



Synthesis, sensor activity and logic behaviour of a novel bichromophoric system based on rhodamine 6G and 1,8-naphthalimide



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ABSTRACT

A novel fluorescence sensing system based on rhodamine 6G and 1,8-naphthalimide fluorophores was synthesized and investigated. The system was designed as a wavelength-shifting bichromophoric molecule where the 1,8-naphthalimide moiety is an energy “donor” capable of absorbing light and efficiently transferring the energy to a focal Rhodamine 6G “acceptor”. Furthermore, the 1,8-naphthalimide unit was configured on the “fluorophore-spacer-receptor” format. Thus, the distinguishing features of fluorescence resonance energy transfer systems were successfully combined with the properties of photoinduced electron transfer and classical ring-opening sensor systems. The synthesized compound shows excellent signalling properties towards protons as well as Cu^{2+} and Hg^{2+} over the representative metal ions. Due to the remarkable fluorescence changes in the presence of protons, Cu^{2+} and Hg^{2+} ions the novel system is able to act as a two output combinatorial logic circuit with three chemical inputs.

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1. Introduction

Detection of trace amounts of species such as protons and metal ions is of great interest in the fields of chemical, biological, medicinal and environmental sciences [1–6]. In this regard, fluorescence spectroscopy affords an easy way of sensing and imaging cations because of its simplicity and high sensitivity [7–9].

Determination of pH is one of the most important analytical methods in the chemical laboratories and in the industry. pH is a key parameter in clinical analysis, food production, biotechnological processes, waste water treatment procedures, environmental and life sciences [10–16]. Intracellular pH environments play a central modulating role in biosystems, since minor variations in pH

may lead to markedly changed cellular behaviour in proliferation, apoptosis, enzymatic activity and ion transport [17,18]. Accordingly, some illnesses like cancer, stroke and Alzheimer's disease are found to be accompanied with pH changes [19,20]. Hence the development of simple and convenient approaches for detecting pH is of great importance in both cellular analysis and diagnosis.

Developing sensors for selective and sensitive detection of mercury species have received an immense interest due to their extreme toxicity towards humans [21,22]. Mercury is the third most frequently found and second most common toxic heavy metal in the list of the Agency for Toxic Substances and Disease Registry (ATSDR) of the U.S. Department of Health and Human Services [23]. The extreme toxicity of mercury and its derivatives results from its high affinity for thiol groups in proteins and enzymes, leading to the dysfunction of cells and consequently causing health problems [24,25]. Unfortunately, mercury contamination can occur through a variety of natural and anthropogenic sources including oceanic and volcanic emissions, gold mining, and combustion of fossil fuels. Thus, the health concerns over exposure to mercury have

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motivated the exploration of selective and efficient methods for the monitoring of mercury in biological and environmental samples.

Rhodamine fluorophore has consistently demonstrated its potential to construct fluorescent sensors for determination of protons and mercury, ascribing to their spirolactam ring-opening equilibrium [26–30]. The single emission-based probes usually tend to be affected by a variety of factors such as instrumental efficiency and environmental conditions, as well as the concentration of the probe molecule. These interferences can be eliminated by employing ratiometric fluorescent probes, which allow the measurement of changes of the intensity ratio at two emission bands to provide built-in correction for the above-mentioned environmental effects [9,25,27,31,32]. Several strategies, including internal charge transfer (ICT) [33,34], excited-state intramolecular proton transfer (ESIPT) [35] and fluorescence resonance energy transfer (FRET) [36,37], have been adopted to design ratiometric probes. Among them, FRET strategy could provide moderate resolution of the two emission bands and has been widely applied in designing ratiometric probes for bioanalytical applications. In this work, a novel ratiometric fluorescent probe for pH and mercury detection was developed combining the advantages of the FRET based bichromophoric systems and Rhodamine receptor abilities.

Since the first suggestion for Boolean operator at molecular level based on fluorescent chemosensors, the field has rapidly extended from simple switches to more complex molecular systems that are capable of performing a variety of classical logic functions [38–40] and examples of half-adder [41,42], full-adder [43], keypad lock [44], half-subtractor [45], full-subtractor [43], encoder-decoder [46] and a digital comparator [47–49] have been described. Also a smart oligonucleotide-based automaton that plays simple games such as Tic-Tac-Toe have been reported [50]. Such logic functions are of elevated interest for applications such as object coding, intelligent materials, drug delivery and activation, diagnostics or actuation [51,52]. Nevertheless, the physical integration of molecular logic gates is especially important for rational design and implementation towards advanced molecular scale computing. Herein, we propose a cascade of two molecular fluorescent chemosensors that are integrated in logic circuit comprising a FRET bichromophoric system. The examined bichromophoric system was constructed by coupling of a Rhodamine 6G acceptor dye and a photoinduced electron transfer (PET) based 1,8-naphthalimide donor (Scheme 1).

