



A novel BODIPY-based colorimetric and fluorometric dual-mode chemosensor for Hg²⁺ and Cu²⁺



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ABSTRACT

A novel BODIPY-based colorimetric fluorescent sensor with bis[2-(phenylseleno)ethyl]amine as binding site (**Se-1**) for Hg²⁺ and Cu²⁺ has been developed. **Se-1** shows high selectivity and sensitivity toward Hg²⁺ and Cu²⁺ over alkali and transition metal ions. **Se-1** shows a significant red-shift in the absorption spectra from 525 to 571 nm for Hg²⁺ and 590 nm for Cu²⁺, which induces color changes from pink to purple and blue. Upon excitation at 570 nm, **Se-1** upon interaction with Hg²⁺ ions displays a 5-fold fluorescence enhancement with a 2 nm blue-shift, while **Se-1** with Cu²⁺ exhibits a 13-fold fluorescence enhancement and red-shifts from 595 to 610 nm. The binding mode of **Se-1** with Hg²⁺ or Cu²⁺ has been investigated by Job's plot, ESI and ¹H NMR experiments. The absorption and fluorescence of the **Se-1**-Hg²⁺ complex can be reversibly restored to that of the uncomplexed ligand by using EDTA or cysteine, however, the sensing processing of **Se-1** in response to Cu²⁺ ions cannot.

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1. Introduction

Copper is one of the most essential trace heavy metal elements in the human body because copper takes part in various fundamental physiological processes. Copper serves as a catalytic cofactor for a variety of metalloenzymes, such as superoxide dismutase, tyrosinase and cytochrome *c* oxidase [1]. However, if the intake of copper exceeds cellular needs, copper exhibits toxicity, causing serious neurodegenerative diseases, such as Alzheimer's, Menkes and Wilson's diseases due to the displacement of other vital metal ions in enzyme-catalyzed reactions [2]. Mercury, another heavy metal ion, is widely distributed in the environment and one of the most notorious toxic metals. When it is absorbed from the environment, mercury can accumulate in the human body, inducing a variety of diseases in the kidneys, brain and the central nervous system [3]. Thus, developing methods for the detection of these two metal ions have been catching considerable attention in the medical, biological and environmental science.

Comparing to other techniques, fluorescence sensors based on ion-induced optical signal changes have become the most promising candidates for the detection of metal ions because of their many advantages such as simplicity, low cost, high sensitivity, instantaneous response and reproducibility [4]. A typical artificial fluorescence sensor usually contains both a binding site and

a signaling subunit. When the binding site chelates with metal ions, the signaling subunit of the fluorescence sensor will display corresponding changes in fluorescence emission, enabling the quantitative determination of metal ions [5]. Among a variety of dyes, BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-s-indacene) has been one of the most interesting signaling subunits in the artificial fluorescent sensors due to its remarkable photophysical properties, such as strong absorption and emission in the visible region, high fluorescence quantum yield, high molar absorption coefficients, and photochemical stability. Moreover, BODIPY has an amenability to structural modification, which makes the absorption and emission bands of BODIPY easily tune to near infra-red (NIR) or red spectral range [6]. Probes with spectra in this wavelength region are preferable for applications in biological systems because they reduce autofluorescence and limit photodamage of living cells [7]. Recently, a few BODIPY-based fluorescent sensors for the detection of Hg²⁺ [8] and Cu²⁺ [9] upon the visible wavelength excitation have been developed.

In continuation of our interests in developing new fluorescent probes based on BODIPY [10], herein we report a new BODIPY fluorescent sensor derivative (**Se-1**) with bis[2-(phenylseleno)ethyl]amine as the ion recognition unit and a [4-(methoxycarbonyl)phenyl]ethynyl group to extend bathochromic spectral shifts [11] for sensing Cu²⁺ and Hg²⁺ ions. **Se-1** displays significant changes in the absorption and great fluorescence enhancements in CH₃CN upon the addition of Hg²⁺ and Cu²⁺ ions.

