices refer to their luminescence, magnetic or electronic properties. Luminescence is one of the most useful techniques to monitor the operation of molecular devices. A part of this rapidly emerging field is the development of fluorescent sensors where the fluorescence is switched "*off*" or "*on*" as a function of the analyte [4–7]. They can be designed according to a few principles with emphasis on the mechanism of photoinduced electron transfer (PET).

The photoinduced electron transfer (PET) using the "fluorophore–spacer–receptor" format is the most commonly exploited approach for the design of fluorescent sensors and switchers [8,9]. The components are selected so that PET from the receptor to the fluorophore quenches the fluorescence of the system. However, in the presence of a guest, which binds to the receptor engaging its lone pair of electrons, PET communication between the receptor and the fluorophore gets cut off and the fluorescence of the system is recovered. In other words, the presence of a guest is signaled by fluorescence enhancement of the system [10–12].

Naphthalimide derivatives are a special class of environmentally sensitive fluorophores [13–15]. Because of their strong fluorescence and good photostability, the 1,8-naphthalimide derivatives enjoy application in a number of areas including coloration and brightening of polymers [16–22], laser active media [23,24], potential photosensitive biologically units [25], fluorescent markers in biology [26], light emitting diodes [27,28], fluorescence sensors and switchers [29–36], electroluminescent materials [37–39], liquid crystal displays [40] and ion probes [41]. Moreover, these properties are essential when employing such devices in real-time and on-line analysis.

In the last years, a number of papers devoted to problem of synthesis of combined stabilizers containing fragments able to act according to different stabilizing mechanisms have been published. Thus, the hindered amine fragments have been combined with either 2-hydroxybenzophenone [42,43] or 2-hydroxyphenylbenzotriazole UV absorbers [19,44–50]. A significant synergistic stabilizing effect against photodegradation has

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[*] Corresponding author. Tel.: +359 2 8163206.
E-mail address: vlbojin@uctm.edu (V.B. Bojinov).

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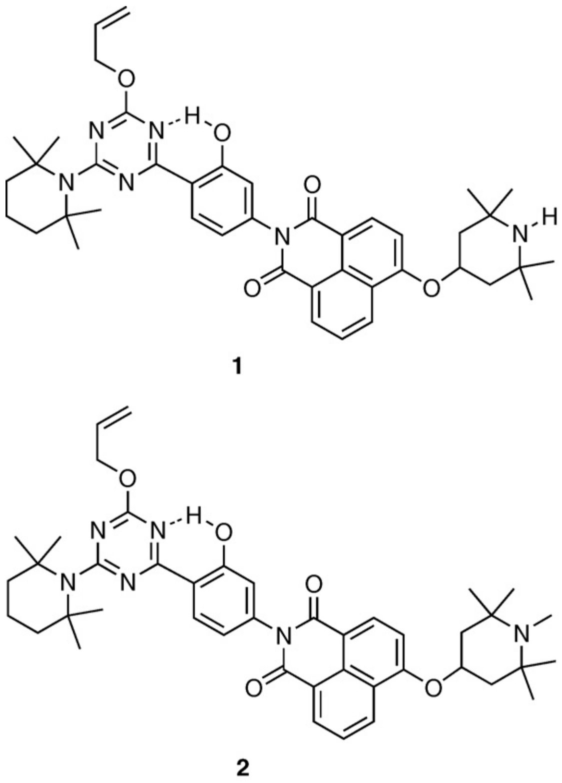

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Scheme 1.

been determined [47]. Recently we have synthesized new polymerizable yellow-green emitting 1,8-naphthalimides, containing built-in *s*-triazine UV absorber and a hindered amine light stabilizer (HALS) fragments, designed as highly photostable additives for "one-step" fluorescent dyeing and photostabilization of polymers [51,52].

These results encouraged our efforts towards the design and synthesis of novel highly photostable blue emitting 1,8-naphthalimide fluorescence sensors. Hence, fluorescent brighteners **1** and **2** (Scheme 1), containing at the 1,8-naphthalimide C-4 position a secondary (2,2,6,6-tetramethylpiperidine) or a tertiary (1,2,2,6,6-pentamethylpiperidine) amine receptor, respectively, were synthesized and investigated by electronic absorption and emission spectroscopy as potential PET sensors for protons and transition metal ions. This paper takes on added significance given the growing body of sensors and other optical devices which employ 1,8-naphthalimide fluorophores.

It was also of interest to investigate photostability of the fluorescent sensors **7** and **8**. In order to receive a more complete comparative picture for the influence of both 2-hydroxyphenyl-*s*-triazine and 2,2,6,6-tetramethylpiperidine fragments on the properties of the examined compounds, previously synthesized 1,8-naphthalimide **4**, not containing a UV absorber moiety [17,30], as well as newly synthesized 1,8-naphthalimides **3** and **5**, not containing a hindered amine moiety (**3**) or not containing both stabilizer fragments (**5**), were involved in the present study as reference compounds (Scheme 2).

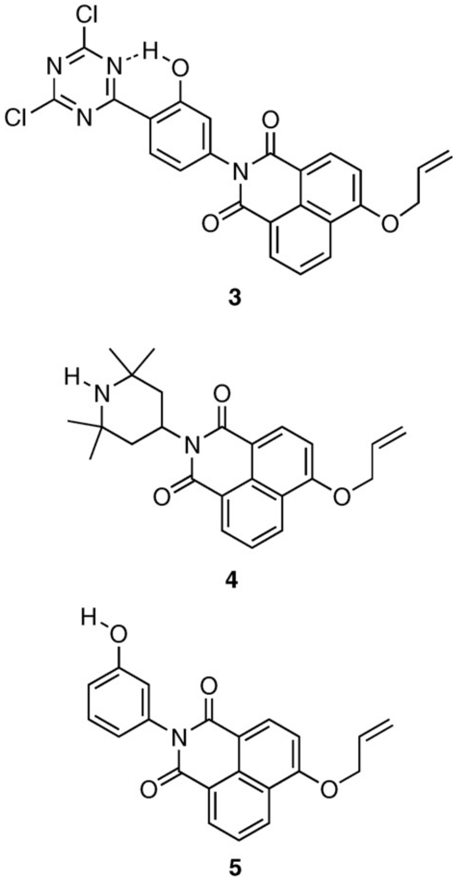
2. Experimental

2.1. Materials

The reference 4-allyloxy-*N*-(2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthalimide **4** [16,17], starting 2-allyloxy-4-(2,2,6,6-tetramethylpiperidin-1-yl)-6-chloro-1,3,5-triazine **7** [44] and 1,2,2,6,6-pentamethylpiperidin-4-ol **10** [45] were synthesized and purified according to the procedures described before. 2,2,6,6-Tetramethylpiperidin-4-ol **9**, cyanuric chloride **11**, 2,2,6,6-tetramethylpiperidine **12**, allyl alcohol **14**, 4-bromo-1,8-naphthalic anhydride **15**, 3-amonophenol **16**, 4-amino-2,2,6,6-tetramethylpiperidine **17**, 18-crown-6 and aluminium (III) chloride (Aldrich, Merck), p.a. grade, was used without purification. All solvents (Merck, Fluka) were of p.a. or analytical grade. $Zn(NO_3)_2$, $Cu(NO_3)_2$, $Ni(NO_3)_2$, $Co(NO_3)_2$ and $Pb(NO_3)_2$ salts were the sources for metal cations. To adjust the pH, very small volumes of sulphuric acid and sodium hydroxide were used. The effect of the metal cations and protons upon the fluorescence intensity was examined by adding $5\,\mu l$ portions of the metal cations stock solution ($8.336 \times 10^{-7}\,mol\,l^{-1}$) to a known volume of the fluorophore solution (3 ml). The addition was limited to 0.045 ml so that dilution remains insignificant.

2.2. Methods

FT-IR spectra were recorded on a Bruker IFS-113 spectrometer at $2\,cm^{-1}$ resolution using KBr discs. The NMR spectra were recorded on a Bruker DRX-250 spectrometer, operating at 250.13 and 62.90 MHz for ^1H and ^{13}C, respectively, using a dual 5 mm probe head. The measurements were carried out in DMSO-d_6 solution at ambient temperature. The chemical shifts (given as δ in ppm) were referenced to tetramethylsilane (TMS) standard. Experiments with 30° pulses, 1 s relaxation delays, 16K time domain points, zero-filled to 64K for protons and 32K for carbons were performed. The distortionless enhancement by polarization transfer (DEPT) spectra were recorded under the conditions used for the ^{13}C NMR spectra at $\tau = (2\,{}^1J_{CH})^{-1} = 3.45\,\mu s$. UV/vis spectra were



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4

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Scheme 2.

recorded on a Hewlett Packard 8452A spectrophotometer with 2 nm resolution at room temperature. The corrected excitation and fluorescence spectra were taken on a PerkinElmer LS 55 fluorescence spectrophotometer. The fluorescence quantum yields (Φ_F) were measured relatively to diphenylanthracene (Φ_{ref} = 0.90) [53]. TLC was performed on silica gel, Fluka F60 254, 20 × 20, 0.2 mm, using as eluant the solvent systems chloroform/methanol = (9:1). The melting points were determined by means of a Kofler melting point microscope.

