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A novel blue fluorescent 4-(1,2,2,6,6-pentamethylpiperidin-4-yloxy)-1,8-naphthalimide pH chemosensor based on photoinduced electron transfer

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Abstract

Three, blue emitting 2,2,6,6-tetramethylpiperidin-4-yloxy-1,8-naphthalimides **1–3** were configured as ‘‘fluorophore-spacer-receptor’’ systems. The photophysical characteristics of the dyes were investigated in water/DMF (4:1, v/v) solution. 1,8-Naphthalimide **1**, which lacks the ‘‘lower’’ amino receptor, and compound **2**, containing a secondary amino receptor at 1,8-naphthalimide 4-oxy moiety, did not show significant changes in emission properties as a function of pH. In contrast to compounds **1** and **2**, 4-(1,2,2,6,6-pentamethylpiperidin-4-yloxy)-1,8-naphthalimide **3** displayed ‘‘*on–off*’’ switching in its fluorescence over a wider pH scale. From the luminescent changes pK_a value of 8.63 was determined. This indicates that the chemosensor **3** would be able to act as highly efficient ‘‘*off–on*’’ fluorescent switcher for pH.

Keywords: 4-Oxy-1,8-naphthalimide; Blue fluorescence; 2,2,6,6-Tetramethylpiperidine; 1,2,2,6,6-Pentamethylpiperidine; Optical sensor; pH sensing; Photoinduced electron transfer

1. Introduction

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 [1,2]. 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 et al. [3], are one of the most popular approaches in design of fluorescent sensors and switchers [4]. 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 the electron transfer to be ‘‘*switched off*’’ and in turn the emission to be ‘‘*switched on*’’ [5].

Environment-sensitive fluorophores are a special class of chromophore [6], of which solvatochromic fluorophores such as 1,8-naphthalimide derivatives, are particularly useful. Because of their strong fluorescence and good photostability, the 1,8-naphthalimide derivatives enjoy application in a number of areas including the colouration of polymers [7], laser active media [8], potential photosensitive biologically units [9], fluorescent markers in biology [10], analgesics in medicine [11], light emitting diodes [12], photoinduced electron transfer sensors [13], fluorescence switchers [14], electroluminescent materials [15], liquid crystal displays [16] and ion probes [17].

A series of 1,8-naphthalimide derivatives, containing different 4-aminoalkyl moieties, with good ‘‘*off–on*’’ switching of fluorescence upon encountering the correct target have been synthesized [5,6,13,14]. Owing to the basicity of the amine group, these serve as fluorescent pH sensors which are finding use in physiology research [18]. In contrast, there are no

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examples which employ 2,2,6,6-tetramethylpiperidine as the basic PET receptor. Recently, we have synthesized new polymerizable blue emitting 1,8-naphthalimides, containing 2,2,6,6-tetramethyl- and 1,2,2,6,6-pentamethylpiperidine fragments, for use as additives for "one-step" brightening and photostabilization of polymers [19]. Therefore, it was of interest to see if 2,2,6,6-tetramethylpiperidin-4-yloxy analogues of the 1,8-naphthalimide fluorophores would shed further light on this issue. This issue takes on added significance given the growing body of sensors and other optical devices which employ 1,8-naphthalimide fluorophores [5,6]. Hence, compounds **1–3** (Scheme 1) were investigated by electronic absorption and emission spectroscopy.

2. Experimental

2.1. Materials

1,8-Naphthalimides **1–3** were synthesized by consecutive reactions of 4-bromo-1,8-naphthalic anhydride first with 2,2,6,6-tetramethylpiperidin-4-ylamine (compound **1**) or allylamine (compounds **2** and **3**) in anhydrous ethanol at 60 °C and then with allyl alcohol (compound **1**), 2,2,6,6-tetramethylpiperidin-4-ol (compound **2**) or 1,2,2,6,6-pentamethyl-piperidin-4-ol (compound **3**) under phase transfer catalysis conditions as described before [19]. 2,2,6,6-Tetramethylpiperidin-4-ylamine, 2,2,6,6-tetramethylpiperidin-4-ol, 1,2,2,6,6-pentamethylpiperidin-4-ol, 4-bromo-1,8-naphthalic anhydride, allyl alcohol and allylamine (Fluka), p.a. grade, was used without purification. All solvents (Fluka, Merck) were of p.a. or analytical grade.

