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## Sensing behavior and logic operation of a colorimetric fluorescence sensor for $\text{Hg}^{2+}/\text{Cu}^{2+}$ ions



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### ABSTRACT

A BODIPY-based **1** as a colorimetric fluorescence sensor was synthesized, and its metal sensing property was investigated. **1** displayed high selectivity and sensitivity towards  $\text{Hg}^{2+}$  and  $\text{Cu}^{2+}$  ions among 15 different metal cations. The addition of  $\text{Hg}^{2+}$  and  $\text{Cu}^{2+}$  ions into **1** in  $\text{CH}_3\text{CN}$  resulted in a significant bathochromic shift of the UV absorption spectra from 533 nm to 560 nm and 593 nm, respectively, changing the corresponding colors from pink to purple and blue. When excited at 530 nm, the fluorescence intensity of **1** was quenched over 75% upon addition of  $\text{Hg}^{2+}$  ions, while **1** with  $\text{Cu}^{2+}$  ions exhibited significant fluorescence enhancement with a 23 nm red-shift. Based on these results, three logic gates (OR, IMPLICATION, and INHIBIT) were obtained by controlling the chemical inputs.

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### 1. Introduction

Molecular logic gates, with a potential application in molecular computers, have become an active field in supramolecular chemistry because of present trends in electronic device miniaturization [1–4]. Since the pioneering work by de Silva [5], many fluorescent chemosensors have been constructed as molecular logic gates by using chemically encoded information (such as anions, cations, pH, and light) as inputs, and absorption and/or fluorescence signals as outputs due to various advantages, including high sensitivity, low cost, and real-time detection [6–8]. In particular, fluorescent chemosensors capable of recognizing and sensing heavy or transition metal cations are more interesting as molecular logic gates for future molecular computing because these sensors can also detect trace and important heavy metal elements in the environment and biological systems [9–24]. Alternatively, colorimetric fluorescence sensors that recognize the analyte to cause a certain degree of hypsochromic or bathochromic shift of the UV absorption spectrum with a corresponding color change, have recently attracted considerable scientific attention due to the feasibility of naked-eye detection of analytes without additional requirements [25,26].

The present study is part of our ongoing research on the development of BODIPY-based fluorescent chemosensors [27–31], where we synthesized a BODIPY-based colorimetric fluorescence sensor (**1**) with

bis[2-(phenylseleno)ethyl]amine as a receptor, and also analyzed its photophysical properties. **1** showed high selectivity and sensitivity for  $\text{Hg}^{2+}$  and  $\text{Cu}^{2+}$  ions with color changes visible with the naked eye. Furthermore, by operating in absorbance and fluorescence mode with  $\text{Hg}^{2+}$  and  $\text{Cu}^{2+}$  ions as chemical inputs, **1** was used for mimicking various logic functions including OR, INHIBIT, and IMPLICATION.

### 2. Experimental

#### 2.1. Materials

All chemicals (analytical grade) were obtained from commercial sources and used without further purification. The metal salts (spectroscopic grade) [ $\text{AgClO}_4$ ,  $\text{AlClO}_4 \cdot 9\text{H}_2\text{O}$ ,  $\text{Ba}(\text{ClO}_4)_2$ ,  $\text{Ca}(\text{ClO}_4)_2$ ,  $\text{Cd}(\text{ClO}_4)_2$ ,  $\text{Co}(\text{ClO}_4)_2$ ,  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Fe}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ ,  $\text{Fe}(\text{ClO}_4)_3$ ,  $\text{Hg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{KClO}_4$ ,  $\text{Mg}(\text{ClO}_4)_2$ ,  $\text{NaClO}_4$ ,  $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ , and  $\text{Zn}(\text{ClO}_4)_2$ ] were purchased from J&K Chemical Company and used without further purification.  $\text{CH}_3\text{CN}$  (spectroscopic grade) was purchased from Energy Chemical Company. Bis(2-phenylselenoethyl)amine (**2**) [32] and 5-chloro-4,4-difluoro-3-(4-(ethynyl)phenylethynyl)-8-(4-tolyl)-4-bora-3a,4a-diaza-s-indacene (**3**) [33] were synthesized as described previously.

