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The design, synthesis and photophysical properties of two novel 1,8-naphthalimide fluorescent pH sensors based on PET and ICT

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ABSTRACT

The changes in the photophysical properties of two novel, yellow-green emitting pH chemosensors namely a 1,8-naphthalimide dye and its condensed heterocyclic derivative, as a function of pH were investigated in water/ethanol. The 1,8-naphthalimide dye displayed on–off pH sensing properties owing to photoinduced electron transfer, while its condensed heterocyclic derivative revealed off-on-off pH sensor activity derived from simultaneous photoinduced electron transfer and internal charge transfer. In alkaline media the fluorescence of the 1,8-naphthailimide dye was quenched owing to photoinduced electron transfer being disabled in acidic media. The pK_a of the 1,8-naphthailimide dye was 5.49, which defines the dye as a highly efficient "*off–on*" switch. For the heterocyclic 1,8-naphthalimide derivative two fluorescence quenching processes at different pH were observed, one with a pK_a value of 6.08 and a second with a pK_a value of 3.95. These results indicate that the heterocyclic derivative would be able to act as an efficient "*off–on–off*" fluorescent pH switch.

1. Introduction

Fluorescent chemosensors and switches have been actively investigated in recent years because of their high sensitivity and rapid response. They are designed on two basic principles – photoinduced electron transfer (PET) and internal charge transfer (ICT) [1,2]. The photoinduced electron transfer (PET) using the "*fluorophore-spacer-receptor*" format is the most commonly exploited approach for the design of fluorescent sensors and switches [3,4]. The components are chosen so that PET from the receptor (usually an amino group) 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 is isolated and fluorescence of the system is recovered. In other words, the presence of a guest is signalled by fluorescence enhancement of the system [5]. In contrast with PET systems, in the ICT chemosensors the receptor is directly attached to the electron-donating/withdrawing unit that is conjugated to the fluorophore an electron-withdrawing/donating unit [1,2]. During excitation of the system the fluorophore undergoes donor-acceptor intramolecular charge transfer. The subsequent change in the dipole moment results in a Stokes shift that depends on the guest near to the fluorophore. Thus it can be predicted that the presence of a guest near by the donor/acceptor moiety will change the photophysical properties of the fluorophore because it will affect the efficiency of ICT [6,7].

Naphthalimide derivatives are a special class of environmentally sensitive fluorophores [8,9]. As a consequence of their strong fluorescence and good photostability 1,8-naphthalimide derivatives have found application in a number of areas including colouration of polymers [10,11], laser active media [12,13], fluorescent markers in biology [14], anticancer agents [15] and analgesics in medicine [16], fluorescence switches and sensors [17,18], light emitting diodes [19,20], electroluminescent materials [21,22], liquid crystal displays [23,24].

The synthesis of a new yellow-green emitting 1,8-naphthalimide chemosensor, diester derivative, containing a tertiary amine receptor, was recently reported by us [25]. The 1,8-naphthalimide derivative was prepared using accessible materials in high yield and showed high pH sensor activity. Therefore it was of interest to see if other ester analogues of the 1,8-naphthalimide fluorophore would shed further light on this issue. The present study reports on the design, synthesis and photophysical properties of two novel 1,8-naphthalimide fluorescent pH sensors. This issue takes on added

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significance given the growing body of sensors and other optical devices which employ 1,8-naphthalimide fluorophores [1,2]. Hence, compounds **4** and **5** (Scheme 1) were synthesized in one synthetic procedure and investigated by electronic absorption and emission spectroscopy.

2. Experimental

2.1. Materials

The starting 4-bromo-1,8-naphthalic anhydride **1** was prepared according to the reported procedure [26]. Ethylene diamine and methyl acrylate (Fluka, Merck), p.a. grade, were used without purification. All solvents (Fluka, Merck) were pure or of spectroscopic grade.

2.2. Methods

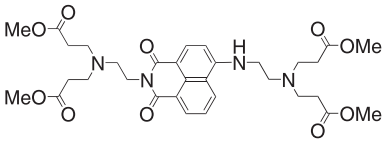
FT-IR spectra were recorded on a Varian Scimitar 1000 spectrometer. The ^{1}H NMR spectra were recorded on a Bruker DRX-250 spectrometer, operating at 250.13 MHz. TLC was performed on silica gel, Fluka F60 254, 20 × 20, 0.2 mm. The melting points were determined by means of a Kofler melting point microscope. The UV–VIS absorption spectra were recorded on a spectrophotometer Lambda 25 (Perkin Elmer). The corrected fluorescence spectra were taken on a Perkin Elmer LS55 spectrofluorimeter. The fluorescence quantum yields (Φ_F) were measured relatively to Coumarin 6 ($\Phi_F = 0.78$ in ethanol) [27].