2.3. Synthesis

*2.3.1. Synthesis of intermediate (**8**)*

To a solution of 3.11 g of 2-allyloxy-4-(2,2,6,6-tetramethylpiperidin-1-yl)-6-chloro-1,3,5-triazine **7** (10 mmol) and 1.34 g of $AlCl_3$ (10 mmol) in 100 ml of xylene, 3.68 g of 4-bromo-*N*-(3-hydroxyphenyl)-1,8-naphthalimide **6** (10 mmol) were added at room temperature. The resulting mixture was heated slowly to 60 °C and stirred at this temperature for 3 h. Then the reaction mixture was heated slowly to 90 °C, held at this temperature for 5 h and finally, the mixture was stirred under reflux for 8 h. After cooling the resulting solution was poured into 150 g of ice. Organic phase (xylene) was removed and the water phase was acidified to pH 2 with 10% hydrochloric acid. The solid was collected by filtration, washed with fresh water and dried. Silica gel chromatography (chloroform/methanol = 9:1) afforded 3.92 g (61%) of 4-bromo-*N*-{4-[4-allyloxy-6-(2,2,6,6-tetramethylpiperidin-1-yl)-1,3,5-triazin-2-yl]-3-hydroxyphenyl}-1,8-naphthalimide **8** as a pale brown solid. FT-IR (KBr), cm^{-1}: 3080 (νOH···N); 3066 (νCH=); 1704 (ν^{as}C=O); 1670 (ν^{s}C=O); 1592 (νC=C); 1338 (νN–C–N). ^1H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 10.23 (s, 1H, OH); 8.78 (dd, 1H, *J* = 8.5 Hz, *J* = 1.2 Hz, naphthalimide 5-H); 8.72 (dd, 1H, *J* = 7.3 Hz, *J* = 1.2 Hz, naphthalimide 7-H); 8.63 (d, 1H, *J* = 8.1 Hz, naphthalimide 3-H); 8.44 (d, 1H, *J* = 8.1 Hz, naphthalimide 2-H); 7.82 (dd, 1H, *J* = 8.5 Hz, *J* = 7.3 Hz, naphthalimide 6-H); 7.42 (d, 1H, *J* = 7.9 Hz, phenyl 5-H); 7.28 (m, 2H, phenyl 2-H and 6-H); 6.12 (m, 1H, allyl CH=); 5.33 (d, 1H, J_{trans} = 17.2 Hz, allyl H*CH*=); 5.21 (d, 1H, J_{cis} = 10.2 Hz, allyl H*CH*=); 4.90 (s, 2H, allyl OCH_2); 1.83 (m, 6H, piperidine 3 × CH_2); 1.46 (s, 12H, piperidine 4 × CH_3). Elemental analysis: Calculated for $C_{33}H_{32}BrN_5O_4$ (MW 642.54) C 61.69, H 5.02, N 10.90%; Found C 62.01, H 4.93, N 11.03%.

*2.3.2. General preparation procedure for fluorescent 1,8-naphthalimides (**1**) and (**2**)*

To a mixture of 0.94 g of 2,2,6,6-tetramethylpiperidin-4-ol **9** (6 mmol) or 1.03 g of 1,2,2,6,6-pentamethylpiperidin-4-ol **10** (6 mmol) in 15 ml of DMF, 0.83 g of finely ground potassium carbonate (6 mmol) and 0.08 g of 18-crown-6 (0.3 mmol, 5 mol%), a solution of intermediate **8** (3.86 g, 6 mmol) in 15 ml of DMF was added at room temperature. The resulting mixture was vigorously stirred and heated to 80 °C for 4 h, then cooled to room temperature and the solution was poured into 300 ml of water. The precipitate was filtered off and washed with water. The crude product was dissolved in a mixture solvent of minim water and ethanol (100 ml), and the undissolved residue was filtered off and dried. The latter then was extracted with chloroform to give after evaporation of the solvent 2.85 g (66%) of 1,8-naphthalimide **1** or 3.12 g (71%) of 1,8-naphthalimide **2** as pale yellow solid.

*4-(2,2,6,6-Tetramethylpiperidin-4-yloxy)-N-{4-[4-allyloxy-6-(2,2,6,6-tetramethylpiperidin-1-yl)-1,3,5-triazin-2-yl]-3-hydroxyphenyl}-1,8-naphthalimide (**1**).* FT-IR (KBr), cm^{-1}: 3378 (νNH); 3078 (νOH···N); 3064 (νCH=); 2918 (νCH_3); 1694 (ν^{as}C=O); 1656 (ν^{s}C=O); 1596 (νC=C); 1332 (νN–C–N). ^1H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 10.08 (s, 1H, OH); 8.67 (dd, 1H, *J* = 8.4 Hz, *J* = 1.1 Hz, naphthalimide 5-H); 8.44 (dd, 1H, *J* = 7.2 Hz, *J* = 1.2 Hz, naphthalimide 7-H); 8.16 (d, 1H, *J* = 8.1 Hz, naphthalimide 2-H); 7.63 (d, 1H, *J* = 8.0 Hz, phenyl 5-H); 7.59 (dd, 1H, *J* = 8.4 Hz, *J* = 7.2 Hz, naphthalimide 6-H); 7.25 (m, 2H, phenyl 2-H and 6-H); 7.03 (d, 1H, *J* = 8.1 Hz, naphthalimide 2-H); 6.11 (m, 1H, allyl CH=); 5.30 (d, 1H, J_{trans} = 17.1 Hz, allyl H*CH*=); 5.22 (d, 1H, J_{cis} = 10.4 Hz, allyl H*CH*=); 5.06 (m, 1H, piperidine CH); 4.88 (d, 2H, *J* = 4.8 Hz, allyl OCH_2); 2.92 (br.s, 1H, piperidine NH); 2.34 (dd, 2H, *J* = 11.9 Hz, *J* = 3.8 Hz, piperidine CH_2); 1.82 (m, 6H, piperidine 3 × CH_2); 1.66 (t, 2H, *J* = 11.8 Hz, piperidine CH_2); 1.46 (s, 12H, piperidine 4 × CH_3); 1.29 (s, 6H, piperidine 2 × CH_3); 1.13 (s, 6H, piperidine 2 × CH_3). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 171.8 (triazine Ar–C=N), 165.2 (triazine N=C–O), 161.8 (triazine N=C–N), 159.1 (Ar–C–OH), 157.9 (2 × C=O), 154.9 (Ar–C–O), 142.2 (Ar–*C*–N–C=O), 136.8 and 124.6 (Ar–C), 133.8 (allyl CH=), 131.7, 129.9, 129.1, 122.8, 118.7, 114.9, 106.6 and 97.6 (Ar–CH), 118.8 (Ar–*C*–C=N), 114.7 (allyl CH_2=), 111.5 (Ar 2 × *C*–C=O), 74.3 (allyl OCH_2), 64.2 (piperidine C–O), 53.8 (piperidine 2 × CH_2), 51.9 (piperidine 2 × N–*C*–Me), 47.5 (piperidine 2 × NH–*C*–Me), 39.3 (piperidine 2 × CH_2), 31.1 and 29.6 (piperidine 4 × CH_3), 28.2 and 26.7 (piperidine 4 × CH_3), 16.6 (piperidine CH_2). Elemental analysis: Calculated for $C_{42}H_{50}N_6O_5$ (MW 718.88) C 70.17, H 7.01, N 11.69%; Found C 69.82, H 6.93, N 11.81%.