2.2. Methods

UV/vis spectra were recorded on a Hewlett Packard 8452A spectrophotometer with 2 nm resolution at room temperature. The fluorescence spectra were taken on a Perkin Elmer LS 45 fluorescence spectrophotometer. Fluorescence quantum yields were determined on the basis of the absorption and fluorescence spectra. Diphenylanthracene ($\Phi_{\text{ref}} = 0.90$) was used as standard [20].

3. Results and discussion

3.1. Design of the dyes

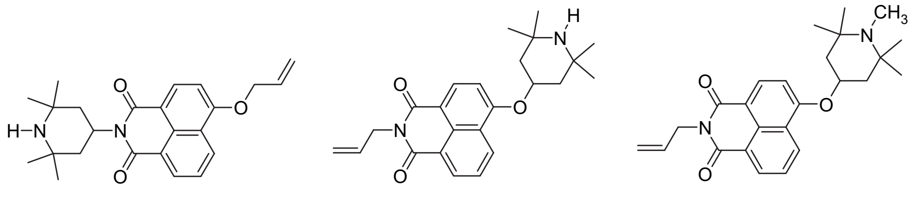
The three dyes (**1–3**) were designed for determining pH changes in the physiological pH range. They are based on the "*fluorophore-spacer-receptor*" model, where the 4-oxy-1,8-naphthalimide moiety is the fluorophore and the 2,2,6,6-tetramethylpiperidine amine or 1,2,2,6,6-pentamethylpiperidine amine is the proton receptor. The hydrocarbon part of the piperidine fragment serves as 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 of the piperidine amine would increase the oxidation potential of the receptor, and as such, thermodynamically disallow the electron transfer [21]. Consequently, the emission would be "*switched on*". Thus we expect the fluorescence to be strong in acidic media.

3.2. Photophysical characterization of the dyes

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

Basic absorption and fluorescent characteristics of the fluorescent brighteners **1–3** such as the absorption and fluorescence (λ_F) maxima, extinction coefficient ($\log \varepsilon$), Stokes shift ($\nu_A - \nu_F$), oscillator strength (f), fluorescent both quantum (Φ_F) and energy (E_F) yields were measured in DMF solution and presented in Table 1.

In DMF solution, the fluorescent brighteners **1–3** displayed intense blue fluorescence due to the charge transfer in the 1,8-naphthalimide moieties from the electron-donating alkoxy substituents at C-4 position to the electron-accepting carbonyl groups. The absorption maxima (λ_A) of compounds **1–3** were in the UV region at 356–368 nm, while the fluorescence emission was observed in the visible region with well pronounced maxima (λ_F) at 433–437 nm. Data presented in Table 1 show that the different substituents at the *N*-imide and C-4 atoms have a small effect on both the absorption and the fluorescence maxima. Fig. 1 displays the absorption and fluorescence



1 **2** **3**

Scheme 1.

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

Compound	λ_A (nm)	log ε (l mol^{-1} cm^{-1})	λ_F (nm)	$\nu_A - \nu_F$ (cm^{-1})	f	Φ_F	E_F
1	364	4.223	437	4589	0.301	0.46	0.383
2	356	4.163	433	4995	0.298	0.25	0.206
3	368	4.373	437	4291	0.393	0.12	0.101

spectra of the fluorescent brightener **1** as a typical example for the spectra of all compounds under study.

