

基于氟硼二吡咯染料的汞离子荧光分子探针的合成与光谱性质

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摘要: 合成了一种中位-苯甲酰基取代的氟硼二吡咯类染料衍生物(**1**)并研究了它的金属离子传感性能。在甲醇溶液中,染料 **1** 显示出显著的对汞离子具有选择性的“开-关”型亲离子荧光团响应,而对其他一些代表性碱金属、碱土金属、过渡金属及重金属离子等都没有明显的荧光响应;同时染料 **1** 在对所检测的金属离子中,通过其溶液颜色的改变对汞离子显示出明显的选择性显色行为,以便实现对汞离子的“裸眼检测”。

关键词: 氟硼二吡咯染料; 汞离子; 电子转移; 分子识别; 荧光探针

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Synthesis and Spectroscopic Studies of Molecular Fluorescent Probe for Hg²⁺ Detection Based on Boron Dipyrromethene Fluorophore

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Abstract: A novel boron-dipyrromethene (BDP) derivative **1** with benzyloxy subunit at meso-position was synthesized and its metal ion sensing properties were investigated. In methanol, dye **1** exhibits pronounced “on-off-type” fluorescence response with high selectivity towards Hg²⁺ among the representative alkali-, alkaline earth-, transition- and heavy-metal ions, and dye **1** also shows a significant Hg²⁺ selective chromogenic behavior over the other tested metal ions by changing the color of the solution, which makes possible the “naked-eye detection” of Hg²⁺.

Key words: boron-dipyrromethene (BDP) fluorophore; Hg²⁺; molecular recognition; electron transfer; fluorescent probe

Mercury distributed in water, air and soil can accumulate in animal and human body and induce various diseases such as prenatal brain damage and motion disorders because of its severe immunotoxic, genotoxic, and neurotoxic effects^[1-2]. As a consequence, it is very important to develop high selective and

sensitive sensors for the detection of Hg²⁺ ions in various chemical systems^[3-4], and the design and synthesis of lots of Hg²⁺-indicating sensors have been made over the past decades^[5-8]. In this case, the design of molecules that can induce prominent spectroscopic changes upon selective binding of Hg²⁺ ions is highly

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desirable for ease of quantifications and signal transductions. However, some reported Hg^{2+} -responsive sensors display drawbacks such as low selective discrimination between chemically closely related cations, or not easy to synthesize complicated macrocycle fluorophore and selective ionophore^[9-10].

Recently boron-dipyrromethene (BDP) dyes have received increasing interest in the construction of selective and efficient fluorescent chemical probes because they possess many distinctive and desirable properties such as high molar extinction coefficients, high quantum efficiencies of fluorescence, narrow absorption and emission bands, relative insensitivity to towards pH value and solvent polarity, and resistance to photobleaching. More importantly, their building block synthesis allows the development of various analogues emitting from 500 to 800 nm^[11-12]. These properties have made them promising applications in light-harvesting system^[13], supramolecular fluorescent gels^[14], solar cells^[15], fluorescent sensors or probes for ion sensing signaling^[12,16], etc. In addition, Many BDP derivative-based fluorescent sensors have also been widely applied for the recognition and determination of Hg^{2+} ^[17-18]. We report here the synthesis and spectroscopic properties of a novel meso-substituted BDP derivative **1**, and the prepared ionophore shows highly efficient Hg^{2+} selective chromogenic and definite on off-type fluoroionophoric switching properties in methanol solution over a wide range of metal cations.

1 Experimental

1.1 Instruments

^1H NMR spectra were recorded on a Bruker DRX400 spectrometer and referenced to the residual proton signals of the solvent. The Mass spectra were measured with a Bruker Daltonics Autoflex IITM MALDI-TOF spectrometer. IR spectra were recorded on Bruker Vector 22 spectrometer with KBr pellets in the 4 000 ~400 cm^{-1} region. UV-Visible spectra were recorded on a UV-3100 spectrophotometer. Fluorescence spectra were measured on an Aminco Bowman 2 Luminescence spectrophotometer with a

xenon arc lamp as the light source.

1.2 Procedures for metal ion sensing

Stock solutions of the metal ions ($100 \mu\text{mol} \cdot \text{L}^{-1}$) were prepared in deionized water. A stock solution of **1** ($5 \mu\text{mol} \cdot \text{L}^{-1}$) was prepared in CH_3OH . In fluorescent titration experiments, a 2 mL solution of **1** ($5 \mu\text{mol} \cdot \text{L}^{-1}$) was filled in a quartz optical cell of 1 cm optical path length, and the Hg^{2+} stock solution was added to the quartz optical cell gradually. In selectivity experiments, the test samples were prepared by placing appropriate amounts of metal ion stock solution into 2 mL solution of **1** ($5 \mu\text{mol} \cdot \text{L}^{-1}$). During fluorescence measurements, the excitation wavelength was 490 nm and emission spectra were collected in the range of 500~600 nm. The titration data were fitted according to the procedure described in the references^[19-20].

