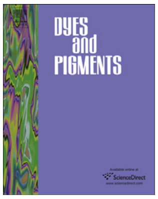
Dyes and Pigments 131 (2016) 9–17

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig



Synthesis, chemosensing properties and logic behaviour of a novel ratiometric 1,8-naphthalimide probe based on ICT and PET

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ARTICLE INFO

Article history:
Received 6 February 2016
Received in revised form
26 March 2016
Accepted 28 March 2016
Available online 30 March 2016

Keywords:
1,8-Naphthalimide
Photoinduced electron transfer (PET)
Internal charge transfer (ICT)
Ratiometric fluorescence probe
Three input disabled-XNOR
Disabled-INHIBIT and disabled-IMPLICATION logic gates
Two output combinatorial logic circuit

ABSTRACT

A novel fluorescence sensing 1,8-naphthalimide designed on the "*receptor$_1$-fluorophore-spacer-receptor$_2$*" model is synthesized and investigated. The novel probe comprising aminotriazole and hydroxyphenyl substituents is capable to operate simultaneously via ratiometric ICT and PET signalling mechanism. The synthesized compound shows excellent signalling properties towards protons, hydroxyl anions and Cu^{2+} ions. Due to the remarkable fluorescence changes in the presence of these analytes the system is able to act as a two output combinatorial logic circuit with three chemical inputs. Input$_3$-Disabled XNOR, INHIBIT and IMPLICATION logic gates were obtained. Because of the parallel action of disabled-XNOR and disabled-INHIBIT gates a magnitude digital comparator with disable capability is achievable.

1. Introduction

Over the past years, design and development of molecular systems, which are able to detect specific guest species at low concentration and to provide significant changes in their electrical, electronic, magnetic or optical signals, have been the subject of great interest in research [1–8]. Among them, fluorescent probes have received much attention due to their advantageous properties such as high sensitivity, high selectivity, rapid response time and cheap instrumentation. Also they are excellent diagnostic tools in the medicine and biology since they enable us to spy on events in living cells and organism with high spatial resolution and minimal perturbation to living systems [9–14].

Two common principles for fluorescence molecular switches are used: photoinduced electron transfer (PET) and internal charge transfer (ICT) [15–18]. PET regularly occurs when certain organic systems interact with light, and the format of "fluorophore-spacer-receptor" is the most commonly exploited approach for the design of fluorescent sensors and switches [19–22]. The fluorophore is covalently linked to a receptor with a non-π-electron-conjugating spacer group (usually alkyl group with two carbons). Typically, the receptor contains an amino group, the electrons of which can bind electron poor analytes. In this model the components are chosen so that PET from the receptor to the fluorophore excited state quenches the fluorescence of the system prior to recognition. Upon recognition of the analyte, which binds to the receptor, engaging its lone-pair electrons, the PET process is no longer possible and the fluorescence of the system is recovered [23–26]. 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 electron-withdrawing/electron-donating unit [27–29]. During excitation of the system the fluorophore undergoes donor-acceptor intramolecular charge transfer which strongly depends on the microenvironment of the fluorophore. Thus, recognition of a guest affects the ICT efficiency that changes the energy between ground and excited state and results in shifting of the fluorophore electronic spectra [30–32]. The attractiveness of the ICT sensors lies on their two-channel output signals - colour change and fluorescence variation allowing the possibility to design a ratiometric fluorescent probes [33–36]. According to the ratiometric method, analyte concentration can be quantified by using the ratio of intensities of fluorescence peaks at two different wavelengths for the analyte free and analyte bound probe. Such

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http://dx.doi.org/10.1016/j.dyepig.2016.03.051
0143-7208/

self-calibration using two emission bands can eliminate the influence of probe concentration, environmental conditions and instrumental efficiency [37–40]. This method allows precise and quantitative analysis and imaging even in complicated systems reducing the problems of autofluorescence, scattering and stability under illumination during fluorescent sensing within many biological and industrial matrices [41–43].

The simultaneous action of PET and ICT sensing signal outputs could provide new and interesting properties. The amalgamation of PET and ICT pathways has provided examples of multilevel logic systems with multiple logic functions, including arithmetic operations by modulation of the fluorescence output [44–48]. The molecules capable of carrying out a variety of sensing functions simultaneously, and to compute a composite result autonomously, have great potential for real-life applications such as object coding and imaging, intelligent materials, drug delivery and activation, diagnostics or actuation [49–59].

Recently we have prepared an ICT and PET based 1,8-naphthalimide bichromophore as a multileveled molecular logic system. However this system didn't exhibit fluorescent ratiometric response which restricts the functionality of the prepared logic system in fluorescent mode. Therefore, in this work we pay attention to the synthesis and fluorescence sensing properties of a novel 1,8-naphthalimide based fluorescent ratiometric probe **2** (Scheme 1) which operates simultaneously via ratiometric ICT and PET signalling mechanism. The optical chemosensing behaviour of the synthesized compound was studied and sequential logic circuits on molecular level were designed.

2. Experimental

2.1. Materials

Commercially available 4-chloro-1,8-naphthalic anhydride, *p*-aminophenol and 3-amino-1,2,4-triazole (Aldrich) were used without purification. All solvents (Aldrich, Fisher Chemical) were pure or of spectroscopy grade. $Zn(NO_3)_2$, $Cu(NO_3)_2$, $Ni(NO_3)_2$, $Co(NO_3)_2$, $Pb(NO_3)_2$, $Fe(NO_3)_3$, $Hg(NO_3)_2$ and $Cd(NO_3)_2$ salts were the sources for metal cations (all Aldrich salts at p.a. grade).

