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Sensor activity and logic behaviour of PET based dihydroimidazonaphthalimide diester

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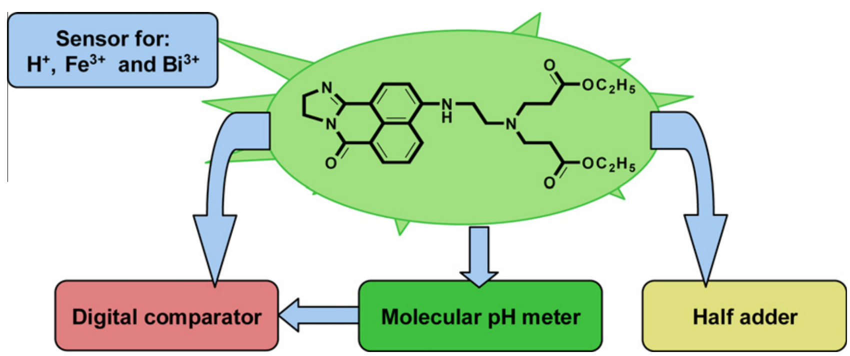
HIGHLIGHTS

- ► Novel naphthalimide derivative is designed as PET based sensor according the "*fluorophore-spacer-receptor*" model.
- ► The sensor naphthalimide efficiently detects protons, Bi^{3+} and Fe^{3+} ions.
- ► The ability of the system to act as multi-functional logic device is demonstrated.
- ► The molecule acts as a molecular pH metre, digital comparator and half-adder.
- ► The novel comparator serves as a fundamental element for control of pH windows.

GRAPHICAL ABSTRACT



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ABSTRACT

An ester terminated dihydroimidazonaphthalimide as multi-functional logic device is presented. Due to the optical changes as a function of pH this simple molecule is able to act as a molecular pH metre, a digital comparator and a half-adder. It was demonstrated that the dihydroimidazonaphthalimide comparator could be used as a fundamental element of an optical device for control of pH windows. Also, the ability of the device to detect metal ions in DMF and in water/DMF (3:1, v/v) at different pHs has been evaluated by monitoring the changes of its fluorescence intensity. Among the tested metal ions (Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Bi^{3+}, Hg^{2+} and Ag^{+}) only Fe^{3+} and Bi^{3+} were efficiently detected. In water/DMF (3:1, v/v) XOR and XNOR logic gates are presented using pH and Fe^{3+} as chemical inputs based on encoding binary digits of logical conventions.

Introduction

Development of new sensors with improved characteristics (selectivity, sensitivity etc.) is a challenging and necessary task in the 21st century, marked by the technological booms consequences [1–5]. Because of the high sensitivity, high speed, and safety the fluorescent chemosensors and switches have been actively investigated in the recent years. The photoinduced electron transfer (PET) using the "*fluorophore-spacer-receptor*" format is the most commonly exploited approach for the design of the fluorescent sensors and switchers [6]. 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, PET communication between the receptor and the fluorophore gets cut off and the fluorescence of the system is recovered. In other words, the presence of a guest is signalled by fluorescence enhancement of the system [7,8].

The area of molecular devices has advanced considerably during the past few years. The extension of the concept of a device to the

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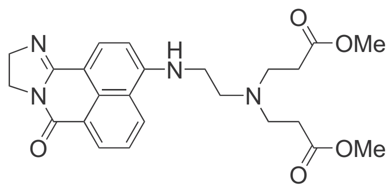

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Scheme 1.

molecular level is of interest, not only for basic research, but also for the growth of nanoscience and the development of nanotechnology [9]. 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. [10,11]. The "*off*" and "*on*" states of the molecular-level devices refer to their luminescence, magnetic or electronic properties. The first suggestion to execute logic operations at the molecular level dated from 1988 [12], but the field was developed only five years later by experimental demonstration of an analogy between the molecular sensors and the logic gates [13]. The field has recently extended from simple switches to more complex molecular systems that are capable of performing a variety of classical logic functions [14–19] and examples of half-adder [20], full-adder [21], keypad lock [22,23], half-subtractor [24–26], full-subtractor [27], encoder-decoder [28].

Recently we have synthesized an ester functionalized dihydroimidazonaphthalimide sensor **1** (Scheme 1). This simple compound was isolated as a by-product throughout the synthesis of other naphthalimide derivative [29]. Sensor **1** is an "*off–on–off*" pH fluorescent switch based simultaneously on both photoinduced electron transfer (PET) and internal charge transfer (ICT) which undergoes a colour change with transition from alkaline to acidic media.