#### 2.2. Instrumentations

$^1\text{H}$  NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer using tetramethylsilane (TMS, 0.00 ppm) as an internal standard. Mass spectra were recorded on a Hewlett–Packard 5989A mass

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spectrometer (ESI mode). High-resolution mass data were obtained with a Kratos MS50TC instrument. UV–Vis absorption spectra and steady-state emission spectra were obtained using a Perkin Elmer Lambda 40 UV–Vis spectrophotometer and a Perkin Elmer LS-55 fluorescence spectrophotometer, respectively. Freshly prepared samples in 1-cm quartz cells were used for all the UV–Vis absorption and emission measurements. The samples for spectroscopic measurements were prepared as follows. A sensor **1** solution (2.0  $\mu\text{M}$  in spectroscopic grade acetonitrile) and different metal ions aqueous solutions (0.1 M in deionized water) were first prepared. Then different metal ions aqueous solution (2  $\mu\text{L}$ ) were added into sensor **1** solution (2 mL). After mixing for 2 min, the mixture solution was measured at room temperature.

### 2.3. Synthesis

Bis(2-phenylselenoethyl)amine **2** (46 mg, 0.12 mmol) and **3** (35 mg, 0.08 mmol) were dissolved in  $\text{CH}_3\text{CN}$  (15 mL), and stirred at room temperature for 2 h under argon. After evaporating the solvent,  $\text{H}_2\text{O}$  (30 mL) was added. The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 20$  mL), then dried by  $\text{Na}_2\text{SO}_4$  and evaporated. The crude product was purified by column chromatography on silica gel, eluting with a mixture of  $\text{CH}_2\text{Cl}_2$  and petroleum ether (2:1, v/v) to give red solid **1**. Yield: 77%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J = 8.4$  Hz, 2H), 7.54–7.52 (m, 4H), 7.49 (d,  $J = 8.4$  Hz, 2H), 7.46 (d,  $J = 8.2$  Hz, 2H), 7.36 (d,  $J = 8.2$  Hz, 2H), 7.33 (d,  $J = 8.0$  Hz, 2H), 7.29 (d,  $J = 8.0$  Hz, 4H), 6.87 (d,  $J = 5.3$  Hz, 1H), 6.59 (d,  $J = 3.9$  Hz, 1H), 6.27 (d,  $J = 3.9$  Hz, 1H), 6.17 (d,  $J = 5.3$  Hz, 1H), 4.04 (t,  $J = 7.5$  Hz, 4H), 3.52 (s, 1H,  $\text{C}\equiv\text{C}$ ), 3.19 (t,  $J = 7.5$  Hz, 4H), 2.43 (s, 3H,  $\text{CH}_3$ ). ESI-MS:  $m/z$  788.9 [M – H] $^+$ . HRMS [M – H] $^+$ : calcd. for  $\text{C}_{42}\text{H}_{33}\text{BF}_2\text{N}_3\text{Se}_2$  788.1111, found 788.1075 (Scheme 1).

## 3. Results and discussion

### 3.1. Colorimetric recognition of $\text{Hg}^{2+}$ and $\text{Cu}^{2+}$

The colorimetric sensing ability of **1** in  $\text{CH}_3\text{CN}$  was investigated upon the addition of 15 different metal cations ( $\text{Ag}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Hg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ). As shown in Figs. 1, **1** displayed two absorption bands at 343 nm and 533 nm, corresponding to  $\text{S}_2 \leftarrow \text{S}_0$  and  $\text{S}_1 \leftarrow \text{S}_0$  transition of BODIPY, respectively [34, 35]. When excess amounts of these metal cations (50 equiv.) were added to the  $\text{CH}_3\text{CN}$  solution with **1**, the UV–Vis absorption spectra exhibited no visible changes, except for  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  ions. Upon the addition of  $\text{Hg}^{2+}$  ions, the main absorption peak corresponding to the  $\text{S}_1 \leftarrow \text{S}_0$  transition shifted bathochromically to 560 nm. However, for  $\text{Cu}^{2+}$  ions, a new strong absorption peak at 593 nm with a shoulder at 555 nm appeared, instead of the disappearance of the main absorption peak. Fig. 2 shows the absorption spectra of **1** in  $\text{CH}_3\text{CN}$  solution (2  $\mu\text{M}$ ) upon the addition of different concentrations of  $\text{Hg}^{2+}$  and

