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Fluorescent 4-(2,2,6,6-tetramethylpiperidin-4-ylamino)-1,8-naphthalimide pH chemosensor based on photoinduced electron transfer

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Abstract

Two isomeric 2,2,6,6-tetramethylpiperidinyl-4-amino-1,8-naphthalimides **5** and **7** were configured as "fluorophore–spacer–receptor" systems. Photophysical characteristics of the dyes were investigated in water/DMF (4:1, v/v) solution. Compound **5**, which lacks the amino receptor at the 1,8-naphthalimide 4-amino moiety, did not show any changes in the emission properties as a function of pH. In contrast to compound **5**, 4-(2,2,6,6-tetramethylpiperidin-4-ylamino)-1,8-naphthalimide **7** displayed "*on–off*" switching in its fluorescence as a function of pH. From the luminescent changes pK_a value of 8.18 was determined. This indicates that the chemosensor **7** would be able to act as highly efficient "*off–on*" fluorescent switcher for pH.

Keywords: 4-Amino-1,8-naphthalimide; 2,2,6,6-Tetramethylpiperidine; Fluorescence; Optical sensor; pH sensing; Photoinduced electron transfer (PET)

1. Introduction

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]. The "*off*" and "*on*" states of the molecular devices refer to their luminescence, magnetic or electronic properties. 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 [2].

The photoinduced electron transfer (PET) system using the "fluorophore–spacer–receptor" format, developed by de Silva [3], is one of the most popular approaches to the 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 chromophores. Their spectroscopic behaviour is dependent on the physicochemical properties of surrounding environment. Particularly useful are solvatochromic fluorophores that display sensitivity to the polarity of the local environment, such as 4-amino-1,8-naphthalimide derivatives [5c,6]. Because of their strong yellow-green fluorescence and good photostability, the 1,8-naphthalimide derivatives have found application in a number of areas including 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]. Moreover, these properties are essential when employing such devices in real-time and on-line analysis.

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 examples which employ 2,2,6,6-tetramethylpiperidine as the basic PET receptor. Recently, we have synthesized a new polymerizable yellow-green 1,8-naphthalimides, containing

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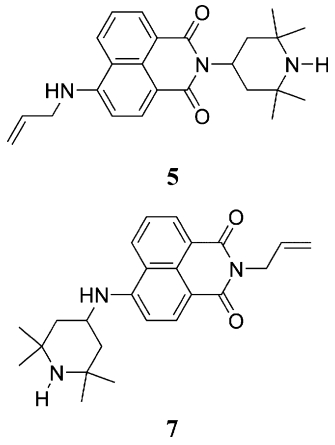

Scheme 1.

a 2,2,6,6-tetramethylpiperidine fragment, for use as additives for "one-step" fluorescent dyeing and photostabilization of polymers [19]. Therefore, it was of interest to see if 2,2,6,6-tetramethylpiperidine analogues of the 4-aminoalkyl-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 4-amino-1,8-naphthalimide fluorophores [6]. Hence, compounds **5** and **7** were synthesized by improved procedure and investigated by electronic absorption and emission spectroscopy (Scheme 1).

2. Experimental

2.1. Materials

The starting 4-nitro-1,8-naphthalic anhydride **1** [10,16c] as well as the intermediates 4-nitro-*N*-(2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthalimide **3** [19a] and 4-nitro-*N*-allyl-1,8-naphthalimide **6** [20] were prepared according to the reported procedures. 2,2,6,6-Tetramethylpiperidin-4-ylamine **2** and allylamine **4** (Fluka), p.a. grade, was used without purification. All solvents (Fluka, Merck) were of p.a. or analytical grade.

2.2. Methods

FT-IR spectra were recorded on a Bruker IFS-113 spectrometer at 2 cm^{-1} resolution using KBr discs. The ^1H NMR spectra (chemical shifts are given as δ in ppm) were recorded on a Bruker DRX-250 spectrometer, operating at 250.13 MHz. The 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. Rhodamine 6G was used as standard ($\Phi_{ref} = 0.95$). 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 of dyes

2.3.1. General preparation procedure for 1,8-naphthalimide dyes 5 and 7

To a solution of intermediate **3** or **6** (5 mmol) in 50 ml of DMF, 0.43 g of allylamine **4** ($d = 0.76$, 7.5 mmol) or 0.78 g of 2,2,6,6-tetramethylpiperidine-4-ylamine **2** ($d = 0.91$, 5 mmol), respectively were added at room temperature. After 24 h (TLC control in a solvent system chloroform/methanol = 9:1), the resulting solution was poured into 300 ml of water. The precipitate was filtered off and washed with water. The crude product was dissolved in a hot mixture solvent of water (5 ml) 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. Re-crystallization from ethanol–water (30:70, vol.%) afforded 1.80 g (92%) of 4-allylamino-*N*-(2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthalimide **5** and 1.51 g (77%) of 4-(2,2,6,6-tetramethylpiperidin-4-ylamino)-*N*-allyl-1,8-naphthalimide **7** as yellow-orange crystals.