2.3. Synthesis of sensors *4* and *5*

4-Bromo-1,8-naphthalic anhydride **1** (4 g, 14 mmol) was dissolved in ethylene diamine (100 mL) and the resulting solution was heated under reflux for 18 h. The solution was allowed to cool and the ethylene diamine was distilled under vacuum to afford a crude product, containing compounds **2** and **3**. A solution of the crude product (an unseparated mixture of **2** and **3**) in methanol (30 mL) was added to a solution of methyl acrylate (11.9 mL, 140 mmol) in methanol (50 mL). The ensuing mixture was stirred for 3 days at room temperature to afford a clear solution. The pure compounds **4** (yellow oil) and **5** (yellow solid, m.p. 127–129 °C) were obtained after silica gel chromatography using dichloromethane as eluent.

2.3.1. 2-{2-[bis(2-methoxycarbonylethyl)-amino]-ethyl}-6-{2-[bis (2-methoxycarbonylethyl)-amino]-ethylamino}-benzo[de] isoquinoline-1,3-dione (*4*)

Yield: 2.88 g (32%). $R_f = 0.58$; *n*-hexane:acetone = (1:1). FTIR (oil) cm^{-1}: 3382 (ν*NH*); 2952 and 2831 (ν*CH*); 1730 (ν*C*OOCH$_3$); 1682 (ν^{as}N–*C*=*O*); 1643 (ν^{s}N–*C*=*O*). ^{1}H NMR (CDCl$_3$, 250 MHz) δ ppm: 8.56 (dd, 1H, $J = 7.3$ Hz, $J = 1.0$ Hz, benzo[*de*]isoquinoline 7-CH); 8.44 (d, 1H, $J = 8.4$ Hz, benzo[*de*]isoquinoline 4-CH); 8.38 (dd, 1H, $J = 8.5$ Hz, $J = 1.0$ Hz, benzo[*de*]isoquinoline 9-CH); 7.60 (dd, 1H, $J = 7.3$ Hz, $J = 8.4$ Hz benzo[*de*]isoquinoline 8-CH); 6.66 (d, 1H, $J = 8.5$ Hz, benzo[*de*]isoquinoline 5-CH); 6.31 (m, 1H, NH); 4.24 (t, 2H, $J = 7.3$ Hz, (CO)$_2$NC*H*$_2$); 3.56 (s, 12H, 4 × OC*H*$_3$); 3.43 (m, 2H, ArNHC*H*$_2$); 2.85 (m, 12H, 2 × N(C*H*$_2$)$_3$); 2.49 (m, 8H, 4 × *C*H$_2$COOCH$_3$). Elemental analysis: Calculated for $C_{32}H_{42}N_4O_{10}$ (MW 642.7) C 59.80, H 6.59, N 8.72%; Found C 60.01, H 6.57, N 8.69%.



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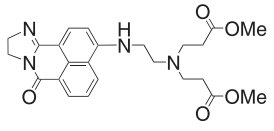


5

Scheme 1.

2.3.2. 3-{2-[bis(2-methoxycarbonylethyl)-amino]-ethylamino}-9,10-dihydro-7H-benzo[de]imidazo[1,2-b]isoquinolin-7-one (*5*)

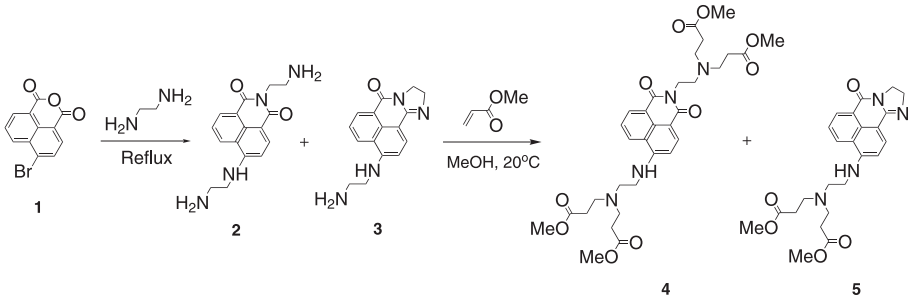
Yield: 3.55 g (56%). $R_f = 0.19$; *n*-hexane:acetone = (1:1). FTIR (KBr) cm^{-1}: 3310 (ν*NH*); 2923 and 2853 (ν*CH*); 1730 (ν*C*OOCH$_3$); 1652 (N–*C*=*O*). ^{1}H NMR (DMSO-d_6, 250 MHz) ppm: 8.38 (d, 1H, $J = 8.3$ Hz, benzo[*de*]imidazo[1,2-*b*]isoquinolin 6-CH); 8.33 (d, 1H, $J = 7.3$ Hz, benzo[*de*]imidazo[1,2-*b*]isoquinolin 4-CH); 8.11 (d, 1H, $J = 8.3$ Hz, benzo[*de*]imidazo[1,2-*b*]isoquinolin 1-CH); 7.62 (dd, 1H, $J = 7.3$ Hz, $J = 8.4$ Hz benzo[*de*]imidazo[1,2-*b*]isoquinolin 5-CH); 6.97 (t, 1H, $J = 5.0$ Hz, NH); 6.72 (d, 1H, $J = 8.3$ Hz, benzo[*de*]imidazo[1,2-*b*]isoquinolin 2-CH); 4.02 (m, 4H, 9-CH$_2$ and 10-CH$_2$); 3.59 (m, 2H, ArNHC*H*$_2$); 3.52 (s, 6H, 2 × OC*H*$_3$); 2.77 (m, 6H, N(C*H*$_2$)$_3$); 2.46 (m, 4H, 2 × *C*H$_2$COOCH$_3$). Elemental analysis: Calculated for $C_{24}H_{28}N_4O_5$ (MW 452.5) C 63.70, H 6.24, N 12.38%; Found C 63.91, H 6.15 N 12.51%.