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

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

The Stokes shift values of the compounds under study between 4291 cm^{-1} and 4995 cm^{-1} were common for the 1,8-naphthalimide derivatives [22].

The oscillator strength (f) shows the effective number of electrons whose transition from ground to excited state gives the absorption area in the electron spectrum. Values of the oscillator strength were calculated using Eq. (2) where $\Delta\nu_{1/2}$ is the width of the absorption band (cm^{-1}) at 1/2 (ε_{max}) [23].

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

The values of the oscillator strength for the 1,8-naphthalimides **1–3** were 0.298–0.393, which is in agreement with previous investigations where 1,8-naphthalimide derivatives have oscillator strength values in the range 0.30–0.45 depending on the experimental conditions [19b,24].

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 diphenylanthracene ($\Phi_{ref} = 0.90$) as a standard according to Eq. (3) [20], 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.

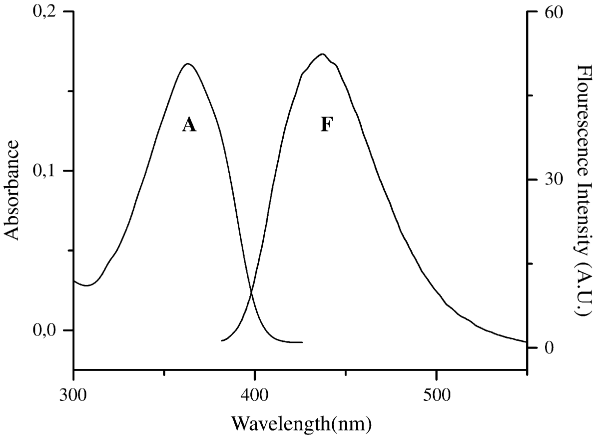


Fig. 1. Absorption and fluorescence spectra of 1,8-naphthalimide **1**, recorded in DMF at concentration 10^{-5} mol l^{-1}.

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

The energy yield of fluorescence E_F (Table 1), calculated by Eq. (4), could also be used instead of Φ_F [7b].

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

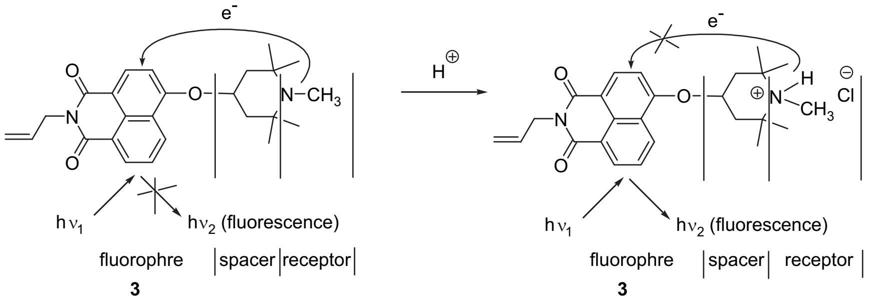
As can be seen (Table 1), the quantum yield of fluorescence of 1,8-naphthalimides **2** and **3** is lower in comparison with the data for compound **1**. This phenomenon might be caused by the possible PET process from the piperidine nitrogen donor (proton receptor) to the 4-oxy-1,8-naphthalimide fluorophore through the piperidinyl spacer [3,4]. Thus the fluorescence of the 4-oxy-1,8-naphthalimide fluorophore is quenched (Scheme 2). Furthermore, as demonstrated experimentally by de Silva et al. [21a] only the receptor that is directly attached to the 4-oxy moiety (the ‘lower’ moiety) is capable of quenching the fluorophores excited state (compounds **2** and **3**). This is due to the fact that molecules like **1–3** have high exited state dipole moments that arise from their Internal Charge Transfer (ICT) excited state nature. In the case of **1–3**, the oxy moiety 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” amine (compound **1**) to transfer an electron to the naphthalimide excited state [14a].