In this work, how to convert the "*off–on–off*" sensing properties of the hydroimidazonaphthalimides in a molecular pH metre was illustrated. Several logic gates were achieved and a molecular comparator was constructed. It was demonstrated that the simultaneous operation of the molecular comparator and the "*off–on–off*" molecular pH metre could be used for pH control. Also, the ability of **1** to detect metal ions was investigated.

Experimental

Materials

The investigated dihydroimidazonaphthalimide diester (**1**) was synthesized as described before [29]. Dimethylformamide (DMF) used in the study was of spectroscopic grade (Aldrich). The pH values were adjusted by addition of NaOH and HCl aqueous solution. $Zn(NO_3)_2$, $Cu(NO_3)_2$, $Ni(NO_3)_2$, $Co(NO_3)_2$, $Pb(NO_3)_2$, $Fe(NO_3)_3$, $Hg(NO_3)_2$, $Bi(NO_3)_3$, $Cd(NO_3)_2$ and $AgNO_3$ salts were the sources for metal cations and used as obtained from Aldrich.

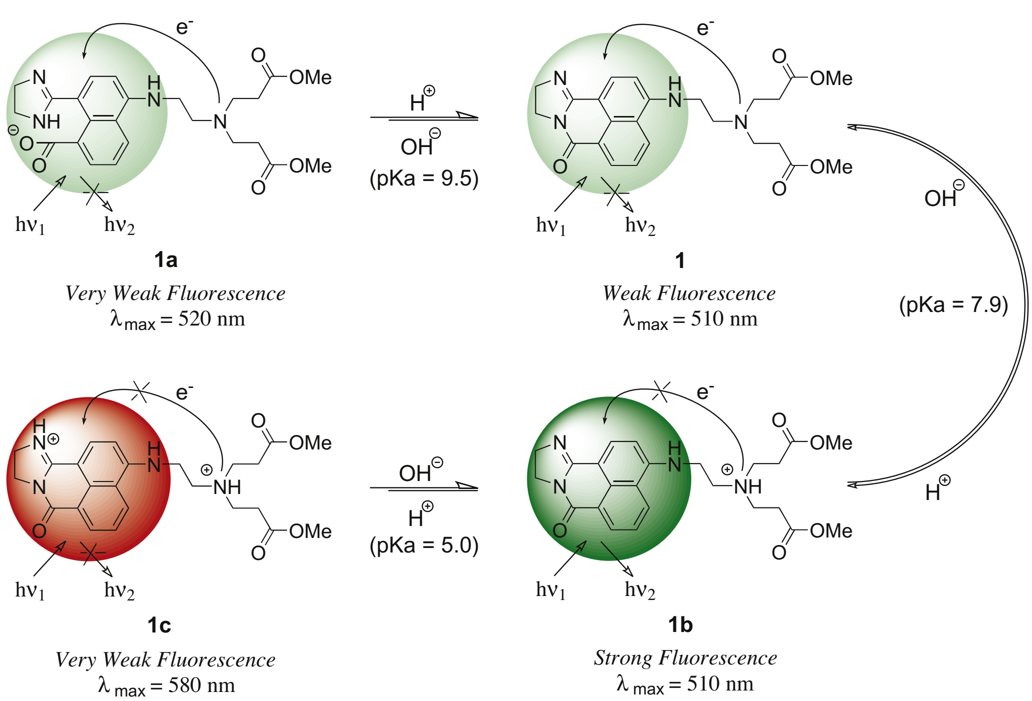
Methods

The pH was measured with a pH metre Metrohm 704, which was standardized with Aldrich buffers. Absorption measurements were performed with a Hewlett Packard 8452A spectrophotometer and fluorescent spectra were recorded on a Scinco FS-2 fluorescence spectrophotometer. All the experiments were performed at room temperature (25.0 °C). A 1 × 1 cm quartz cuvette was used for all spectroscopic analysis. The effect of the metal cations and protons upon the fluorescence intensity was examined by adding 4 or 10 μL portions of the metal cations stock solution (1.0×10^{-5} mol L^{-1}) to a known volume of the fluorophore solution (4 mL). The addition was limited to 50 μL so that dilution remains insignificant.

Results and discussion

Influence of pH on the fluorescence properties of the dye

In slightly alkaline solution sensor **1** shows fluorescence in the range between 450 and 700 nm with maximum at 510 nm. At



Scheme 2.