3. Results and discussion

3.1. Design and synthesis of pH sensors

The dyes under study were designed as ester-functionalized 1,8-naphthalimide fluorophores for determining pH changes over a wider pH scale. The 1,8-naphthalimide chromophore was selected as the fluorescent core of the synthesized compounds because of its chemical stability and high fluorescence efficiency. Sensor **4** is based on the "*fluorophore-spacer-receptor*" model, where the 4-amino-1,8-naphthalimide moiety is the fluorophore and the branching amines are the proton receptors. The ethylene spacer between the fluorophore and the receptors 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 the 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 [28,29]. Consequently the emission would be "*switched on*". Thus we expect the fluorescence of compound **4** to be amplified in acidic media. Compound **5** was also configured on the "*fluorophore-spacer-receptor*" format. However its pH sensing properties should be considered as a function of two simultaneous effects – PET and ICT. The PET process would quench fluorescence emission of the fluorophore in alkaline media. The same behaviour of compound **5** should be expected in stronger acidic media. After protonation of its imine (C=N) nitrogen the ICT interaction would be affected and the fluorescence of the system quenched [30]. That is why it was predictable that the emission of sensor **5** would be in "*on-state*" at neutral media and "*switched off*" in both acidic and alkaline media.

The novel compounds were synthesized in two steps by one synthetic procedure as shown in Scheme 2. First, a mixture of yellow-green emitting intermediates **2** and **3** was obtained by refluxing of 4-bromo-1,8-naphthalic anhydride **1** in ethylene diamine. Then the mixture of intermediates **2** and **3** was converted into a mixture of the desired sensors **4** and **5** by exhaustive Michael addition to excess of methyl acrylate [31]. The pure sensors **4** and **5** were obtained after silica gel column chromatography.



Scheme 2.

The new compounds **4** and **5** were characterized and identified by their melting points, TLC (R_f values), elemental analysis data, UV–VIS, fluorescence, FT-IR and ^{1}H NMR spectroscopy. For instance, in the ^{1}H NMR spectra of novel pH sensor **4**, a triplet resonance at 4.24 ppm for two protons was observed (Fig. 1A). This is an usual characteristic for the methylene protons in *N*-position of the 1,8-naphthalimide ring, which is different from the corresponding resonance for the yellow-green emitting sensor **5** that shows multiplet resonance for four protons at 4.02 (Fig. 1B). Furthermore, the ^{1}H NMR spectra of the both sensors **4** and **5** contain peaks in range of 3.59–2.46 ppm, attributed to the protons for the branching amino esters.

3.2. Photophysical characterization of the sensors

It is well known that photophysical properties of the 1,8-naphthalimide derivates depend mainly on the polarization of their chromophoric system. Light absorption in this molecule generates a charge transfer interaction between the substituents at C-4 position and the carbonyl groups. In general, the derivatives with alkoxy groups are colourless and blue emitting, while the amino substituted 1,8-naphthalimides are yellow coloured with green fluorescence [32,33]. The basic photophysical characteristics of the examined compounds in different solvents (ethanol and chloroform) are listed in Table 1.

As can be seen from the data presented in Table 1, in both solvents the longest-wavelength absorption maximum of compound **5** appears in the visible region at $\lambda_A = 422–432$ nm, while the corresponding absorption maxima of compound **4** is bathochromically shifted by 8–10 nm to $\lambda_A = 430–442$ nm, which is surely connected with the different electron-accepting ability of the imine and carbonyl functions in different fluorophores. This could be due to destabilization of the ICT excited state nature in case of compound **5** (imine function) to the larger extent, resulting in more energy being required to access the excited state.

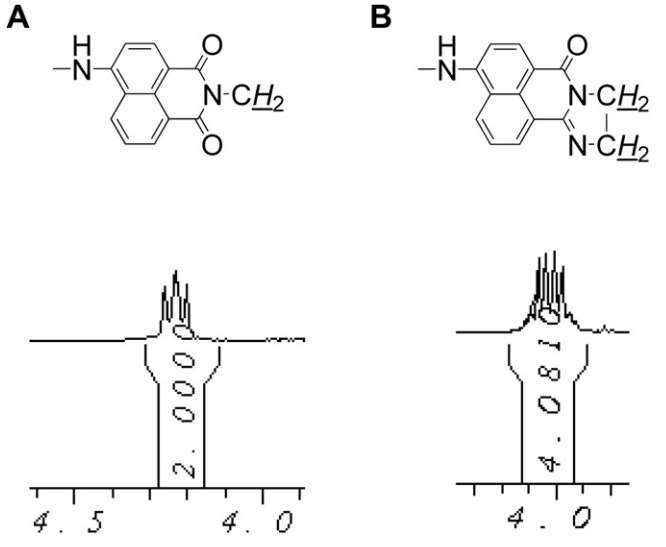


Fig. 1. The ^{1}H NMR methylene resonances of sensors **4** (A) and **5** (B) in a range of about 3.8–4.4 ppm.