The results obtained suppose PET pH sensor properties of the fluorescent brighteners **2** and **3**, containing 4-oxypiperidine moiety at the C-4 position of the 1,8-naphthalimide fluorophore. This was the reason to investigate the photophysical behaviour of compounds **2** and **3** in water/DMF (4:1, v/v) at different pH values.

3.3. Dependence of pH on the fluorescent intensity of compounds 2 and 3

Basic photophysical characteristics of the fluorescent brighteners **2** and **3** in distilled water/DMF (4:1, v/v) solution (pH = 6.18) are represented in Table 2. There was no significant difference in the absorption spectra of the compounds if compared to those recorded in DMF (Table 1). 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.

In water/DMF (4:1, v/v) solution both compounds are blue emitting. However, the fluorescence intensity of the fluorescent brightener **3** is higher than that of compound **2** (Table 2).



Scheme 2.

Obviously, in the case of compound **2** the oxidation potential of the receptor increases less than that of compound **3** after the protonation of the amino moieties, and as such, thermodynamically disallows the electron transfer to a lower extent. The fluorescence enhancement of compound **3** can be assigned to protonation of the basic piperidine amine in the weakly acidic medium (pH = 6.18), which disallows PET (Scheme 2).

Family of fluorescence emission spectra of **2** as a function of pH was recorded in water/DMF (4:1, v/v) and plotted in Fig. 2. As seen, compound **2** 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 = 1.84).

In contrast to the above results, in alkaline solution for compound **3** only a week emission was observed between 400 and 550 nm (Fig. 3), with λ_F at 457 nm. However, upon acidification the emission was gradually increased as demonstrated in Fig. 3. After careful titration from pH 12 to 3, the emission maximal had shifted to 448 nm, and the emission intensity had enhanced more than six times (FE = 6.43). 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. These changes are due to the protonation of the piperidine amino moiety of compound **3**. 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.

Compound **3** is thus highly efficient "*off–on*" switcher for pH. This switching process was also found to be reversible. Fig. 4 shows the changes in the fluorescence emission spectra of **3** as a function of pH. From these changes the emission is "*switched off–on*" between ca. pH 7 and 10.

Taking the part of the graph located between pH 6 and 11, the pH dependence on the fluorescence intensity has been calculated by Eq. (5) [21b].

Table 2
Fluorescence characteristics ($\lambda_{ex} = \lambda_A$) of 1,8-naphthalimides **2** and **3** at concentration 10^{-5} mol l^{-1} in water/DMF (4:1, v/v)

Compound	λ_{ex} (nm)	log ε (l mol^{-1} cm^{-1})	λ_F (nm)	Intensity[a]	$\nu_A - \nu_F$ (cm^{-1})	f
2	362	4.224	442	238.4	4999	0.358
3	370	4.406	448	380.3	4706	0.456

[a] Fluorescence intensity at λ_F, arbitrary units.

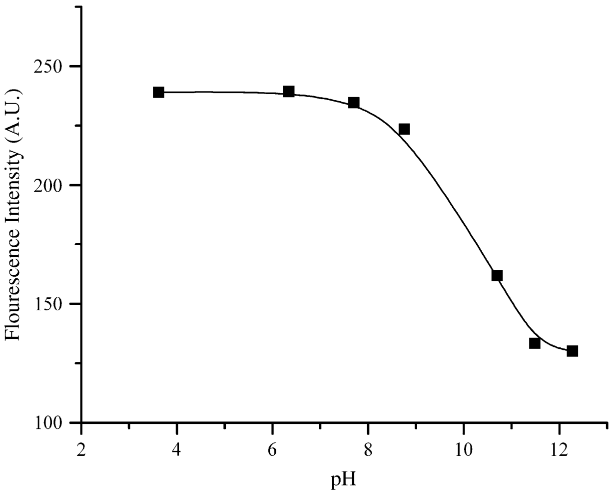


Fig. 2. Effect of pH on the fluorescence intensity (λ_{ex} = 362 nm) of **2** in water/DMF (4:1, v/v).