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2. Experimental

2.1. Materials

All reagents and solvents (analytical grade and spectroscopic grade) were obtained commercially and used without further purification. THF was distilled from sodium prior to use. The metal salts [AgClO₄, Ba(ClO₄)₂, Ca(ClO₄)₂, Cd(ClO₄)₂, Co(ClO₄)₂, Cu(ClO₄)₂·6H₂O, Copper(I) thiophene-2-carboxylate, Fe(ClO₄)₂·H₂O, Fe(ClO₄)₃·6H₂O, Hg(ClO₄)₂·3H₂O, KClO₄, Mg(ClO₄)₂, NaClO₄, Ni(ClO₄)₂·6H₂O, Pb(ClO₄)₂·3H₂O and Zn(ClO₄)₂] were purchased from Aldrich. Bis(2-phenylselenoethyl)amine (**1**) [12] and 5-chloro-4,4-difluoro-3-(4-(methoxycarbonyl)phenylethynyl)-8-(4-tolyl)-4-bora-3a,4a-diaza-s-indacene (**2**) [10d] were synthesized according to the corresponding literature.

2.2. Instrumentations

¹H and ¹³C NMR spectra were recorded at room temperature with a Bruker Avance 400 instrument operating at a frequency of 400 MHz for ¹H and 100 MHz for ¹³C nuclei. ¹H NMR spectra in CDCl₃ were referenced to tetramethylsilane (δ = 0.00 ppm) as an internal standard. ¹³C NMR spectra in CDCl₃ were referenced to the CDCl₃ (δ = 77.16 ppm) signal. Mass spectra were recorded on a Hewlett-Packard 5989A mass spectrometer (ESI mode). High-resolution mass data were obtained with a Kratos MS50TC instrument. X-ray diffraction measurements were made on a BRUKER SMART 1000 CCD diffractometer equipped with graphite crystal monochromatized Mo Kα radiation (λ = 0.71073 Å) at 291(2) K. The structure was solved by direct methods with the SHELXS-2000 program, and refined anisotropically by full-matrix least-squares methods for all non-H atoms. All H atoms were added according to theoretical calculations and refined isotropically.

UV–vis absorption spectra were recorded on a Perkin Elmer Lambda 40 UV–vis spectrophotometer. Corrected steady-state excitation and emission spectra were obtained by using a Perkin Elmer LS-55 fluorescence spectrophotometer. Freshly prepared samples in 1-cm quartz cells were used for all UV–vis absorption and emission measurements. All spectroscopic measurements were taken with solutions with 2.0 μM of **Se-1** in spectroscopic grade acetonitrile and various concentrations of metal salts, EDTA and cysteine in deionized water at room temperature.

2.3. Synthesis

To a solution of **2** (47 mg, 0.1 mmol) in CH₃CN (15 mL), bis[2-(phenylseleno)ethyl]amine (57 mg, 0.15 mmol) was added. The reaction mixture was stirred at room temperature for 3 h under

argon. After evaporating the solvent, 30 mL of water was added and the aqueous layer was extracted with CH₂Cl₂ (3 × 40 mL), dried by Na₂SO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel, eluting with a mixture of CH₂Cl₂ and petroleum ether (2:1, v/v) to give red solid **Se-1** (5-*N*-bis(2-phenylselenoethyl)amino-4,4-difluoro-3-(4-(methoxycarbonyl)phenylethynyl)-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene). Yield: 85%. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.99 (2H, d, *J* = 8.0 Hz), 7.69 (2H, t, *J* = 8.0 Hz), 7.53 (4H, m), 7.27 (10H, m), 6.76 (1H, d, *J* = 5.2 Hz), 6.62 (1H, d, *J* = 4.0 Hz), 6.32 (1H, d, *J* = 4.0 Hz), 5.73 (1H, d, *J* = 5.2 Hz), 3.98 (4H, t, *J* = 8.0 Hz), 3.91 (3H, s, OCH₃), 3.11 (4H, t, *J* = 8.0 Hz), 2.43 (3H, s, Ar-CH₃). ¹³C NMR (100 Mz, CDCl₃) δ (ppm): 166.9, 139.2, 136.5, 135.7, 134.1, 134.0, 133.7, 133.6, 131.9, 131.5, 131.3, 130.5, 129.5, 129.0, 128.9, 128.8, 128.7, 127.9, 124.8, 120.7, 118.9, 114.1, 95.0, 87.3, 63.8, 53.5, 52.3, 21.5 ppm. ESI-MS: *m/z* 821.86 [M-H]⁺. HRMS [M-H]⁺: calcd. for C₄₂H₃₅BF₂N₃O₂Se₂ 822.1121, found 822.1130.