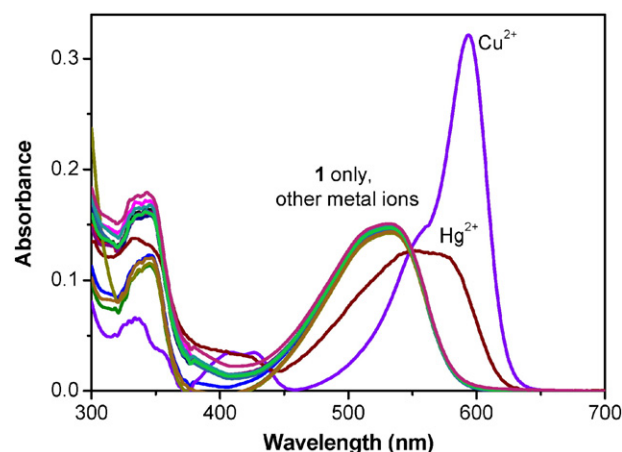
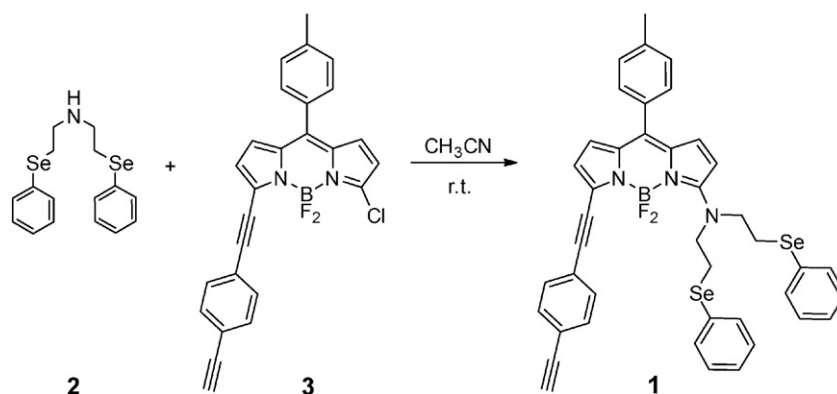


Fig. 1. UV–Vis absorption spectra of **1** (2.0  $\mu\text{M}$ ) in the presence of metal ions (100  $\mu\text{M}$ ) in  $\text{CH}_3\text{CN}$ .

$\text{Cu}^{2+}$  ions ranging from 0 to 20  $\mu\text{M}$  and 0–15  $\mu\text{M}$ , respectively. As shown in Fig. 2a, with an increase in the concentration of  $\text{Hg}^{2+}$  ions, the intensity at 533 nm decreased gradually and red-shifted to 560 nm, resulting in a naked-eye color change from pink to purple (as shown in the top row of Fig. 3). Three well-defined isosbestic points at 356, 439, and 548 nm emerged during the titration process, indicating an equilibrium process between **1** and **1**- $\text{Hg}^{2+}$ . Increasing the concentration of  $\text{Cu}^{2+}$  ions resulted in a gradual decrease in the original peak of **1** at 533 nm, followed by formation of a new strong peak at 593 nm with three isosbestic points at 362, 440, and 549 nm (Fig. 2b). The drastic color change from pink to blue was easily observed with the naked eye. All of the above results indicated that **1** detected  $\text{Hg}^{2+}$  and  $\text{Cu}^{2+}$  metal ions colorimetrically, without any cumbersome labor and the need for a sophisticated instrument [25,26].

### 3.2. Fluorescent recognition of $\text{Hg}^{2+}$ and $\text{Cu}^{2+}$

The sensing behavior of **1** to the above mentioned metal ions was further investigated by fluorescence emission spectra, which gave results similar to that of the UV–Vis absorption spectra. As shown in Figs. 4 and 5, **1** showed a fluorescence emission peak maximum at 590 nm when excited at 530 nm. However, the fluorescence intensity of **1** was quenched over 75% upon the addition of  $\text{Hg}^{2+}$  ions. Interestingly,  $\text{Cu}^{2+}$  ions induced significant fluorescence enhancement and a large red-shift from 590 nm to 617 nm. Also, addition of  $\text{Cu}^{2+}$  ions resulted in the color change of **1** solution from orange to pink (Fig. 3). Stimulation of other metal ions caused no remarkable changes in the emission peak and emission intensity of **1**. Using the fluorescence titration data (Fig. 5) and the Benesi-Hildebrand method [36], the



Scheme 1. Synthetic route to sensor **1**.

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