The emission spectra of the two compounds under study in both solvents, obtained after excitation at 420 nm showed the approximately the same tendency (Table 1). The emission of compound **5** was observed in the visible region with well-pronounced maxima (λ_F) at 496–536 nm, while the emission of compound **4** was bathochromically shifted by 27–40 nm to $\lambda_F = 519–546$ nm.

The Stokes shift ($\nu_A - \nu_F$) is an important parameter for the fluorescent compounds that indicates the differences in the properties and structure of the fluorophores between the ground state S_0 and the first excited state S_1. The Stokes shifts (cm^{-1}) were calculated by Eq. (1).

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

The Stokes shift values for compound **4** (3988 cm^{-1} in chloroform and 4309 cm^{-1} in ethanol) and for compound **5** (3535 cm^{-1} in chloroform and 4491 cm^{-1} in ethanol) are typical for the 1,8-naphthalimide derivatives [30,34] and do not indicate remarkable changes in the geometry of the first singlet excited state due to the excitation.

The ability of the molecules to emit the absorbed light energy is characterized quantitatively by the fluorescence quantum yield (Φ_F). The quantum yields of fluorescence were calculated using Coumarin 6 ($\Phi_F = 0.78$ in ethanol) as a standard according to Eq. (2) [35], where A_{ref}, S_{ref}, n_{ref} and A_{sample} S_{sample}, n_{sample} represent the absorbance at the exited wavelength, the integrated emission band area and the solvent refractive index of the standard and the sample, respectively.

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

Table 1
Photophysical characteristics of sensors **4** and **5** in ethanol and chloroform.

Compound	Ethanol				Chloroform			
	λ_A (nm)	ε (l mol^{-1} cm^{-1})	λ_F[a] (nm)	Φ_F	λ_A (nm)	ε (l mol^{-1} cm^{-1})	λ_F[a] (nm)	Φ_F
4	442	11,844	546	0.11	430	12,152	519	0.44
5	432	12,942	536	0.08	422	13,878	496	0.38

[a] Fluorescence maxima at $\lambda_{ex} = 420$ nm.

Table 2
Photophysical characteristics of sensors **4** and **5** in water/ethanol (4:1, v/v).

Compound	λ_A (nm)	ε (l mol^{-1} cm^{-1})	λ_F (nm) [a]	Φ_F
4	450	11,153	545	0.09
5	430	12,723	537	0.04

[a] Fluorescence maxima at $\lambda_{ex} = 420$ nm.

It can be seen that in the more polar ethanol the quantum yields of fluorescence are lower ($\Phi_F = 0.11$ for compound **4** and $\Phi_F = 0.08$ for compound **5**) than the quantum yields in the less polar chloroform ($\Phi_F = 0.44$ for compound **4** and $\Phi_F = 0.38$ for compound **5**). This significant difference is due to the possible photoinduced electron transfer (PET) occurring from the tertiary alkylamine receptors to the fluorophore units in polar ethanol that stabilize the dye charge separated state thus favouring the fluorescence switching by a PET process, which is disallowed in non-polar media causing restoration of the fluorescence emission [36].

3.3. Influence of pH on the absorption properties of the sensors

The compounds under study ware designed as fluorescence sensors for determining pH changes over a wider pH scale. This was the reason to investigate the photophysical behaviour of compounds **4** and **5** in water/ethanol (4:1, v/v) solution (Table 2).

When the UV–VIS spectrum of sensor **4** was recorded in alkaline solution at *ca.* pH 10, a broad absorption band was observed between 350 and 525 nm due to the internal charge transfer (ICT) state with λ_A maximum at 448 nm (Fig. 2). Upon acidification the band was blue shifted with small reductions in its maximum intensity at *ca.* pH 4. However, upon further acidification (pH *ca.* 2) the λ_A became further blue shifted with small intensity enhancements. These changes can be considered to be only minor in respect to the changes in the fluorescence spectra as a function of pH (see Section 3.4). As Gunnlaugsson and co-authors commented for the 1,8-naphthalimide fluorophores the reason for the blue shift is twofold [3]. First, the protonation of the amine receptor will exert some weak charge repulsion on the 4-amino moiety of the fluorophores. However, the major reason is that under the very acidic conditions the push–pull character of the ICT state is partially reduced due to the protonation of the 4-amino moiety itself.