*4-(1,2,2,6,6-Pentamethylpiperidin-4-yloxy)-N-{4-[4-allyloxy-6-(2,2,6,6-tetramethylpiperidin-1-yl)-1,3,5-triazin-2-yl]-3-hydroxyphenyl}-1,8-naphthalimide (**2**).* FT-IR (KBr), cm^{-1}: 3082 (νOH···N); 3068 (νCH=); 2920 and 2878 (νCH_3); 1700 (ν^{as}C=O); 1664 (ν^{s}C=O); 1598 (νC=C); 1334 (νN–C–N). ^1H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 10.13 (s, 1H, OH); 8.66 (dd, 1H, *J* = 8.5 Hz, *J* = 1.2 Hz, naphthalimide 5-H); 8.45 (dd, 1H, *J* = 7.4 Hz, *J* = 1.2 Hz, naphthalimide 7-H); 8.19 (d, 1H, *J* = 8.3 Hz, naphthalimide 2-H); 7.61 (dd, 1H, *J* = 8.5 Hz, *J* = 7.4 Hz, naphthalimide 6-H); 7.49 (d, 1H, *J* = 7.9 Hz, phenyl 5-H); 7.21 (m, 2H, phenyl 2-H and 6-H); 7.05 (d, 1H, *J* = 8.3 Hz, naphthalimide 2-H); 6.10 (m, 1H, allyl CH=); 5.32 (d, 1H, J_{trans} = 17.2 Hz, allyl H*CH*=); 5.23 (d, 1H, J_{cis} = 10.1 Hz, allyl H*CH*=); 5.13 (m, 1H, piperidine CH); 4.92 (d, 2H, *J* = 5.2 Hz, allyl OCH_2); 2.46 (dd, 2H, *J* = 12.0 Hz, *J* = 3.6 Hz, piperidine CH_2); 2.34 (s, 3H, piperidine N–CH_3); 1.79 (m, 6H, piperidine 3 × CH_2); 1.66 (t, 2H, *J* = 11.8 Hz, piperidine CH_2); 1.48 (s, 12H, piperidine 4 × CH_3); 1.31 (s, 6H, piperidine 2 × CH_3); 1.14 (s, 6H, piperidine 2 × CH_3). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 172.1 (triazine Ar–C=N), 164.9 (triazine N=C–O), 162.2 (triazine N=C–N), 158.7 (Ar–C–OH), 157.6 (2 × C=O), 155.3 (Ar–C–O), 141.8 (Ar–*C*–N–C=O), 137.1 and 125.4 (Ar–C), 133.3 (allyl CH=), 132.4, 130.0, 129.6, 123.5, 117.8, 115.3, 107.4 and 98.2 (Ar–CH), 119.1 (Ar–*C*–C=N), 114.2 (allyl CH_2=), 110.9 (Ar 2 × *C*–C=O), 73.8 (allyl OCH_2), 64.8 (piperidine C–O), 54.3 (piperidine 2 × CH_2), 48.5 (piperidine 2 × N–*C*–Me), 44.6 (piperidine NMe), 42.8 (piperidine 2 × NH–*C*–Me), 40.2 (piperidine 2 × CH_2), 35.4 and 32.9 (piperidine 4 × CH_3), 29.8 and 28.5 (piperidine 4 × CH_3), 15.8 (piperidine CH_2). Elemental analysis: Calculated for $C_{43}H_{52}N_6O_5$ (MW 732.91) C 70.47, H 7.15, N 11.47%; Found C 70.80, H 7.24, N 11.59%.

*2.3.3. Synthesis of reference 1,8-naphthalimides (**3**) and (**5**)*

A suspension of 6.93 g of 4-bromo-1,8-naphthalic anhydride **15** (25 mmol) and 2.73 g of 3-aminophenol **16** (25 mmol) in 180 ml of glacial acetic acid was stirred at 110 °C for 8 h. The crude product that precipitated on cooling was filtered off, washed with water and treated with 50 ml of 5% aqueous sodium carbonate. The solid phase was filtered off, washed with water and dried. Re-crystallization from acetic acid afforded 7.64 g (83%) of 4-bromo-*N*-(3-hydroxyphenyl)-1,8-naphthalimide **6** as pale yellow-brown solid.

To a mixture of 0.70 g of allyl alcohol **14** (*d* = 0.85, 12 mmol), 0.16 g of 18-crown-6 (0.6 mmol, 5 mol% to the allyl alcohol) and 0.67 g of finely ground potassium hydroxide (12 mmol) in 30 ml of toluene a suspension of 1,8-naphthalimide **6** (3.68 g, 10 mmol) in 120 ml of toluene was added at room temperature. The resulting mixture was vigorously stirred and heated to 90 °C for 3 h, then cooling to room temperature. The solid phase was filtered off, and the toluene solution was washed with water and dried over anhydrous sodium sulphate. After evaporation of the toluene under reduced pressure the crude product was dissolved in a mixture solvent of minim water and ethanol (100 ml), and the undissolved residue was filtered off. The filtrate then was diluted in 100 ml of water and the precipitated product was filtered off and dried. Recrystallization from ethanol–water (50:50, vol.%) afforded 2.97 g (86%) of 4-allyloxy-*N*-(3-hydroxyphenyl)-1,8-naphthalimide **5** as pale yellow solid. FT-IR (KBr), cm^{-1}: 3288 (νOH); 3072 (νArCH=); 1702 (ν^{as}C=O); 1665 (ν^{s}C=O); 1596 (νC=C); 1340 (νN–C–N). ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 8.65 (dd, 1H, J = 7.4 Hz, J = 1.2 Hz, naphthalimide 5-H); 8.52 (dd, 1H, J = 8.2 Hz, J = 1.2 Hz, naphthalimide 7-H); 8.14 (d, 1H, J = 8.1 Hz, naphthalimide 3-H); 7.78 (dd, 1H, J = 8.2 Hz, J = 7.4 Hz, naphthalimide 6-H); 7.22 (m, 3H, phenyl 2-H, 5-H and 6-H); 7.09 (d, 1H, J = 8.1 Hz, naphthalimide 3-H); 6.81 (dd, 1H, J = 8.0 Hz, J = 1.6 Hz, phenyl 4-H); 6.26 (br.s, 1H, OH); 6.02 (m, 1H, allyl CH=); 5.28 (d, 1H, J_{trans} = 17.4 Hz, allyl H*CH*=); 5.17 (d, 1H, J_{cis} = 10.2 Hz, allyl H*CH*=); 4.89 (d, 2H, J = 4.9 Hz, allyl OCH$_2$). Elemental analysis: Calculated for $C_{21}H_{15}NO_4$ (MW 345.35) C 73.03, H 4.38, N 4.06%; Found C 69.67, H 4.46, N 3.99%.

To a solution of 1.48 g of cyanuric chloride **11** (8 mmol) and 1.07 g of AlCl$_3$ (8 mmol) in 80 ml of xylene, 2.76 g of 4-allyloxy-*N*-(3-hydroxyphenyl)-1,8-naphthalimide **5** (8 mmol) were added at room temperature. The resulting mixture was heated slowly to 60 °C and stirred at this temperature for 3 h. Then the reaction mixture was heated slowly to 90 °C, held at this temperature for 5 h and finally, the mixture was stirred under reflux for 8 h. After cooling the resulting solution was poured into 120 g of ice. Organic phase (xylene) was removed and the water phase was acidified to pH 2 with 10% hydrochloric acid. The solid was filtered off, washed with fresh water and dried. Silica gel chromatography (chloroform/methanol = 9:1) afforded 2.37 g (60%) of 4-allyloxy-*N*-[4-(4,6-dichloro-1,3,5-triazin-2-yl)-3-hydroxyphenyl]-1,8-naphthalimide **3** as a pale yellow solid. FT-IR (KBr), cm^{-1}: 3064 (νCH=); 3018 (νOH$\cdots$N); 1700 (ν^{as}C=O); 1668 (ν^{s}C=O); 1652 (νC=N); 1598 (νC=C). ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 9.89 (s, 1H, OH); 8.68 (d, 1H, J = 8.0 Hz, naphthalimide 5-H); 8.56 (d, 1H, J = 7.3 Hz, naphthalimide 7-H); 8.20 (d, 1H, J = 8.3 Hz, naphthalimide 2-H); 7.71 (t, 1H, J = 7.7 Hz, naphthalimide 6-H); 7.39 (d, 1H, J = 7.8 Hz, phenyl 5-H); 7.18 (m, 2H, phenyl 2-H and 6-H); 7.08 (d, 1H, J = 8.3 Hz, naphthalimide 3-H); 6.05 (m, 1H, allyl CH=); 5.30 (d, 1H, J_{trans} = 17.6 Hz, allyl H*CH*=); 5.17 (d, 1H, J_{cis} = 10.3 Hz, allyl H*CH*=); 4.92 (d, 2H, J = 5.2 Hz, allyl OCH$_2$). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 173.5 and 172.7 (2 × triazine N=C–Cl), 169.4 (triazine Ar–C=N), 159.2 (Ar–C–OH), 155.5 and 154.8 (2 × C=O), 153.2 (Ar–C–O), 140.5 (Ar–*C*–N–C=O), 136.4 (Ar–*C*–C=N), 133.9 (allyl CH=), 131.7 (Ar–CH), 130.8 (Ar–C), 129.9 and 128.6 (2 × Ar–CH), 124.7 (Ar–C), 124.1 (Ar–CH), 121.1 (Ar–*C*–C=O), 119.6 (Ar–CH), 115.4 (allyl CH$_2$=); 114.8 (Ar–CH), 112.8 (Ar 2 × *C*–C=O), 106.3 and 101.2 (2 × Ar–CH), 72.7 (allyl OCH$_2$). Elemental analysis: Calculated for $C_{24}H_{14}Cl_2N_4O_4$ (MW 493.30) C 58.43, H 2.86, N 11.36%; Found C 58.71, H 2.94, N 11.48%.

