



# Benzo[e]indolium derivatives in aqueous solutions: Reaction with bisulfite and successive interaction with $\text{Cu}^{2+}$ and $\text{Hg}^{2+}$

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## ABSTRACT

A new benzo[e]indolium derivative **1** including pyridyl and thienyl groups was synthesized and characterized, which failed to response to  $\text{Hg}^{2+}$  or  $\text{Cu}^{2+}$  in aqueous system. However, it is interesting that when it reacted with bisulfite in HEPES buffer, the in situ generated ensemble as **1**-SO<sub>3</sub>H displayed dramatic absorption and fluorescence changes after adding  $\text{Cu}^{2+}$  or  $\text{Hg}^{2+}$ , which were contrary to the changes of **1** upon the addition of bisulfite ions. By contrast, the other two derivatives **2** and **3** showed the almost similar trends of spectral changes, which were short of ligating atoms N or S. The further investigation of <sup>1</sup>H NMR spectra changes of **1** showed that C–SO<sub>3</sub>H bond may be interrupted because the good binding capacity of  $\text{Hg}^{2+}$  and  $\text{Cu}^{2+}$  with O of C–SO<sub>3</sub>H weaken the binding force of C–SO<sub>3</sub>H, which resulted in the recovery of ethylene with benzo[e]indolium block. The DFT calculations results further confirmed it.

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## 1. Introduction

In recent years, optical molecular probes have been drawn much attention because of their simplicity, sensitivity and virtues in real-time observation and visualization. There have been many molecular probes reported for anions [1–4], metal ions [4–6] and some small molecules [4,7–9]. Benzoindolium derivatives, as one of the most important organic functional dyes, have been widely used in optical discs [10,11], biological analysis [12], organic solar cells [13] and nonlinear optical materials [14] due to their good optical properties including wide spectral spectrum and high extinction coefficient. Moreover, benzoindolium derivatives also display potential applications in recognizing molecules because of their water-solubility. Currently, they have been intensively concerned in detecting  $\text{HSO}_3^-/\text{SO}_3^{2-}$  [2,15–21],  $\text{HS}^-$  [22–24] and  $\text{CN}^-$  [15,24–26] for an increasing attention to the environment protection and human healthy. The investigations of these benzoindolium were focused on the detection process including optical changes, detection limits, response time and their nucleophilic addition reaction mechanisms. It should be noted that most of these reported compounds presented selective, sensitive, rapid, and a naked-eye response to  $\text{HSO}_3^-/\text{SO}_3^{2-}$  over other physiologically anions and biothiols.

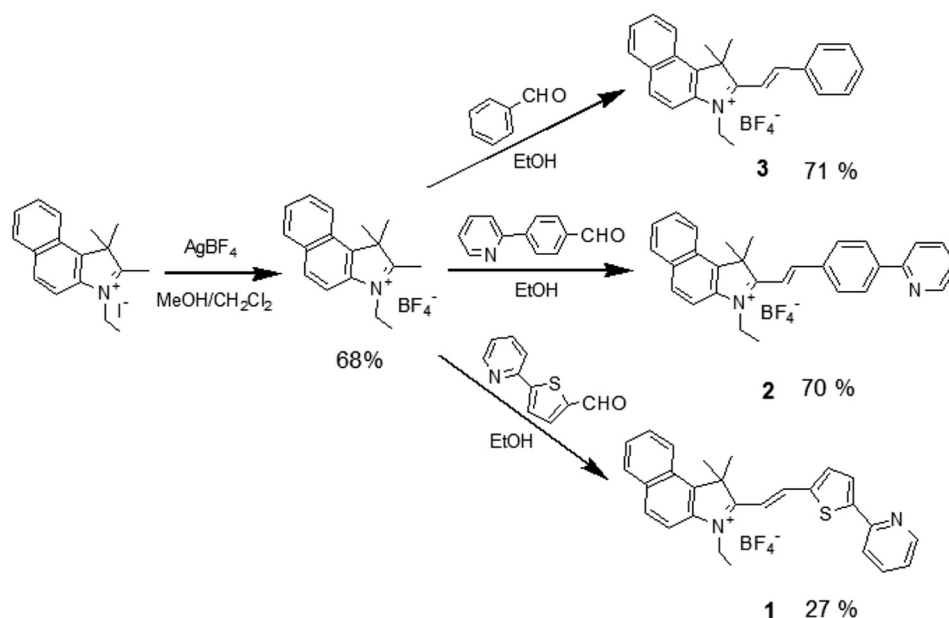
On the other hand, heavy metals such as mercury and copper have caused serious environmental problems. Mercury ions, when they