In contrast to the minor changes in the absorption properties of sensor **4** at different pH values sensor **5** showed a colour change

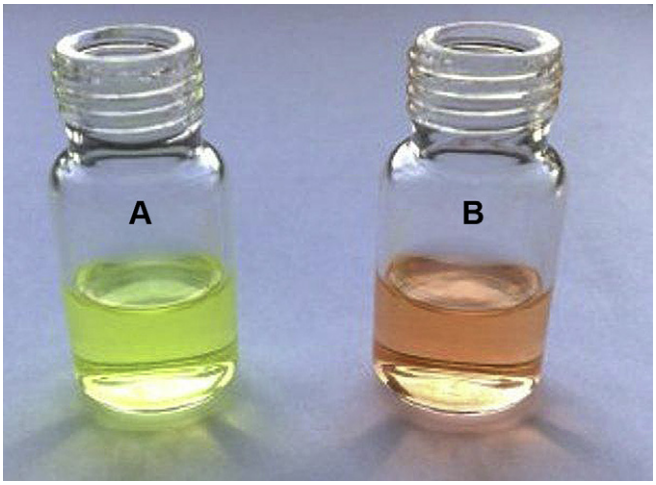


Fig. 3. The colour change of sensor **5** in water/ethanol (4:1, v/v) solution on addition of hydrochloric acid.

which could be observed visually upon addition of hydrochloric acid the colour of the alkaline solution changed from yellow (Fig. 3A) to red (Fig. 3B).

The influence of pH on the absorbance of sensor **5** is illustrated in the Fig. 4. Upon acidification of the alkaline solution the absorption maximum intensity at 436 nm decreases and disappears at about pH 2.6. Simultaneously a new longer-wavelength absorption band at 472 nm appears at pH 8 that increases with further acidification of the solution. This phenomenon was probably due to the protonation of the imine (C=N) nitrogen that enhanced the "push–pull" character of the ICT transition and caused a considerable batochromic shift (44 nm) of the absorption band.

In contrast to the work of Qian et al. [30], the absorption spectra of compound **4** showed no isosbestic point, suggesting that a simple equilibrium between two species is missing probably due to their different solubility resulting in the concentration change.

3.4. Influence of pH on the fluorescence properties of the sensors

The changes in the fluorescence spectra of compound **4** in water/ethanol (4:1, v/v) solution ($\lambda_{ex} = 420$ nm) at different pH

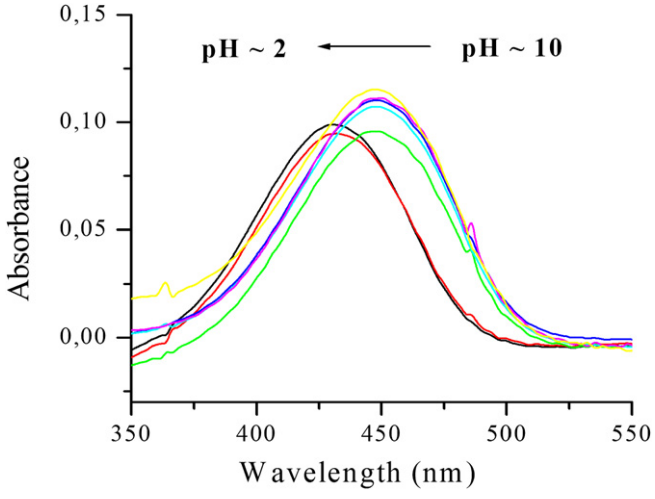


Fig. 2. Absorption spectra of sensor **4** in water/ethanol (4:1, v/v) solution at different pH values.

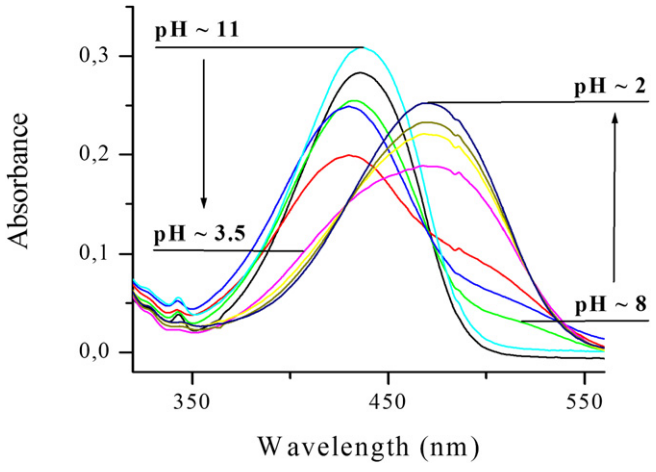


Fig. 4. Absorption spectra of sensor **5** in water/ethanol (4:1, v/v) solution at different pH values.