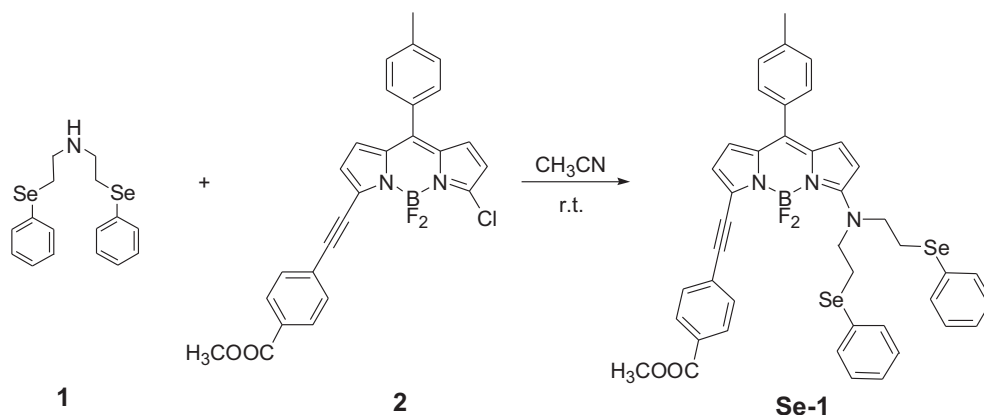
3. Results and discussion

3.1. Synthesis

Se-1 was facily synthesized by the substitution reaction of **1** [12] with **2** [10d] in excellent (85%) yield (Scheme 1). The structure of **Se-1** was confirmed by ¹H NMR and ¹³C NMR spectroscopic, ESI-MS and HRMS data, and single-crystal X-ray diffraction methods. The single crystal of **Se-1** suitable for X-ray diffraction studies was grown by slow evaporation of *n*-hexane into the solution of **Se-1** in CHCl₃. **Se-1** crystallized in the triclinic system, space group *P*₁. The crystallographic data for **Se-1** are listed in Table S1 (Supplementary data). As shown in Fig. 1, the boron atom adopted distorted tetrahedral geometry, with the B–F and B–N bond distances being 1.376(7), 1.382(7), 1.556(7) and 1.574(8) Å, and the angles around boron atom ranging from 106.8(4) to 111.7(5)°, which was similar to the previously reported structures of BODIPY derivatives [13]. The central six-membered ring formed with the boron atom and two adjacent pyrrole five-membered rings of the BODIPY skeletons in **Se-1** was almost planar, and the plane defined by F–B–F atoms of **Se-1** was perpendicular (87.95°) to that of BODIPY core. The dihedral angle between the tolyl ring at the *meso*-position and the BODIPY core was 45°. The C17=C18 triple bond and the C19–C24 aryl ring were almost coplanar (dihedral angle is 0.678°), suggesting efficient conjugation within the entire chromophore.

3.2. Spectral characteristics of **Se-1** with Hg²⁺ and Cu²⁺

The UV–vis and fluorescence titration experiments of **Se-1** with Hg²⁺ and Cu²⁺ were performed in CH₃CN. Fig. 2 shows



Scheme 1. Synthetic route to fluorescent sensor **Se-1**.

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