2.3.1.1. 4-Allylamino-N-(2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthalimide (5). FT-IR (KBr), cm^{-1}: 1700 ($\nu^{as}C{=}O$); 1665 ($\nu^{s}C{=}O$); 1646 ($\nu C{=}N$); 1598 ($\nu C{=}C$). ^1H NMR (250.13 MHz, $CDCl_3$) ppm: 8.55 (d, 1H, $J = 7.4$ Hz, 1,8-naphthalimide 5-H); 8.42 (d, 1H, $J = 7.8$ Hz, 1,8-naphthalimide 2-H); 8.12 (dd, 1H, $J = 7.5$ Hz, $J = 1.1$ Hz, 1,8-naphthalimide 7-H); 7.62 (t, 1H, $J = 7.5$ Hz, 1,8-naphthalimide 6-H); 6.71 (d, 1H, $J = 7.8$ Hz, 1,8-naphthalimide 3-H); 6.02 (m, 1H, allyl CH=); 5.69 (m, 1H, piperidine CH); 5.50 (br.s, 1H, NH); 5.36 (dd, 1H, $J_{trans} = 17.3$ Hz, $J = 1.1$ Hz, allyl HCH=); 5.30 (dd, 1H, $J_{cis} = 10.5$ Hz, $J = 1.1$ Hz, allyl HCH=); 4.08 (td, 2H, $J = 5.4$ Hz, $J = 1.1$ Hz, allyl NCH_2); 2.53 (t, 2H, $J = 11.9$ Hz, piperidine CH_2); 2.15 (br.s, 1H, piperidine NH); 1.64 (dd, 2H, $J = 12.1$ Hz, $J = 2.5$ Hz, piperidine CH_2); 1.38 (s, 6H, piperidine 2 × CH_3); 1.22 (s, 6H, piperidine 2 × CH_3).

2.3.1.2. 4-(2,2,6,6-Tetramethylpiperidin-4-ylamino)-N-allyl-1,8-naphthalimide (7). FT-IR (KBr), cm^{-1}: 1695 ($\nu^{as}C{=}O$); 1660 ($\nu^{s}C{=}O$); 1658 ($\nu C{=}N$); 1594 ($\nu C{=}C$). ^1H NMR (250.13 MHz, $CDCl_3$) ppm: 8.58 (d, 1H, $J = 7.3$ Hz, 1,8-naphthalimide 5-H); 8.47 (d, 1H, $J = 7.9$ Hz, 1,8-naphthalimide 2-H); 8.08 (dd, 1H, $J = 7.4$ Hz, $J = 1.1$ Hz, 1,8-naphthalimide 7-H); 7.60 (dd, 1H, $J = 7.4$ Hz, $J = 7.3$ Hz, 1,8-naphthalimide 6-H); 6.74 (d, 1H, $J = 7.9$ Hz, 1,8-naphthalimide 3-H); 5.99 (m, 1H, allyl CH=); 5.26 (dd, 1H, $J_{trans} = 17.2$ Hz, $J = 1.2$ Hz, allyl HCH=); 5.20 (dd, 1H, $J_{cis} = 10.4$ Hz, $J = 1.2$ Hz, allyl HCH=); 5.10 (d, $J = 6.1$ Hz, 1H, NH); 4.79 (d, 2H, $J = 4.9$ Hz, allyl NCH_2); 4.09 (m, 1H, piperidine CH); 2.17 (dd, 2H, $J = 11.8$ Hz, $J = 2.2$ Hz, piperidine CH_2); 1.79 (br.s, 1H, piperidine NH); 1.39 (s, 6H, piperidine 2 × CH_3); 1.22 (m, 8H, piperidine 2 × CH_3 and piperidine CH_2).

3. Results and discussion

3.1. Design and synthesis of dyes

The two dyes (**5** and **7**) were designed for determining pH changes in the physiological pH range. They are based on