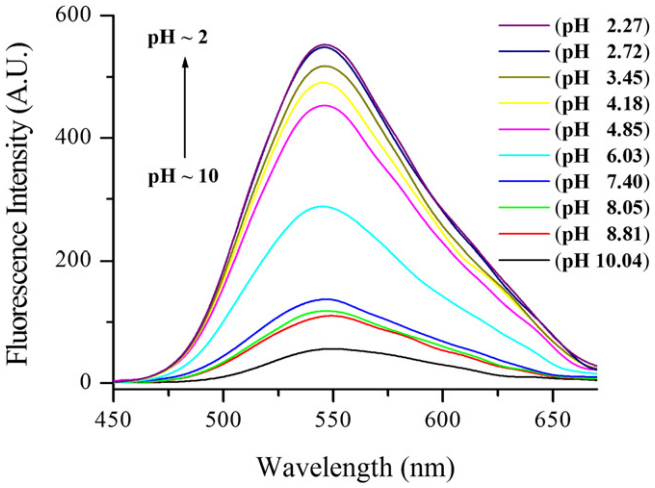
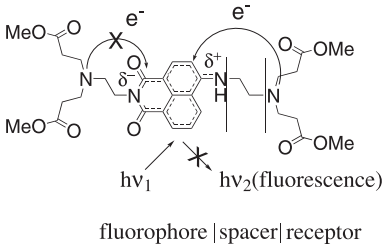


Fig. 5. Fluorescence spectra (λ_{ex} = 420 nm) of sensor **4** in water/ethanol (4:1, v/v) solution at different pH values.

values are depicted in Fig. 5. In alkaline media 1,8-naphthalimide **4** showed fluorescence in the range between 450 and 700 nm, with a maximum at 550 nm. As can be seen, upon acidification the emission intensity was gradually increased with the decrease of the pH and fluorescence maximum was shifted to 546 nm. The amplification of fluorescence intensity in acid media together with the lower fluorescence quantum yield in ethanol than the quantum yield in chloroform indicates that for compound **4** a PET process quenches the fluorescence of the system (Scheme 3).

Upon recognition of the analyte (protons or transition metal ion) the ester-branching amine would increase the oxidation potential of the receptor, and as such, thermodynamically disallow the electron transfer and the emission would be "*switched on*" [37] (Scheme 3). Furthermore, as we demonstrated experimentally, the branching ester receptor in the *N*-position of the 1,8-naphthalimide (the "*upper*" receptor) is unable to involve the fluorophore in a PET process [38]. This fact suggests that only the receptor directly attached to the 4-amino moiety (the "*lower*" receptor) is capable of quenching the excited state of the fluorophore.

The remarkable difference in the behaviour of the receptors in the 4-position and the *N*-position of the sensor **4** can be easily rationalized according to Scheme 4. The 4-aminonaphthalimide fluorophore in sensor **4** is a "*push–pull*" π-electron system with a 4-amino donor and 1,8-naphthalimide acceptor. This arrangement



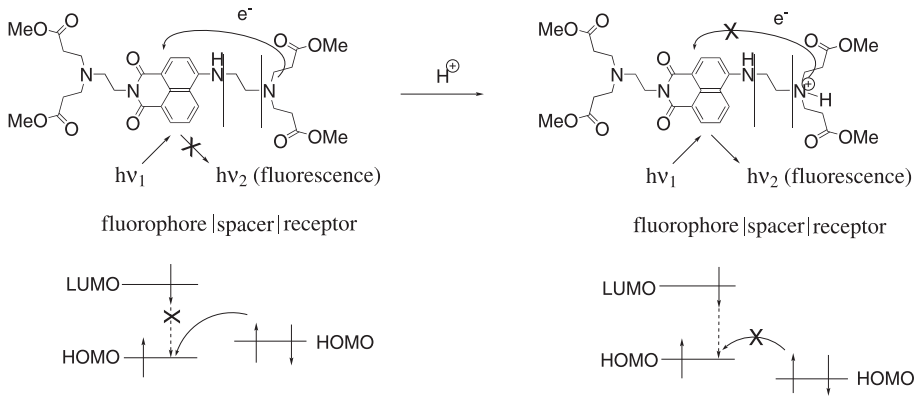
Scheme 4.

leads to strong internal charge transfer (ICT) in the lowest excited singlet state and considerable dipole character (positive pole at the 4-amino terminus). A large dipole moment in the excited state gives rise to a strong photogenerated electric field. Such a molecular electric field can, depending on its sign and magnitude, inhibit or accelerate a transiting electron in the 1,8-naphthalimide unit. Thus the fluorescence quenching PET process is observed only if the electron leaving the unprotonated amine donor can enter the space of the 4-aminonaphthalimide fluorophore across the 4-position with its attractive electric field (Scheme 4). The corresponding PET path from the unprotonated amino receptor in *N*-position is just as feasible thermodynamically but requires the electron to enter the fluorophore across the imide moiety with its repulsive electric field and is not observed [39].

The changes in the fluorescence intensity as a function of pH for compound **4** should be related to the protonation of its "*lower*" amine receptors bonded in the C-4 position of the 1,8-naphthalimide. 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 is substantially removed. Sensor **4** is thus an efficient "*off–on*" switcher for pH. The changes in the fluorescence intensity of **4** as a function of pH are presented in Fig. 6. After careful titration from *ca.* pH 10 to *ca.* pH 2 the emission intensity of sensor **4** had enhanced by approximately ten times (FE = 9.90). The data clearly show that the emission is "*switched off–on*" between *ca.* pH 8 and 5. This switching process was also found to be reversible.