enter the human body, bring damages to human organs including the heart, brain, lungs, liver, and kidney [27,28]. An excessive intake of copper leads to neurodegenerative diseases and oxidative stress probably by its involvement in the procedure of reactive oxygen species [29]. Hence, detection and recognition of these metal ions have gathered much attention owing to its importance [4–6,30–34]. However, most of them only can be operated in organic solvents or organic-aqueous system that organic solvent is predominant. Therefore, the design and development of optical probes that do function well in water is significant and necessary. Some efforts have been devoted to exploring benzoindolium derivatives as metal ions probes [35,36]. The results showed that benzoindolium derivatives have advantages over other common dyes when they were used as probe in water. However, few of them were reported to detecting mercury or copper ions due to their strong affinity with oxygen atom [37,38].

Herein, benzo[e]indolium derivative **1** involving pyridyl and thienyl group was synthesized to detect metal ions in aqueous system (see Scheme 1). By contrast, the other two benzo[e]indolium derivatives **2** and **3** were also synthesized according to the routes depicted as Scheme 1. As expected, all these three compounds failed to detect metal ions in aqueous system such as  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (1: 8, v/v) or  $\text{CH}_3\text{CN}/\text{HEPES}$  solution (pH 7.0, 1: 8, v/v), despite that **1** can provide S coordination atom and a nitrogen coordination atom. Interestingly, their in-situ generated systems with bisulfites (abbreviated as **1**-SO<sub>3</sub>H, **2**-SO<sub>3</sub>H and **3**-SO<sub>3</sub>H) are all susceptible to  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  in  $\text{CH}_3\text{CN}/\text{HEPES}$  solutions and showed obvious spectral changes. It is notable that the presence of some common metal ions ( $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,

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Scheme 1. Synthetic routes of compounds 1–3.

$\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Al}^{3+}$ ) did not induce any significant spectra changes of these ensembles in comparison with  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$ . As results, all these in-situ generated system of compounds 1–3 with bisulfite can be used as probes to detect  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$ , and their sensitivity was not significantly affected by these commonly coexistent metal ions. Based on the structures of compounds 1, 2 and 3, it can be found that the sensing unit mainly depended on the  $-\text{SO}_3\text{H}$  group. The  $^1\text{H}$ NMR spectral changes of 1 and DFT calculations of three compounds verified that the presence of the  $-\text{SO}_3\text{H}$  group that probably donated electrons to metal ions  $\text{Cu}^{2+}$  or  $\text{Hg}^{2+}$  resulted in fracture of  $\text{C}-\text{SO}_3\text{H}$  and recovery of the benzo[e]indolium block with ethylene.

## 2. Experimental Section

### 2.1. Materials and Physical Measurements

All solvents were commercially available and used without further purification unless specified. 2,3,3-Trimethyl-1-ethylbenzo[e]indolium iodide [15] and 4-(2-pyridyl)benzaldehyde [39] were prepared by the methods described in the literatures and confirmed by  $^1\text{H}$  NMR spectra. Herein, NMR spectra were recorded on Bruker Avance-400 and TCI IITM 600 MHz spectrometers at room temperature. Dimethyl sulfoxide ( $\text{DMSO}-d_6$ ) or  $\text{CDCl}_3$  was used as solvent with tetramethylsilane (TMS) as an internal standard. Mass spectra were obtained on a G6520 Q-TOF LC/MS spectrometer. UV–Vis absorption spectra were measured using a Shimadzu UV-2550 spectrophotometer. All fluorescence spectra were measured on a Hitachi F-7000 fluorescence spectrometer at room temperature. The PMT voltage was 400 V, and the excitation and emission slit width were 10 and 10 nm, respectively. The excitation wavelengths used for compound 1, 2 and 3 were 380, 371 and 320 nm, respectively. Quantum efficiency measurements in HEPES buffers were carried out at room temperature with  $\lambda_{\text{ex}} = 350$  nm. The solution of quinine sulfate in 0.1 mol  $\text{dm}^{-3}$  sulfuric acid ( $\phi = 0.58$ ) was used as a reference [40].

