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An efficient multiple-mode molecular logic system for pH, solvent polarity, and Hg^{2+} ions

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ABSTRACT

A novel fluorophore 1,3-bis(1,1,3-trimethyl-1*H*-benzo[*e*]indol-2(3*H*)-ylidene)propan-2-one (**L**) was synthesized and fully characterized by ^{1}H NMR, ^{13}C NMR, HRMS, and X-ray single-crystal structural analysis. Compound **L** is a pH-controlled molecular switch due to its protonation. The fluorescence change in protic polar solvents means that this compound also could be used as a protic solvent polarity sensor. Among the considered metal ions, the fluorescence of compound **L** could be quenched completely by Hg^{2+} ions with a high selectivity. Based on these fluorescence characters, this fluorescent dye **L** has promising applications as a multiple-mode molecular logic system.

1. Introduction

Developing a wide variety of supramolecular systems performing as elementary electronic devices, such as switches, sensors, logic gates, and molecular-level machines, is an intense research area and of tremendous significance to the development of miniaturized device components.[1] Potential applications of these components in optical and electronic molecular-scale computational devices have attracted considerable effort to this research area.[2]

A significant amount of work has been devoted to obtain specific molecule that is able to change one or several macroscopic properties in response external inputs.[3] The design of fluorescent signaling molecules has attracted a great deal of attention.[4] Many supramolecular systems, the emission properties of which can be modulated by external inputs, such as temperature, pH, redox potential, solvent polarity, and metal ions, have been reported.[5–9] There are few molecular systems behaving as 'multiply configurable' fluorescent indicators.[10]

Merocyanine dyes are heterocyclic chromophores that are extensively used in a number of areas (i.e., as photographic sensitizers, for nonlinear optics, and in chemotherapy).[11] Recently, they have also been employed as sensors of protein conformation and protein interactions in live cell imaging.[12] Here, we design a merocyanine dye, **L** (Scheme 1), which has a carbonyl bearing two benzo[*e*]indoline fragments at both ends. At both sides, **L** has nitrogen atoms (trialkylamine moiety), which could be protonated. In fact, basic donor amino groups can also act as fluorescence quenchers.[13] On account of the nitrogen atoms with lone electron pairs, which can form coordinate bonds, **L** is propitious to recognize special metal ion with high selectivity due to its structure. Based on these results, a pH switch was achieved. Meanwhile, a highly fluorescent material displaying novel solvent polarity-tunable blue-green fluorescence emission was presented, which was clearly different from the behaviors of solvent polarity sensors previously reported. Otherwise, this molecule has a selective detection of Hg^{2+} ions.

As a class of molecular devices, fluorescent logic gates play a pivotal role in molecular computation because they are detectable as a single molecule and can simultaneously treat multiple inputs.[14,15] Within the past decade, many fluorescent logic gates showing NOT, AND, OR, XOR, NOR, NAND, and INHIBIT operations, and combinational logic circuits incorporating single logic gates have been reported.[16] In the same way, the molecule we reported here could demonstrate three different logic functions (NAND, NOR, and INHIBIT) operated by solvent polarity, proton (H^+), and Hg^{2+} as inputs.

2. Results and discussion

The synthetic route to the merocyanine receptor (**L**) is illustrated in Scheme 1. 1,1,2,3-Tetramethyl-1*H*-benzo[*e*]indolinium iodide (**1**) and 2-methylene-1,1,3-trimethyl-1*H*-benzo[*e*]indoline (**2**) were prepared according to the literature method.[17] Treatment of **2** with an appropriate amount of triphosgene and $AlCl_3$ afforded the symmetrical structural **L**. Compounds **1**, **2**, and **L** have been

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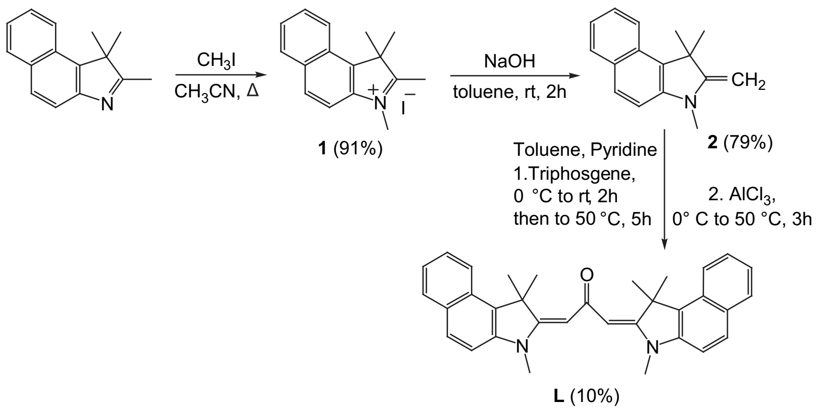

Scheme 1. Synthesis of merocyanine receptor **L**.

characterized by ^1H NMR spectroscopy, ^{13}C NMR spectroscopy, and HRMS (ESI) spectrometry. Compound **L** was also characterized crystallographically.