2.4. Photodegradation of fluorescent 1,8-naphthalimides

The study on the photodegradation of the fluorescent 1,8-naphthalimides was conducted in a solar simulator SUNTEST CPS equipment (Heraeus, Germany), supplied with an arc air-cooled Xenon lamp (Hanau, 1.1 kW, 765 W m^{-2}), at ambient temperature. The irradiation of dyes was performed in DMF solution at concentration 10^{-5} mol l^{-1}. The changes in the 1,8-naphthalimide concentration were followed spectrophotometrically by the changes of the absorption maxima using the method of a standard calibration curve.

3. Results and discussion

3.1. Design of 1,8-naphthalimides (**1**) and (**2**)

The aim of the present study was to synthesize multifunctional fluorescence sensing 1,8-naphthalimide brighteners, containing both 2-(2-hydroxyphenyl)-1,3,5-triazine UV absorber and 2,2,6,6-tetramethylpiperidine radical scavenger fragments as well as an unsaturated allyl function usable for simultaneously chemically fluorescent brightening and photostabilization of polymers.

The two 1,8-naphthalimides (**1** and **2**) were designed to act as photostable detectors of environment pollution by transition metal cations and protons. They were configured on the “fluorophore-spacer-receptor” model, where the 4-oxy-1,8-naphthalimide moiety is the fluorophore and the piperidine amine in the C-4 substituent is the analyte receptor. The hydrocarbon part of the piperidine fragment serves as a spacer that covalently separates the two units. In these particular cases, it was predicted that a PET process (an electron transfer 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 or respective metal complex formation of the piperidine amine would increase the oxidation potential of the receptor, and as such, thermodynamically disallow the electron transfer [54,55]. Consequently the emission would be “*switched on*”. Thus, we expect the fluorescence to be strong in acidic media and transition metal cations environment.

3.2. Synthesis of the target and reference fluorescent brighteners

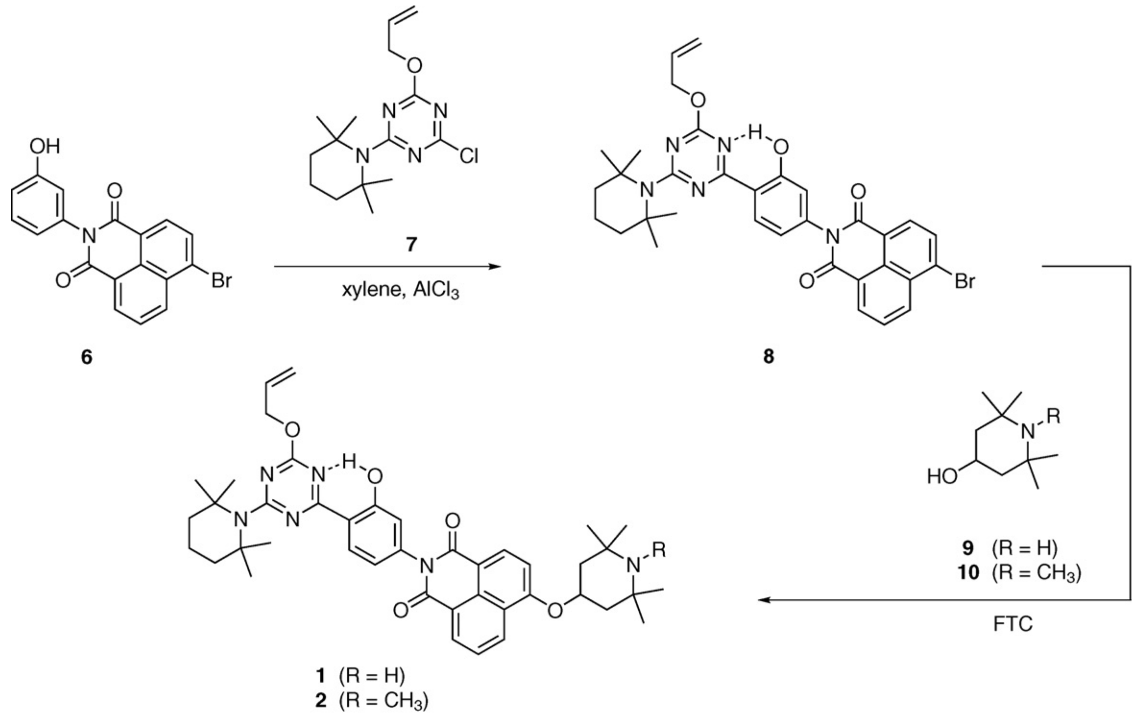
The synthesis of the novel 1,8-naphthalimides **1** and **2** was performed in two steps as it is shown in Scheme 3. First, the intermediate **8** was obtained by Friedel–Crafts acylation of 4-bromo-*N*-(3-hydroxyphenyl)-1,8-naphthalimide **6** with *s*-triazinylpiperidine **7** in xylene.

In order to obtain the target fluorescent 1,8-naphthalimides **1** and **2** and functionalize them with an analyte receptor in one step, the bromine in the intermediate **8** was substituted under phase transfer catalysis conditions with the commercially available 2,2,6,6-tetramethylpiperidin-4-ol **9** (Aldrich) for compound **1** or with the previously synthesized 1,2,2,6,6-pentamethylpiperidin-4-ol **10** [45] for compound **2**.

The starting *s*-triazinylpiperidine **7** was synthesized in two steps as described before [44] by *N*-acylation of 2,2,6,6-tetramethylpiperidine **12** with the commercially available cyanuric chloride (Merck) in xylene at 110 °C, and subsequent nucleophilic substitution of the second chlorine in the intermediate **13** with allyl alcohol under phase transfer catalysis conditions (PTC) at room temperature (Scheme 4).

Reference 1,8-naphthalimides **3**, **4** and **5** were synthesized following Scheme 5. Compound **4** was obtained in two steps as described before [16,17] by acylation of 4-amino-2,2,6,6-tetramethylpiperidine **17** with 4-bromo-1,8-naphthalic anhydride **15**, and subsequent nucleophilic substitution of the bromine in the intermediate **18** with the commercially available allyl alcohol **14**.

4-Bromo-1,8-naphthalic anhydride **15** was also used as a starting material for the preparation of reference 1,8-naphthalimides **3** and **5**. First, 4-bromo-*N*-(3-hydroxyphenyl)-1,8-naphthalimide **6**, the starting material for the synthesis of novel fluorescent brighteners **1** and **2** (Scheme 3), was synthesized by *N*-acylation of 3-aminophenol **16** with 4-bromo-1,8-naphthalic anhydride **15**. Reference 1,8-naphthalimide **5** was obtained by nucleophilic substitution of the bromine in the compound **6** with the commercially available allyl alcohol **14** under phase transfer catalysis conditions at room temperature by analogy with the method described



Scheme 3.

before [56]. Reference 1,8-naphthalimide **3** was synthesizes by Friedel–Crafts acylation of 4-allyloxy-*N*-(3-hydroxyphenyl)-1,8-naphthalimide **5** with the commercially available cyanuric chloride **11** in xylene.

The synthesized compounds were fully characterized by their melting points, TLC (R_f values) and UV/vis spectra (Table 1) and identified by elemental analysis data, FT-IR, ^{1}H and ^{13}C NMR spectra. The target 1,8-naphthalimides (**1** and **2**) and reference compounds (**3**–**5**) were additionally characterized by fluorescence maxima, Stokes shifts (ν_A–ν_F) and quantum yields of fluorescence (Φ_F). The data are presented in Table 2.