2.2. Methods

FT-IR spectra were recorded on a Varian Scimitar 1000 spectrophotometer. The ^{1}H NMR spectra (chemical shifts are given as δ in ppm) were recorded on a Bruker Avance II+ 600 instrument operating at 600 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 Hewlett Packard 8452A. The fluorescence spectra were taken on a Scinco FS-2 spectrofluorimeter. The fluorescence quantum yields (Φ_F) were measured relatively to Coumarin 6 ($\Phi_F = 0.78$ in ethanol [60]) as a standard. All the experiments were performed at room temperature (25.0 °C). A 1 × 1 cm quartz cuvette was used for all spectroscopic analysis. To adjust the pH, very small volumes of hydrochloric acid and sodium hydroxide were used. The effect of the metal cations upon the fluorescence intensity was examined by adding portions of the metal cations stock solution to a known volume of the fluorophore solution (10 mL). The addition was limited up to 100 μL so that dilution remains insignificant.

2.3. Synthesis of probe (**2**)

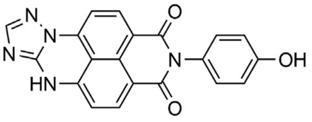
A solution of 4-chloro-1,8-naphthalic anhydride (1.00 g, 0.0043 mol) and *p*-aminophenol (4.7 g, 0.0043 mol) in glacial acetic acid (25 mL) was stirred under reflux for 10 h. After cooling the precipitate was filtered off, washed with water and dried to give 1.32 g of pure 4-chloro-*N*-(4-hydroxyphenyl)-1,8-naphthalimide **1** as brown crystals (1.32 g, 94%, m.p. > 250 °C). Then to a solution of 3-amino-1,2,4-triazole (0.69 g, 8.2 mmol) and KOH (0.9 g, 16 mmol) in DMF (15 mL), a solution of 4-chloro-*N*-(4-hydroxyphenyl)-1,8-naphthalimide **1** (1.32 g, 4.1 mmol) in DMF (5 mL) was added dropwise. The resulting mixture was stirred under reflux for 12 h. After cooling to room temperature, the mixture was poured into water (20 mL) and pH was adjusted do pH 4. The precipitated solids were filtered off and dried to give probe **2** as a yellow solid (0.74 g, 49%, m.p. > 250 °C).

FT-IR (KBr) cm^{-1}: 3309 (ν N-H); 1704 (ν^{s} C=O); 1648 (ν^{as} C=O). ^{1}H NMR (DMSO-d_6, 600 MHz) δ ppm: 9.62 (s, 1H, N-H); 8.48 (d, 1H, J = 7.2 Hz, Naphthalimide H-7); 8.42 (d, 1H, J = 8.1 Hz, Naphthalimide H-2); 8.28 (s, 1H, -N=*CH*-N-); 8.10 (d, 1H, J = 7.1 Hz, Naphthalimide H-6); 7.49 (d, 1H, J = 8.1 Hz, Naphthalimide H-3); 7.06 (m, 2H, Ar*H*); 6.84 (m, 2H, Ar*H*); 5.87 (s, 1H, Ar–*OH*). Elemental analysis: Calculated for $C_{20}H_{11}N_5O_3$ (MW 369.3) C 65.04, H 3.00, N 18.96%; Found C 65.33, H 3.12, N 18.67%.

3. Results and discussion

3.1. Design and synthesis

The novel probe **2** was configured on the "*receptor$_1$-fluorophore-spacer-receptor$_2$*" model (Scheme 2). The aminotriazole 1,8-naphthalimide part in **2** represents the "*fluorophore$_1$-receptor$_1$*" architecture with ICT chemosensing properties, where the 4-amino-1,8-naphthalimide is the fluorophore and the amino group possessing labile hydrogen is the receptor moiety. 1,8-Naphthalimide derivatives are chosen because of their desirable properties, such as excellent photostability, high luminescence efficiency, large Stokes' shift and easy modification of the molecular structure [61–65]. However, the fluorescent ratiometric response is unusual for the naphthalimide probes. The easiest way to obtain 1,8-naphthalimide architecture with fluorescent ratiometric response is to introduce 3-amino-1,2,4-triazole in the *peri*-position to the carbonyl groups [66,67]. Also, the aminotriazole naphthalimides show high water solubility, low cytotoxicity, clear cellular location and membrane permeability in living cells. That is



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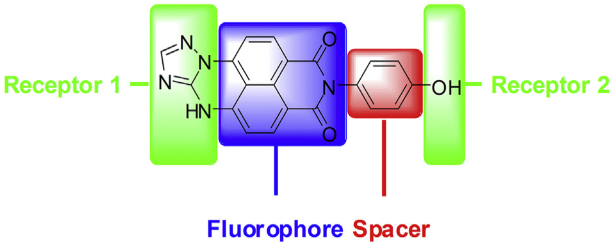
Scheme 1. 1,8-Naphthalimide based probe **2**.



Scheme 2. Design of probe **2** on the "*receptor$_1$-fluorophore-spacer-receptor$_2$*" model.