2. Experimental

2.1. Materials

The intermediate compounds **2** and **3** were prepared according to the reported procedure [53]. Commercially available ethylenediamine and methylacrylate (Aldrich) were used without purification. All solvents (Aldrich, Fisher Chemical) were pure or of

spectroscopy grade. Commercial aqueous buffer solution HEPES (Fisher Chemical) was used as received. $\text{Zn}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$, $\text{Hg}(\text{NO}_3)_2$, and AgNO_3 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 spectrometer. The ^1H NMR spectra (chemical shifts are given in ppm) 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 Hewlett Packard 8452A. The fluorescence spectra were taken on a Scinco FS-2 spectrofluorimeter. The fluorescence quantum yields (Φ_F) were measured relatively to Rhodamine 6G ($\Phi_F = 0.95$ in ethanol [54]) or Coumarin 6 ($\Phi_F = 0.78$ in ethanol [55]) as standards. 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 to 100 μL so that dilution remains insignificant.

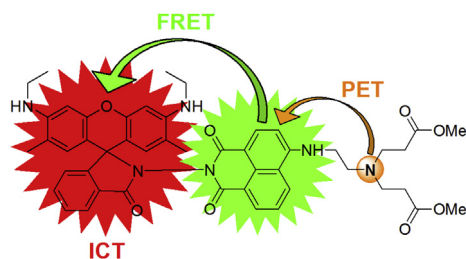
2.3. Synthesis of dyad (**4**)

To a solution of **3** (1.96 g, 3 mmol) in DMF (30 mL), ethylenediamine (6.2 mL, 30 equiv. per reactive nitro group) was added at room temperature. After 48 h, the resulting solution was poured into water. The precipitate was filtered off and washed with water. The final product **4** was obtained as yellow solid after purification by column chromatography using silica gel as a stationary phase and methanol/ammonium hydroxide = 5:0.4 as eluent. In order to remove the silica gel particles, the solid was dissolved in chloroform, resulting solution was filtrated off and the solvent was evaporated in vacuum.

Yield: 1.24 g (62%), m.p. > 250 °C, $R_f = 0.48$ (methanol/ammonium hydroxide = 5:0.4) IR (KBr) cm^{-1} : 3313 and 3224 (ν_{NH} and ν_{NH_2}); 2927 and 2885 (ν_{CH}); 1706 ($\nu^{\text{as}}\text{N}-\text{C}=\text{O}$); 1674 ($\nu^{\text{s}}\text{N}-\text{C}=\text{O}$). ^1H NMR (CDCl_3 -*d*, 250.13 MHz) ppm: 8.18 (d, 1H, $J = 8.4$ Hz, Naphthalimide H-7); 8.11 (m, 1H, 9-Ph H-3); 7.73 (d, 1H, $J = 8.6$ Hz, Naphthalimide H-2); 7.65 (m, 2H, 9-Ph H-4, 9-Ph H-5); 7.56 (d, 1H, $J = 7.2$ Hz, Naphthalimide H-5); 7.29 (m, 1H, 9-Ph H-6); 7.00 (dd, 1H, $J = 8.4$ Hz, $J = 7.2$ Hz, Naphthalimide H-6); 6.51 (m, 3H, Rhodamine H-4, Rhodamine H-5, Naphthalimide 4-NH); 6.21 (d, 1H, $J = 8.6$ Hz, Naphthalimide H-3); 6.05 (s, 1H, Rhodamine H-1); 6.00 (s, 1H, Rhodamine H-8); 3.41 (br.s, 2H, $2 \times \text{NH}$); 3.22 (m, 2H, $\text{NHCH}_2\text{CH}_2\text{NH}_2$); 3.03 (m, 6H, $\text{NHCH}_2\text{CH}_2\text{NH}_2$, Rhodamine $2 \times \text{CH}_2\text{CH}_3$); 1.98 (s, 3H, Rhodamine CH_3); 1.97 (s, 3H, Rhodamine CH_3); 1.20 (m, 8H, NH_2 , Rhodamine $2 \times \text{CH}_2\text{CH}_3$). Elemental analysis: Calculated for $\text{C}_{40}\text{H}_{38}\text{N}_6\text{O}_4$ (MW 666.8) C 72.05, H 5.74, N 12.60%; Found C 72.31, H 5.85, N 12.44%.

2.4. Synthesis of dyad (**5**)

A suspension of Dyad **4** (1.0 g, 1.5 mmol) in methanol (20 mL) was added dropwise over period of 20–30 min to a solution of methylacrylate (1.4 mL, 10 equiv. per reactive amine group) in 2 mL of cooled to 0 °C methanol. The reaction was allowed to warm slowly to room temperature and then stirred for 3 days. The final product was obtained as yellow solid after purification by column chromatography using silica gel as a stationary phase and toluene/ethyl acetate/ethanol = 3:3:1 as eluent. In order to remove the silica



Scheme 1. Rhodamine 6G/1,8-naphthalimide wavelength-shifting bichromophoric system.

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