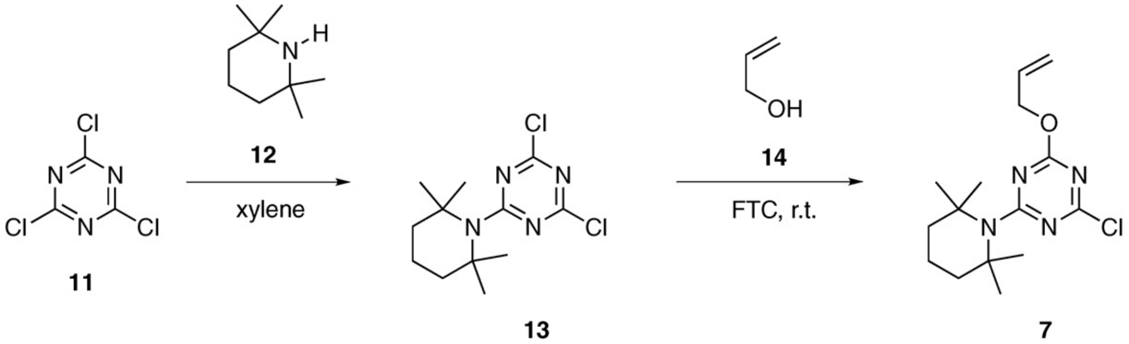
3.3. *Photophysical characterization of fluorescent brighteners (**1**–**5**)*

The light absorption properties of the 4-alkoxy-1,8-naphthalimides under study are basically related to the polarization of the 1,8-naphthalimide molecule on irradiation, resulting from the electron donor-acceptor interaction between the substituent at C-4 position and the carbonyl groups of the chromophoric system, and may be influenced by the environmental effect of the media.

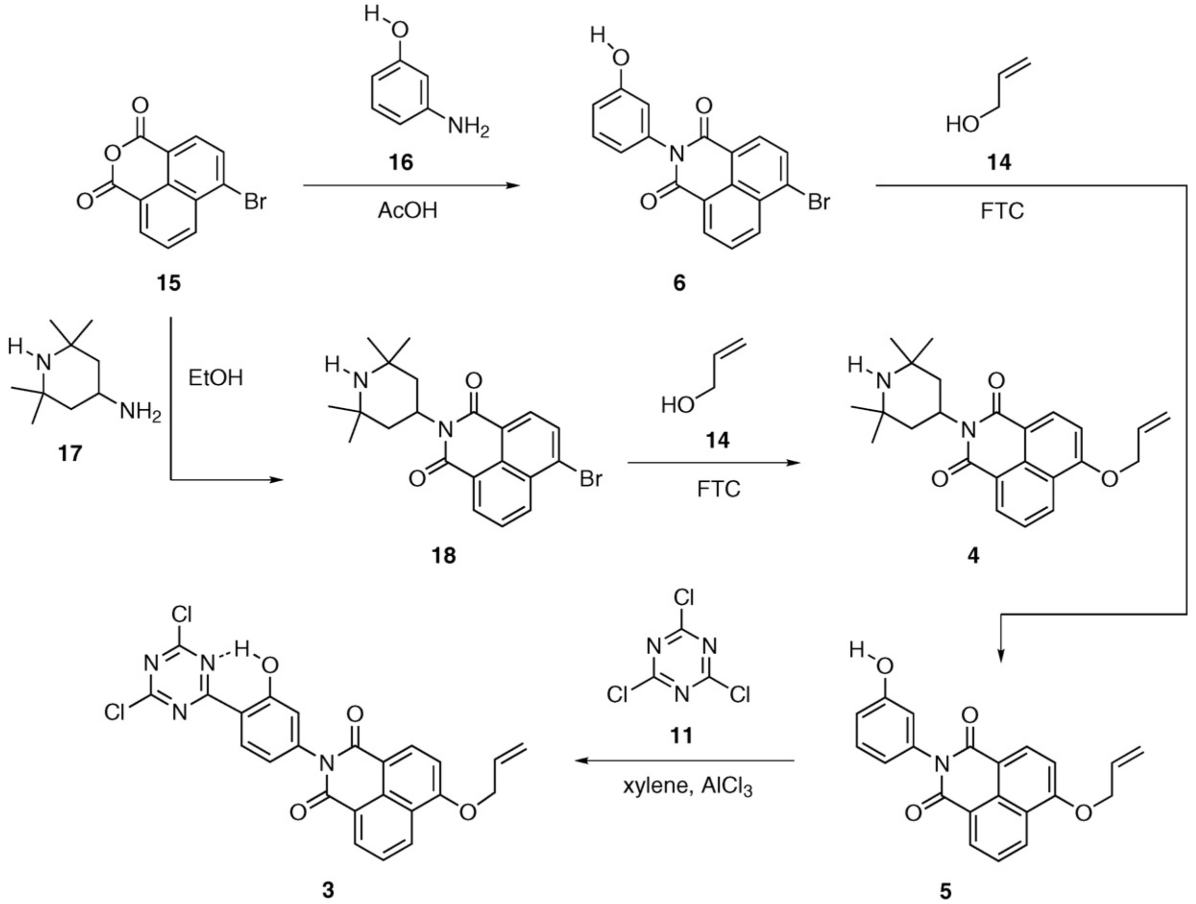
The absorption spectra of the fluorescent brighteners (FBs) **1** and **2** in DMF solution (Fig. 1) clearly show the participation of both UV absorber and 1,8-naphthalimide units in the combined molecules. 2-Hydroxyphenyl-*s*-triazine fragments absorb in the UV region at λ_{A1} = 340–342 nm, while the 1,8-naphthalimide absorption is red shifted to λ_{A2} = 360–362 nm. The dyes' molar absorptivity (ε) in the longest-wavelength band of the absorption spectra is higher than 10,000 l mol^{-1} cm^{-1} (Table 1), indicating that this is a charge transfer (CT) band, due to (π,π^*) character of the $S_0 \rightarrow S_1$ transition.

Basic fluorescent characteristics of novel 1,8-naphthalimides (**1** and **2**) and reference compounds (**3**–**5**) such as the fluorescence (λ_F) maxima, Stokes shift (ν_A–ν_F), oscillator strength (*f*), fluorescent both quantum (Φ_F) and energy (E_F) yields were measured in DMF solution and presented in Table 2.

In DMF solution all compounds under study displayed blue fluorescence due to the charge transfer in the 1,8-naphthalimide moieties from the electron-donating alkyloxy group at C-4 position to the carbonyl groups. The FBs' emission was observed in the visible region with well-pronounced maxima (λ_F) at 440–444 nm. Fig. 2 displays the absorption and fluorescence spectra of the fluorescent dye **1** as a typical example for the spectra of compounds under study. The overlap between absorption and fluorescence bands is



Scheme 4.



Scheme 5.

Table 1
Yields, melting points, retention factors and absorption data for novel compounds **1** and **2**, starting materials **6** and **7**, intermediate **8** and reference naphthalimides **3**–**5** in DMF solution.

Compound	Yield (%)	Mp (°C)	R_f[a]	λ_{A1}[b] (nm)	Log ε (l mol^{-1} cm^{-1})	λ_{A2}[b] (nm)	Log ε (l mol^{-1} cm^{-1})
1	66	246–248	0.30	342	4.286	362	4.242
2	72	215–217	0.42	340	4.323	360	4.259
3	60	>260	0.51	340	4.371	362	4.195
4	88	178–180	0.40	–	–	362	4.247
5	86	195–196	0.56	–	–	360	4.266
6	83	>260	0.68	–	–	344	3.923
7	93	38–40	0.63	–	–	–	–
8	61	247–249	0.59	342	4.359	346	3.968

[a] TLC in a solvent system chloroform/methanol = (9:1).
[b] λ_{A1} and λ_{A2} represent the absorption maxima of 2-(2-hydroxyphenyl)-1,3,5-triazine and 1,8-naphthalimide units in the combined molecules, respectively.

small and an aggregation effect at concentration of 10^{-5} mol l^{-1} has not been observed.

The Stokes shift (ν_A–ν_F) and oscillator strength (f) are important characteristics for the fluorescent compounds. The Stokes shift is a parameter that indicates the difference 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).

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

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

Table 2
Fluorescence characteristics of 1,8-naphthalimides **1**–**5** in DMF solution at concentration 10^{-5} mol l^{-1} ($\lambda_{ex} = \lambda_{A2}$).