### 2.2. Synthesis and Characterizations

**2.2.1. Synthesis of 2,3,3-Trimethyl-1-ethylbenzo[e]indolium Tetrafluoroborate**  
2,3,3-Trimethyl-1-ethylbenzo[e]indolium iodide (0.71 g, 1.95 mmol) and  $\text{AgBF}_4$  (0.39 g, 2.01 mmol) were dissolved in 20 mL of methanol/

dichloromethane (v/v, 1:1). After the mixture was stirred at room temperature for 12 h, the silver(I) salt was removed by centrifugation. Then the clear solution was collected and concentrated to afford an orange solid. Yield: 0.43 g (68%).

### 2.2.2. Synthesis of 5-(2-Pyridyl)thiophene-2-aldehyde

In the solution of 2-bromopyridine (0.50 g, 3.16 mmol) in 40 mL of 1,4-dioxane,  $\text{K}_2\text{CO}_3$  aqueous solution (15 mL, 3 M) and 10 mL of ethanol were added. After the addition of 5-formylthiophene-2 boronic acid (0.59 g, 3.79 mmol),  $\text{PPh}_3$  (0.067 g, 0.19 mmol) and  $\text{Pd}(\text{PPh}_3)_4$  (0.22 g, 0.19 mmol), the resulting suspension was refluxed under  $\text{N}_2$  for 24 h. Then, the mixture was cooled and extracted with dichloromethane. The crude compound was purified by column chromatography on silica gel by using petroleum ether/dichloromethane as eluent. Finally, a pale yellow solid was obtained. Yield: 0.26 g (43%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz): 9.94 (s, 1H), 8.65 (d,  $J = 2.27$  Hz, 1H), 7.79–7.75 (m, 3H), 7.70–7.69 (m, 1H), 7.29–7.28 (m, 1H).

### 2.2.3. Synthesis of 1, 2, and 3

**2.2.3.1. Synthesis of 1.** Under nitrogen atmosphere, 10 mL of dry ethanol solution containing 5-(2-pyridyl)thiophene-2-aldehyde (0.10 g, 0.94 mmol) and 2,3,3-trimethyl-1-ethylbenzo[e]indolium tetrafluoroborate (0.29 g, 0.90 mmol) was refluxed with stirring for 12 h. After cooling, the precipitate was filtrated, collected and washed with petroleum ether/ethyl acetate (v/v, 3:1) to afford a red solid. Yield: 70 mg (27%).  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , 400 MHz): 8.63 (d,  $J = 4.83$  Hz, 1H), 8.59 (d,  $J = 15.98$  Hz, 1H), 8.42 (d,  $J = 8.60$  Hz, 1H), 8.24 (d,  $J = 8.86$  Hz, 1H), 8.19 (d,  $J = 8.22$  Hz, 1H), 8.00–7.97 (m, 2H), 7.93–7.91 (m, 3H), 7.83 (t,  $J = 7.05$  Hz, 1H), 7.76 (t,  $J = 7.16$  Hz, 1H), 7.41–7.39 (m, 1H), 7.24 (d,  $J = 15.89$  Hz, 1H), 4.68–4.62 (m, 2H), 2.22 (s, 6H), 1.62 (t,  $J = 7.37$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ , 100 MHz): 181.48, 154.30, 150.72, 149.92, 145.23, 141.34, 138.93, 138.86, 138.24, 137.39, 133.69, 131.42, 130.12, 128.45, 127.46, 127.23, 126.81, 124.11, 123.21, 119.91, 112.49, 109.85, 99.86, 54.04, 42.66, 25.34, 13.19. MS (Maldi-TOF, CHCA):  $m/z$  calculated for 409.17 ( $\text{M}-\text{BF}_4^-$ ), Found: 409.18.

**2.2.3.2. Synthesis of 2.** According to the similar synthetic procedure for 1, compound 2 was prepared by 4-(2-pyridyl)benzaldehyde. Herein, 2 was obtained as an orange-red solid. Yield: 1.05 g (70%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz): 8.71–8.70 (m, 1H), 8.38 (d,  $J = 8.5$  Hz, 2H),

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