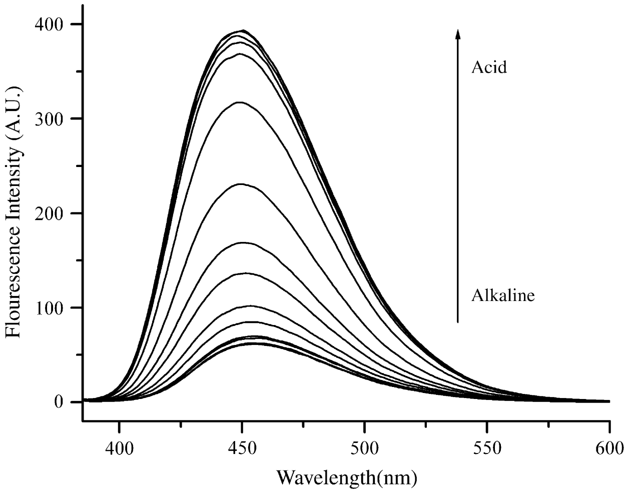


Fig. 3. Changes in the fluorescence spectra of **3** as a function of pH in water/DMF (4:1, v/v). The pH range was from 11.99 to 3.37.

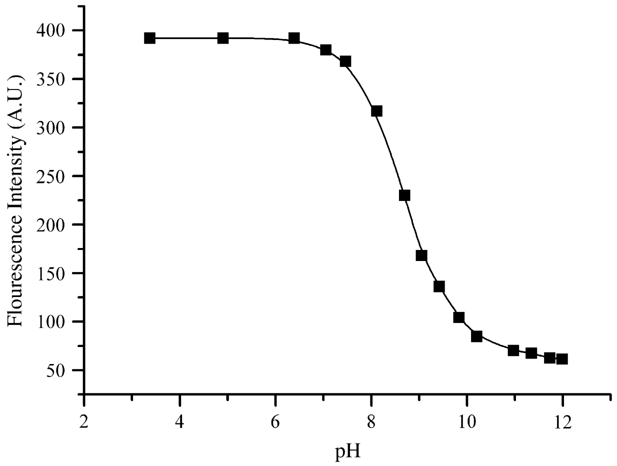


Fig. 4. Effect of pH on the fluorescence intensity ($\lambda_{ex} = 370$ nm) of **3** in water/DMF (4:1, v/v).

$$\log[(I_{F\,max} - I_F)/(I_F - I_{F\,min})] = pH - pK_a \qquad (5)$$

A pK_a value of 8.63 has been found. These results are consistent with compounds of similar nature that were developed before [21a,25]. This shows that the protonation of the outer rim tertiary amines is responsible for the main part of the fluorescence enhancement.

4. Conclusions

Three blue emitting 4-oxy-1,8-naphthalimides **1**–**3**, containing 2,2,6,6-tetramethylpiperidinyl moieties, have been designed as pH PET sensors. Their photophysical properties were studied in both DMF and water/DMF (4:1, v/v) solution. 1,8-Naphthalimide **1**, which lacks the amino receptor at the 1,8-naphthalimide 4-oxy moiety, and compound **2**, containing secondary amino receptor at the 1,8-naphthalimide 4-oxy moiety, did not show significant changes in the emission properties as a function of pH. Conversely, the successive neutralizations of the alkaline solution of 4-(1,2,2,6,6-pentamethylpiperidin-4-yloxy)-1,8-naphthalimide **3** allow the fluorescence to change over a wider pH scale. These changes can be attributed to the protonation of the ‘‘lower’’ tertiary piperidine amino moiety of this compound. 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 value of 8.63 for the 4-(2,2,6,6-tetramethylpiperidin-4-oxy)-1,8-naphthalimide chemosensor **3** indicates that it would be able to act as highly efficient ‘‘*off–on*’’ switcher for pH.

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