Compound	λ_{ex} (nm)	λ_F (nm)	ν_A–ν_F (cm^{-1})	f	Φ_F	E_F
1	362	440	4897	0.243	0.16	0.132
2	360	442	5153	0.225	0.09	0.073
3	362	442	5000	0.214	0.52	0.426
4	362	444	5102	0.205	0.46	0.375
5	360	440	5051	0.221	0.55	0.450

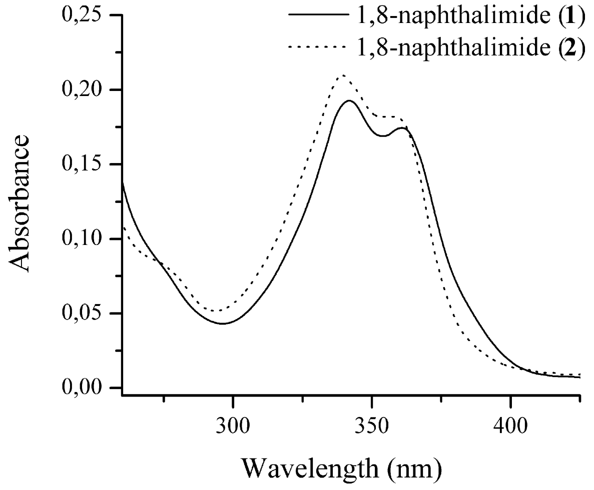


Fig. 1. Absorption spectra of novel 1,8-naphthalimides **1** and **2** in DMF solution at concentration 10^{-5} mol l^{-1}.

strength were calculated using Eq. (2) where $\Delta\nu_{1/2}$ is the width of the absorption band (cm^{-1}) at 1/2 ($\varepsilon_{\max}$) [57].

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

The Stokes shift (4897–5153 cm^{-1}) and oscillator strength (0.205–0.243) values for the FBs **1**–**5** (Table 2) were in accordance with the data for other blue emitting 1,8-naphthalimide derivatives [58,59].

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 relatively to diphenylanthracene (Φ_{ref} = 0.90) as a reference compound [53] 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.

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

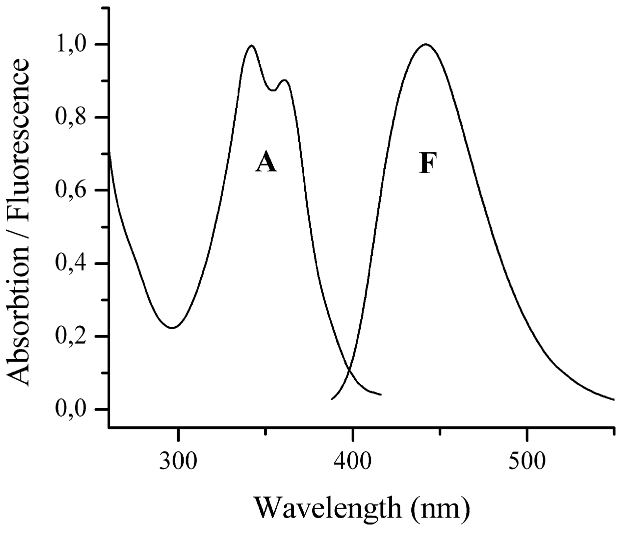


Fig. 2. Normalized absorption (λ_A) and fluorescence (λ_F) spectra of 1,8-naphthalimide **1**.

The energy yield of fluorescence E_F (Table 1), calculated by Eq. (4), could also be used instead of Φ_F [60].

$$E_F = \Phi_F\frac{\lambda_A}{\lambda_F} \tag{4}$$

As can be seen (Table 2), the quantum yield of fluorescence of 1,8-naphthalimides **1** and **2**, possessing 2,2,6,6-tetramethylpiperidin-4-yloxy unit at C-4 position, are lower in respect to those of traditional blue emitting 1,8-naphthalimides, not containing PET receptor (reference compounds **3**–**5**). On the other hand, the quantum yield of fluorescence of 1,8-naphthalimide **2**, containing tertiary amine receptor, was lower than those of 1,8-naphthalimide **1**. This phenomenon might be caused by the possible PET process from the piperidine amine donor (receptor) to the 4-oxy-1,8-naphthalimide fluorophore through the saturated piperidinyl ring. Thus the fluorescence of the 4-oxy-1,8-naphthalimide fluorophore is quenched (Scheme 6). Upon recognition of the analyte (guest proton or transition metal ion) piperidine amine would increase the oxidation potential of the receptor, and as such, thermodynamically disallow the electron transfer and the emission would be "*switched on*" [54,55].

Furthermore, as demonstrated experimentally by de Silva et al., only the receptor that is directly attached to the 1,8-naphthalimide 4-oxy moiety (the "lower" moiety) is capable of quenching the fluorophore excited state [54]. This is due to the fact that molecules like 1,8-naphthalimides **1** and **2** have high exited state dipole moments that arise from their internal charge transfer (ICT) excited state nature. In this case the alkyloxy unit is acting as an electron donor, whereas the imide functions as an electron acceptor. Consequently, a push-pull mechanism is in operation, and due to charge repulsion, disallows the "upper" piperidine amine (compound **4**) to transfer an electron to the naphthalimide excited state [61].

The results obtained suppose PET sensor properties of FBs **1** and **2**, containing "lower" piperidine moiety at C-4 position of the 1,8-naphthalimide fluorophore, which was the reason to investigate their photophysical behaviour in water/DMF (4:1, v/v) at different pH values and in the presence of transition metal ions.

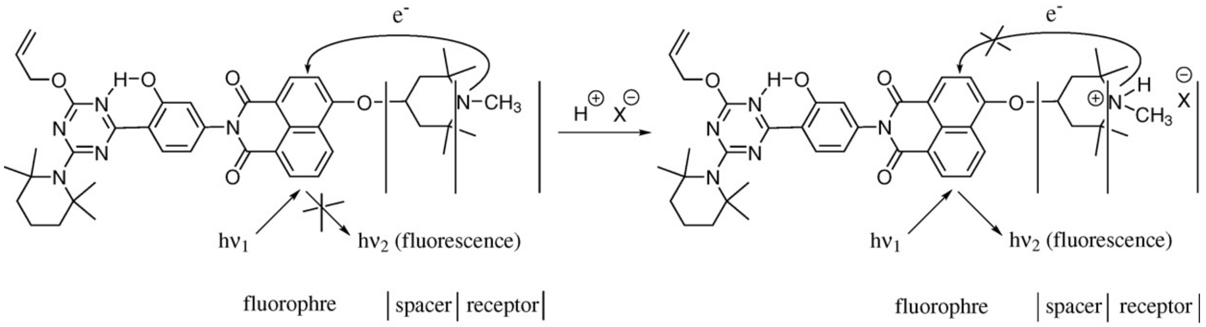
*3.4. Influence of pH on the fluorescent properties of 1,8-naphthalimides (**1**–**5**)*

The photophysical characteristics of the dyes in distilled water/DMF (4:1, v/v) solution are represented in Table 3. Some bathochromic shift of the absorption and fluorescence maxima of the compounds was observed if compared spectra to those recorded in DMF. The oscillator strength values calculated in water/DMF (4:1, v/v) were higher than those in DMF which is well correlated with the increase in the extinction coefficient of the dyes in this medium.

Family of fluorescence emission spectra of the novel 1,8-naphthalimides **1** and **2** and reference compound **4** as a function of pH were recorded in water/DMF (4:1, v/v) and plotted in Fig. 3. Reference 4-allyloxy-1,8-naphthalimide **4**, which lacks the amine receptor at the 4-alkyloxy moiety, did not show any observable changes in the emission properties as a function of pH. The fluorescent enhancement (FE) was insignificant (FE = 1.13).

The fluorescent enhancement (FE) for other reference 1,8-naphthalimides (**3** and **5**), not containing tetramethylpiperidine substituent, as could be expected, was practically missing (FE = 1.04 for 1,8-naphthalimide **3** and FE = 1.01 for 1,8-naphthalimide **5**).

In contrast, 1,8-naphthalimides **1** and **2**, containing amine receptor at their 4-alkyloxy moieties, showed higher fluorescence sensitivity as a function of pH. However, after careful titration from *ca.* pH 12 to 2 the fluorescence enhancement of 1,8-naphthalimide **2**, containing tertiary amine receptor, was considerable higher in respect to that of 1,8-naphthalimide **1**, containing secondary amine



2

2

Scheme 6.

Table 3
Absorption and fluorescence characteristics of 1,8-naphthalimides **1–5** in water/DMF (4:1, v/v) at concentration 10^{-5} mol l^{-1} ($\lambda_{ex} = \lambda_A$).