Taking the part of the graph on Fig. 6 located between pH 3.0 and 9.0, the pK_a value of sensor **4** has been calculated by the Eq. (3) [39]. The pK_a value was calculated to be 5.49 that is consistent with the data for compounds of similar nature that have been previously reported [40].

$$\log[(I_{Fmax} - I_F/I_F - I_{Fmin})] = pH - pK_a \quad (3)$$



Scheme 3.

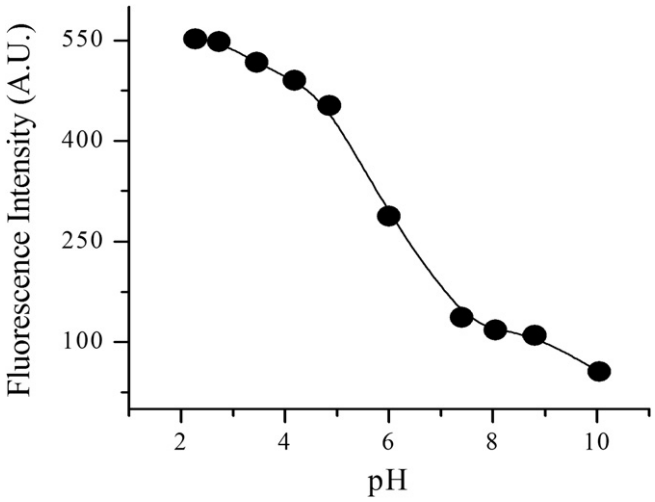


Fig. 6. Effect of pH on the fluorescence intensity of sensor **4** in water/ethanol (4:1, v/v).

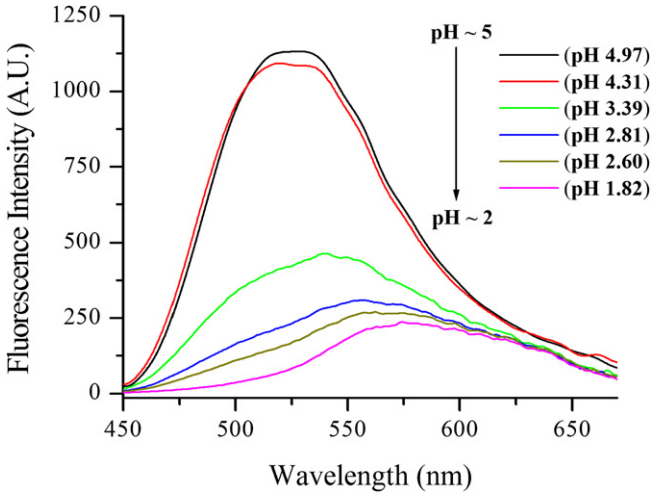


Fig. 8. Fluorescence spectra (λ_{ex} = 420 nm) of sensor **5** in water/ethanol (4:1, v/v) solution in pH range *ca.* 2.0–5.0.

The changes in the fluorescence spectra (λ_{ex} = 420 nm) of compound **5** in water/ethanol (4:1, v/v) solution at different pH values are presented in Figs. 7 and 8. In slightly alkaline solution (pH 8.6) sensor **5** shows fluorescence in the range between 450 and 700 nm, with a maximum at 539 nm. Under these conditions the fluorescence of compound **5** is in "*off-state*", because of the PET quenching from tertiary alkylamine receptor to the fluorophore excited state. Increasing the pH of the solution by the addition of sodium hydroxide from pH 8.6 to *ca.* pH 11.0 expectable initiated additional fluorescence quenching as described in the work of Qian and co-workers by the cleavage of the naphthalene-1,8-dicarboximide ring enabling quenching by molecular vibration [30]. On the contrary, upon acidification of the solution from pH 8.6 to *ca.* pH 5.0 (Fig. 7) the emission intensity of sensor **5** had enhanced (FE = 1.50). This fact is due to the protonation of the tertiary alkylamine receptor that disallows the PET quenching process.

Further acidification of the solution from *ca.* pH 5 to *ca.* pH 2.0 (Fig. 8) significantly quenched the fluorescence intensity of sensor **5** (fluorescence quenching FQ = 4.88) and slightly red-shifted the emission maximum to 575 nm. These changes were a consequence of protonation of the imine (C=N) nitrogen which opened up the non-radiative deexcitation pathway such as solvent effect of water [30].

The changes in the fluorescence intensity of compound **5** as a function of pH are presented in Fig. 9. The graph plotted in the figure clearly shows that the sensor **5** has "*off–on–off*" pH sensing properties with "*on-state*" at about pH 5. For compound **5** two values for pK_a were calculated, one for the protonation of the tertiary amine nitrogen moiety (pK_a = 6.08) and second for the protonation of the imine nitrogen moiety (pK_a = 3.95).