2.1. pH switch

Molecular systems behaving as a fluorescent indicator of the pH window have attracted much attention, because the proton (H^+) concentration is simply and easily controlled.[18] Due to the very low solubility of **L** in water, its properties as a base have been examined in a THF/H_2O mixed solvent. A 50% THF solution of **L** (1.0×10^{-5} M) was titrated with H^+ ($HClO_4$). After addition of H^+, the yellow solution of **L** turned colorless (see the photograph in Fig. 1a). The color bleaching resulted from the progressive disappearance of the absorption band at 441 nm. Meanwhile, upon addition of H^+, a new smaller absorption band with a peak at 393 nm forms and develops, as shown in Figure 2. The absorption makes a blue shift of 48 nm. There is no absorption from 500 to 700 nm, so this segment is not shown in Figure 2.

As shown in the photograph (Fig. 1b), the solution of **L** in 50% THF emits blue fluorescence, which can be considered as 'switched on'. Upon addition of H^+, the blue fluorescence was quenched gradually. It was quenched completely at pH=2, which is considered as 'switched off' as shown in Figure 3. Since compound **L** is not 'ideal' polymethine, the mirror-image relationship of absorption and fluorescence is often abrogated.

In this pH sensing system, with a decrease in pH of the solution, the color was bleached and the fluorescence quenched. This change occurs because of the protonation of the nitrogen atoms (two trialkylamine moieties). The nitrogen atoms change from electron-contributing groups to electron-withdrawing units. After the protonation, the whole conjugated system of the molecule has been separated. Thus, the merocyanine-like chromophore was broken up, which resulted in the blue shift of the absorption spectrum and the quenching of the fluorescence.

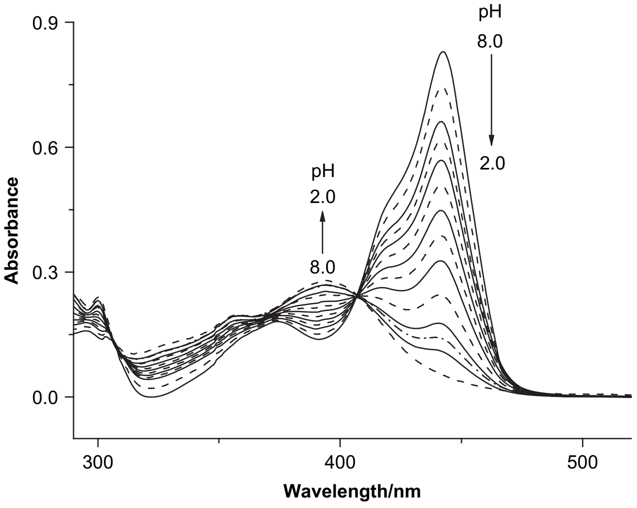

Figure 2. UV–vis spectra in the course of titration of the aqueous THF solution (1.0×10^{-5} M) of **L** with H^+, at 298 K.

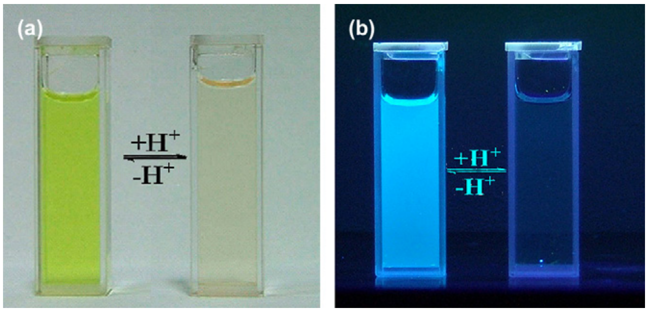

Figure 1. The color change (a) and fluorescence emission (b) responses of **L** (1.0×10^{-5} M in THF/H_2O=1:1) on addition of H^+. Left to right: in the absence (pH=8) and presence (pH=2) of H^+ in KCl (0.1 M) solution at 298 K.

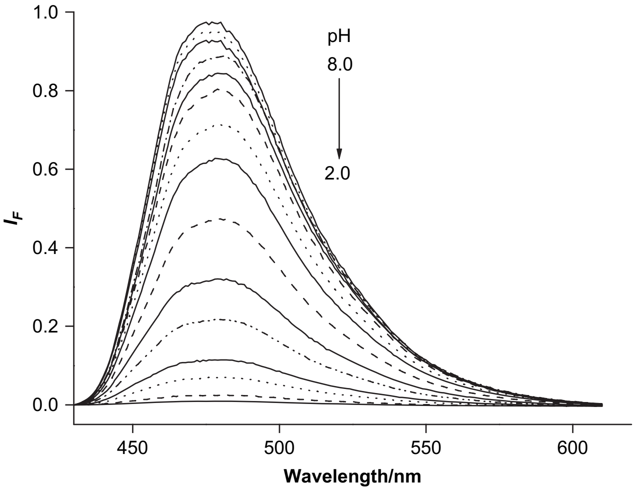

Figure 3. Change in fluorescence spectra (λ_{ex}=410 nm) of **L** (10 μM) with pH in aqueous KCl (0.1 M) solution with 50% THF at 298 K.