Compound	λ_A (nm)	Log ε (l mol^{-1} cm^{-1})	λ_F (nm)	$\nu_A - \nu_F$ (cm^{-1})	f	FE[a]	pK_a
1	366	4.357	446	4902	0.323	2.34	8.08
2	366	4.365	448	5001	0.308	8.11	7.96
3	368	4.307	446	4752	0.316	1.04	–
4	366	4.363	450	5100	0.318	1.13	–
5	364	4.364	446	5051	0.332	1.01	–

[a] Factor for proton-induced fluorescence enhancement FE = I_{Fmax}/I_{Fmin} (I_F: fluorescence intensity, arbitrary units).

receptor (Fig. 3). This shows that the protonation of the outer rim (amine receptor) is responsible for the main part of the fluorescence enhancement. Fig. 4 presents as an example fluorescence changes of the fluorescent brightener **2** over a wider pH scale. As seen protonation of the alkylated amine donor (receptor) drastically alters the electron-donating properties and consequently switching of the PET path from the alkylated amine donor to the 4-oxy-1,8-naphthalimide moiety. The typical naphthalimide emission band of **2** in water/DMF (4:1, v/v) is blue-shifted upon-protonation and red shifted upon deprotonation (Fig. 4). Compared with the fluorescence in the basic medium, protonation of the alkylated amine of compound **2** results in the fluorescence enhancement of the 4-oxy-1,8-naphthalimide fluorophore by 8.11 times. At the same time the fluorescence enhancement of compound **1** was only FE = 2.34. Obviously, in the case of compound **1** the oxidation potential of the receptor (secondary amine) increases less than that of compound **2** after the protonation of the amino moiety, and as such, thermodynamically disallows the electron transfer to a lower extent.

The changes in the fluorescence intensity of the fluorescent brighteners **1** and **2** as a function of pH 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. This switching process was also found to be reversible.

It can be concluded that novel 1,8-naphthalimides **1** and **2**, especially compound **2**, are efficient "*off–on*" switchers for pH. Taking the part of the graphs located between pH 5.0 and 11.0, the pH influence on the fluorescence intensity (I_F) has been calculated by Eq. (5) [55].

$$\log\left[\frac{I_{Fmax} - I_F}{I_F - I_{Fmin}}\right] = pH - pK_a \qquad (5)$$

pK_a values of 8.08 for 1,8-naphthalimide **1** and 7.96 for 1,8-naphthalimide **2** have been found. The results obtained are con-

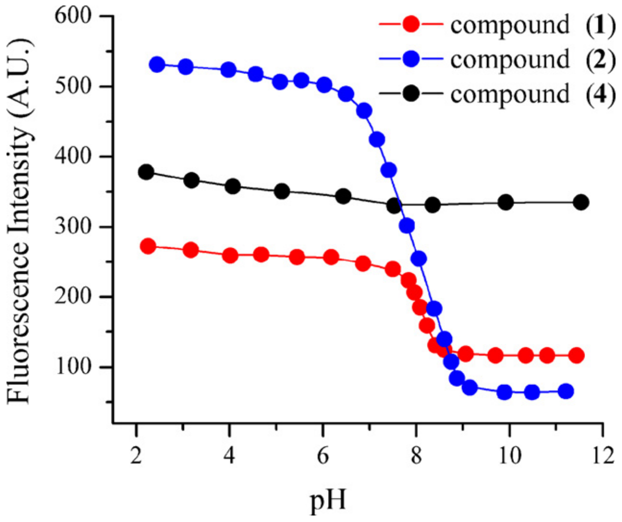


Fig. 3. Effect of pH on the fluorescence intensity of compounds **1**, **2** and **4** in water/DMF (4:1, v/v).

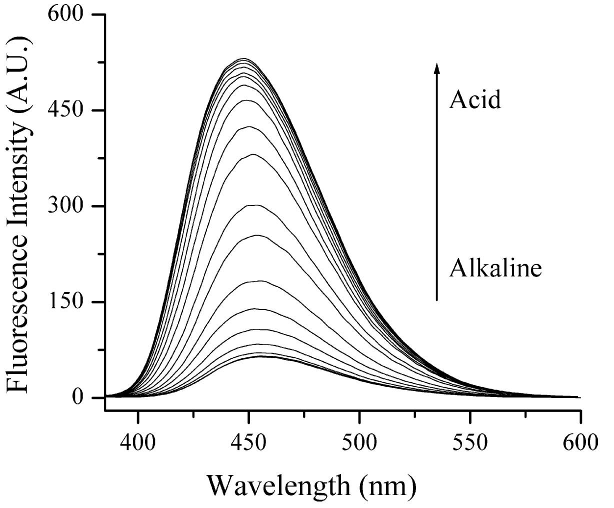


Fig. 4. Changes in the fluorescence spectra of **2** as a function of pH in water/DMF (4:1, v/v). The pH range was from 11.21 to 2.44.

sistent with those for compounds of similar nature that have been developed before [30,55]. These pK_a values also indicate that the novel sensors **1** and **2** would be well suited to monitor changes in the physiological pH range.

*3.5. Influence of metal cations on the fluorescence intensity of 1,8-naphthalimides (**1**) and (**2**)*

The signalling fluorescent properties of novel 1,8-naphthalimides **1** and **2** in the presence of transition metal ions have been investigated spectrophotometrically in DMF with regard to their potential application as PET sensors. DMF has been chosen in all measurements since it is able as a polar solvent to stabilize the dye charge separated state thus favouring the fluorescence switching by PET process. Also DMF guarantees a good solubility of the dye ligands, used metal salts and the respective complexes.

The fluorescence behaviour of the novel compounds (**1** and **2**) throughout the coordination process with different metal ions (Cu^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}) was, as expected, approximately the same as that in the presence of protons. It was found that the coordination of the receptor with the metal ion results in fluorescence enhancement, as it is demonstrated as an example in Fig. 5 for the 2,2,6,6-tetramethylpiperidine substituted 1,8-naphthalimide **1** in the presence of Zn^{2+} ions.

The sensor capacity of the fluorescent brighteners **1** and **2** in respect to different metal ions and their concentration was evaluated on the basis of the fluorescence enhancement values (Fig. 6). The FE = I/I_0 was calculated using minimal (I_0) and maximal (I) fluorescence intensity recorded before and after addition of metal ions. The highest fluorescence enhancement for 1,8-naphthalimides **1** and **2** has been observed in the presence of Zn^{2+} ions (FE = 3.17 and 10.06, respectively). As it is seen (Fig. 6), the FE values for compound **2** in the presence of all types of metal cations are considerably higher as compared to those of compound **1**, which could be related to the best increase in the oxidation potential of the tertiary amine receptor as discussed above (Section 3.4).

The increase in fluorescence intensity was occurred after addition of Zn^{2+} ions in the concentration range of 8.336×10^{-7} to 1.084×10^{-5} mol l^{-1}. Noticeable fluorescence intensity enhancement was observed at Zn^{2+} concentration of 2.5×10^{-6} mol l^{-1} which showed good sensitivity of the investigated compounds (Fig. 7). Raising the cation concentration up to 5.835×10^{-6} mol l^{-1} also induced an increase in the fluorescence. Further augmentation of the metal ions concentration up to 7.503×10^{-6} mol l^{-1} had a small impact on the alteration of fluorescence intensity.

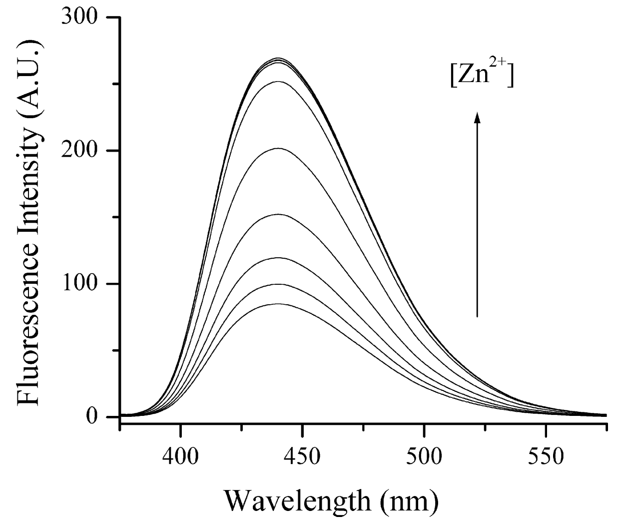


Fig. 5. Fluorescence spectra of **1** (10^{-5} mol l^{-1}) in DMF solution at various concentrations of Zn^{2+}. The concentrations of Zn^{2+} cations are in order of increasing intensity from 0 to 7.503×10^{-6} mol l^{-1}.