In neutral and alkaline media the fluorescence emission of sensor **5** is in an "*off-state*" (Fig. 9) which is due to the PET quenching from ester-branching amine receptor to the fluorophore excited state (Scheme 5). Upon acidification to *ca.* pH 5, the PET process is thermodynamically disallowed because of the protonation of the amine receptor and the fluorescence of **5** is "*switched on*". Further acidification caused protonation of the imine nitrogen (C=N) thus quenching the emission of sensor **5** again and the fluorescence is "*switched off*". That is why sensor **5** shows "*off–on–off*" pH switching properties with "*on-state*" between pH 6 and pH 4. Also, the switching process of sensor **5**, as that of sensor **4**, was found to be reversible.

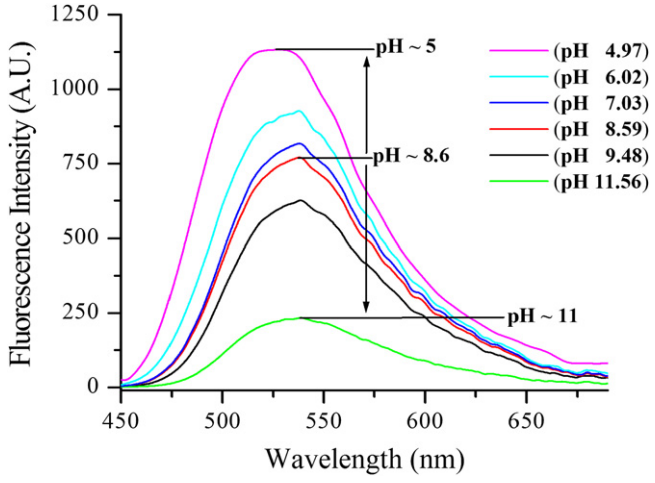


Fig. 7. Fluorescence spectra (λ_{ex} = 420 nm) of sensor **5** in water/ethanol (4:1, v/v) solution in pH range *ca.* 5.0–11.0.

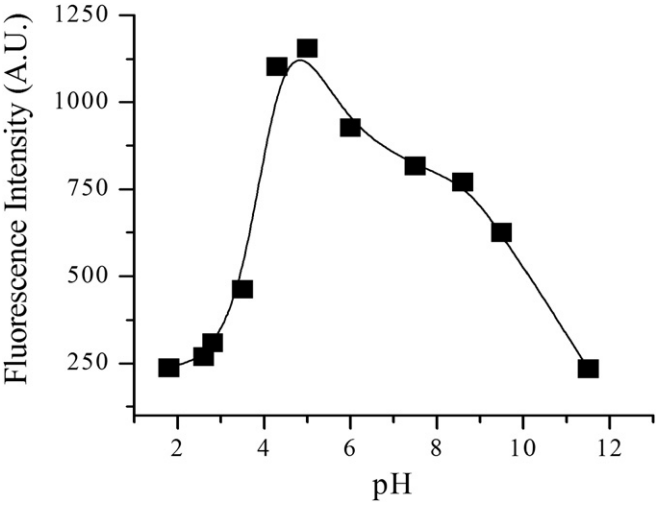
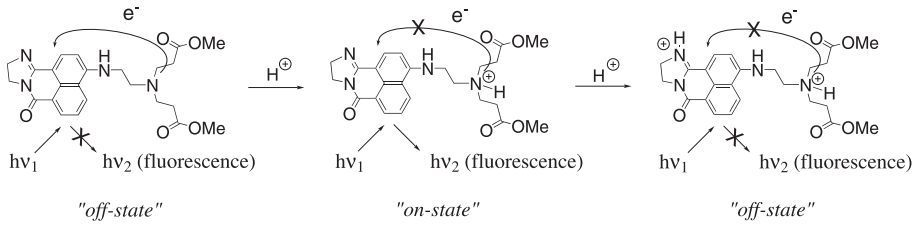


Fig. 9. Effect of pH on the fluorescence intensity of sensor **5** in water/ethanol (4:1, v/v).



Scheme 5.

4. Conclusions

Two novel yellow-green emitting sensors **4** and **5** have been synthesized and their photophysical properties studied. The sensors **4** and **5** were designed as fluorescent switches for determining pH changes over a wide pH scale. In water/ethanol (4:1, v/v) solution 1,8-naphthalimide **4** enhanced its fluorescence intensity *ca.* tenfold (FE = 9.90) in the pH range 2–11. This effect was attributed to the protonation of the tertiary amine receptors, which disallows the PET in the molecule. 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 media and "*switched on*" in acidic environment. The calculated pK_a value of 5.49 for compound **4** indicates that the novel 1,8-naphthalimide would be able to act as efficient "*off–on*" switches for pH. Compound **5** showed weak fluorescence emission intensity in alkaline media as well, that was enhanced (FE = 1.50) upon acidification from pH 8.6 to *ca.* pH 5. This was related again to the protonation of the tertiary amine receptors, which disallow the PET in the system. The pK_a value of 6.08 for this process was calculated. Further acidification from *ca.* pH 5 to *ca.* pH 2.0 quenched the fluorescence of compound **4** (FQ = 4.88), due to the protonation of the imine nitrogen (pK_a = 3.95). These changes indicated that the sensor **5** would be able to act as efficient fluorescence "*off–on–off*" switches for pH determination.

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