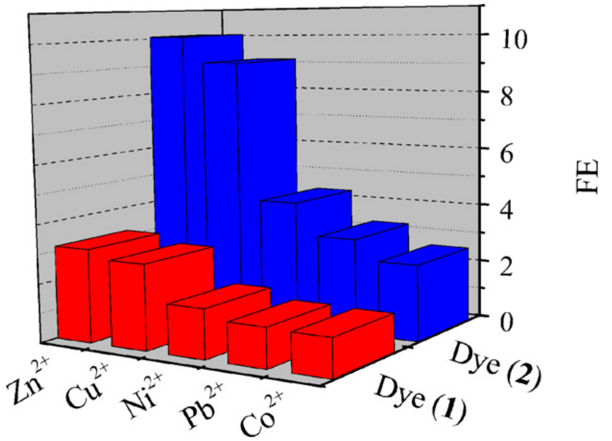


Fig. 6. Fluorescence enhancement (FE) of 1,8-naphthalimides **1** and **2** (10^{-5} mol l^{-1}) in the presence of different metal cations at concentration 7.503×10^{-6} mol l^{-1} in DMF solution.

As discussed above, the fluorescence intensity increased due to the complexation between the piperidine amine receptor and Zn^{2+} ions. Titration plots (Fig. 7) suppose a 1:2 metal/ligand complex formation as it is shown in Scheme 7. Thus the PET process is "*switched off*" and the fluorescence emission of fluorescent brighteners is recovered.

The results obtained reveal a good sensor activity of the novel blue emitting fluorophores, especially possessing tertiary amine receptor fluorescent brightener **2**, indicating their potential as highly efficient "*off–on*" switchers for transition metal ions with pronounced selectivity towards Zn^{2+} and Cu^{2+} ions.

*3.6. Photostability of fluorescent brighteners (**1–5**)*

The fluorescent sensors' photostability is a very important characteristic with regard to their practical usage. To study the influence of both 2,2,6,6-tetramethylpiperidine and 2-(2-hydroxyphenyl)-1,3,5-triazine fragments on the photostability of the novel compounds **1** and **2**, DMF solutions of the compounds were subjected to irradiation in a SUNTEST equipment for 10 h. In order to receive a more complete comparative picture of this

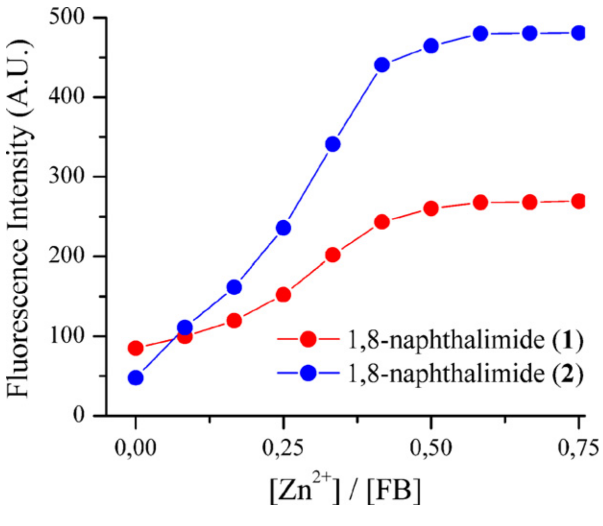
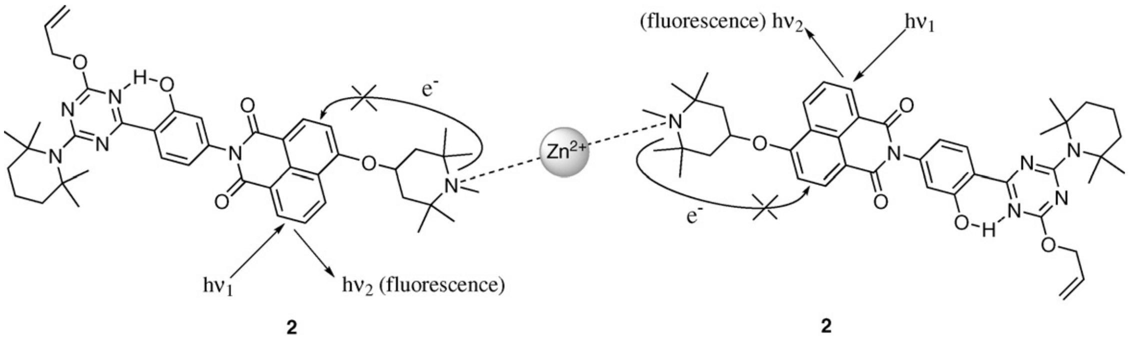


Fig. 7. Changes in the fluorescence maxima of FBs **1** and **2** (10^{-5} mol l^{-1}) upon addition of Zn^{2+} cations with a concentration step of 8.336×10^{-7} mol l^{-1}.



Scheme 7.

influence, previously synthesized 1,8-naphthalimide derivatives (Scheme 2), not containing a hindered amine **3** or UV absorber **4** moieties as well as not containing both stabilizer fragments **5** in their molecules were involved in the present study as reference compounds.

The kinetics of the fluorophores' photodegradation was monitored colorimetrically. As no changes were observed in the dyes absorption maxima (λ_{A2}) during the irradiation, the correlation between the dye concentration and the time of irradiation was monitored using the method of the standard calibration curve (Fig. 8).

As seen (Fig. 8), in DMF solution photostability of the novel compounds **1** and **2**, containing both HALS and UV absorber fragments, was higher than those of reference compounds **3** and **4**, not containing either 2,2,6,6-tetramethylpiperidine or 2-hydroxyphenyl-*s*-triazine fragment in their molecules, which could be explained by a synergistic interaction of the UV absorber and HALS moieties combined in one molecule. The study also showed that the photostability of 1,8-naphthalimide **2**, containing *N*-substituted piperidine moiety, is relatively lower in respect to that of the piperidine *N*-free analogue **1** probably due to the reduced ability of the piperidine nitrogen to form *N*-oxyl radicals.

Photodegradation of reference compound **5**, not containing stabilizer fragments was considerably faster if compared to those of reference dyes **3** and **4**, especially to those of novel fluorophores **1** and **2**. Within 2 h the solution of compound **5** looses significant part of its absorption capacity as a result of photodegradation of the dye chromophoric system.

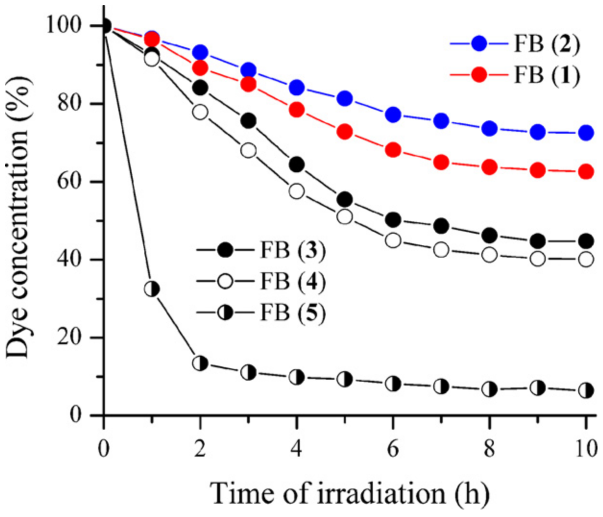


Fig. 8. Photodegradation of 1,8-naphthalimides **1**–**5** in DMF solution.

The results obtained show that the novel compounds **1** and **2** are highly photostable fluorescent brighteners with high potential for use as effective fluorescence detectors of environmental pollution by metal ions and protons.

4. Conclusions

In this paper we have given a comprehensive account of the design and synthesis of two multifunctional 1,8-naphthalimide fluorescent brighteners as highly photostable PET fluorescence sensors for metal ions and protons, containing active fragments of a hindered amine radical scavenger, *s*-triazine UV absorber and a polymerizable allyl function. It was shown that the presence of both a hindered amine and an UV absorber fragments in the fluorophores' molecules considerably improved their photostability in respect to other similar fluorescent brighteners, not containing either an UV absorber or a HALS component. The photophysical properties of novel compounds were studied in DMF and water/DMF (4:1, v/v) solution and discussed. In the presence of metal ions (Cu^{2+}, Pb^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}) and protons these molecules sustained appreciable changes in their fluorescence intensity. These changes can be attributed to coordination of their piperidine amine receptor with the analyte, whereupon the receptor increases its oxidation potential, and as such, thermodynamically disallow the electron transfer and the emission is "*switched on*". It was found that the detecting ability of compound **2** is considerably higher in respect to that of fluorophore **1**, which could be related to the better increase of the tertiary amine oxidation potential in the presence of transition metal ions and protons. The results indicate the potential of the novel compounds, especially that of fluorescent brightener **2**, as highly photostable and efficient "*off–on*" pH switchers and fluorescent detectors for metal ions with pronounced selectivity towards Zn^{2+} and Cu^{2+} ions.

Acknowledgements

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