1.3 Reagents and materials

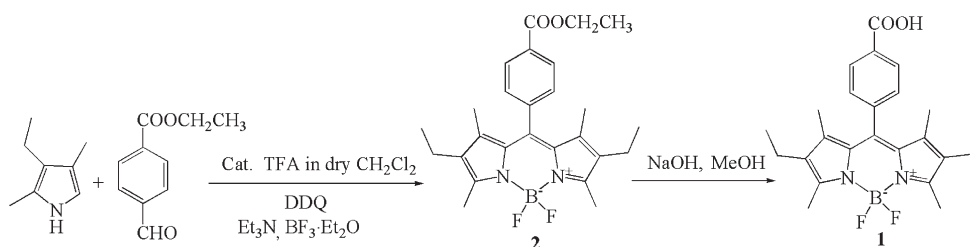
All air- and moisture-sensitive reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. Unless otherwise noted, all reagents or solvents were obtained from commercial suppliers and used as received without further purification. Dry dichloromethane was obtained by refluxing and distilling over CaH_2 . Dry tetrahydrofuran (THF) was distilled from sodium/benzophenone. Triethylamine was obtained by simple distillation. The solvents used for photophysical measurement were of spectroscopic grade without further purification. Chromatographic purifications were conducted by using 40 ~200 μm silica gel obtained from Merck. Thin-layer chromatography (TLC) was performed on silica gel plates coated with fluorescent indicator.

1.3 Synthesis of BDP derivative 1

The synthetic procedures for the preparation of the BDP derivatives are given in Scheme 1. To a solution of 2, 4-dimethyl-3-ethylpyrrole (2 mmol) and 4-ethoxycarbonyl benzaldehyde (1 mmol) in 50 mL of N_2 -saturated dry CH_2Cl_2 was added one drop of trifluoroacetic acid (TFA). The reaction mixture solution was stirred in dark for 3 h at room temperature. A solution of 2, 3-dichloro-5, 6-dicyano-1, 4-benzoquinone (DDQ, 227 mg, 1 mmol) in 20 mL of dry

CH_2Cl_2 was then added, and the solution was stirred for another 1 h. To the mixture, 3 mL of Et_3N was added followed by the addition of 3 mL of $\text{BF}_3\cdot\text{Et}_2\text{O}$. The resulting mixture was stirred for another 1 h and then washed with water. The organic phase was dried over MgSO_4 and concentrated under reduced pressure. The residue was purified by silica-gel column

chromatography and recrystallization from $\text{CHCl}_3/\text{hexane}$ to compound **2** as red crystals. The title compound **1** was obtained by the hydrolysis of **2** in basic methanol at reflux condition. ^1H NMR (400 MHz, CDCl_3): δ 13.2 (s, 1 H), 8.70 (d, $J=8.4$ Hz, 2 H), 7.49 (m, 2 H), 2.42 (s, 6 H), 2.26 (m, 4 H), 1.20 (s, 6 H), 0.91 (m, 6 H).



Scheme 1 Synthetic route for the preparation of **1**

2 Results and discussion

2.1 Spectroscopic properties of **1**

The absorption and steady-state fluorescence spectra of **1** in CH_3OH are shown in Fig.1. The absorption spectrum features with a strong, narrow band centered at 523 nm and a shoulder on the shorter wavelength side centered at about 489 nm, which is typical for the conventional BDP derivatives carrying only alkyl substitutes on the indacene core [21,25]. A considerably weaker and broad absorption band is observed at about 370 nm, which can be ascribed to the $S_0\rightarrow S_2$ transition [22]. The similarity between **1** and those classic BDP derivatives in the absorption spectrum indicates the absence of donor-acceptor interaction in

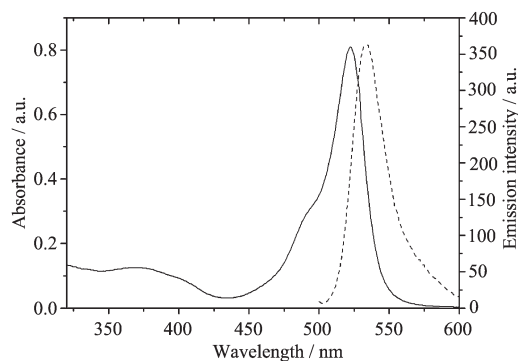


Fig.1 Absorption (solid line) and emission spectra (dashed line) of **1** in CH_3OH

the ground state, which is derived from the decoupled structure between the indacene plane with meso-subunit [23]. Upon excitation at 490 nm, the fluorescence spectrum of **1** shows mirror image shape with a maximum around 533 nm and Stokes shift of 10 nm compared to its absorption spectrum.

2.2 Fluorimetric titrations of **1** with various metal cations

To investigate the utility of compound **1** as the Hg^{2+} -selective fluorescent probe, the selective fluorogenic responses of **1** towards various metal ions were carried out by the fluorescence measurements. Treatment of **1** with 1.0×10^{-4} mol \cdot L $^{-1}$ Hg^{2+} and 2.0×10^{-4} mol \cdot L $^{-1}$ various other metal ions (transition-metal ions of Cu^{2+} , Zn^{2+} , Ni^{2+} and Fe^{3+} , heavy-metal ions of Pb^{2+} and Ag^{+} and alkali-metal and alkaline-earth metal ions of Ca^{2+} , Mg^{2+} , Na^{+} and K^{+}) in MeOH resulted in diverse fluorescence behaviors (Fig.2). Especially with Hg^{2+} , the intense fluorescence of **1** around 533 nm is significantly quenched, and the fluorescence intensity is decreased down to less than 28% of the original value in the presence of 1.0×10^{-4} mol \cdot L $^{-1}$ Hg^{2+} ions. However, the fluorescence intensity of **1** is almost not influenced by addition of 2.0×10^{-4} mol \cdot L $^{-1}$ Mg^{2+} , Ca^{2+} , K^{+} and Ag^{+} ions. On the other hand, among the other metal ions tested, Zn^{2+} , Ni^{2+} , Na^{+} , Cu^{2+} , Fe^{3+} and Pb^{2+} ions also show some

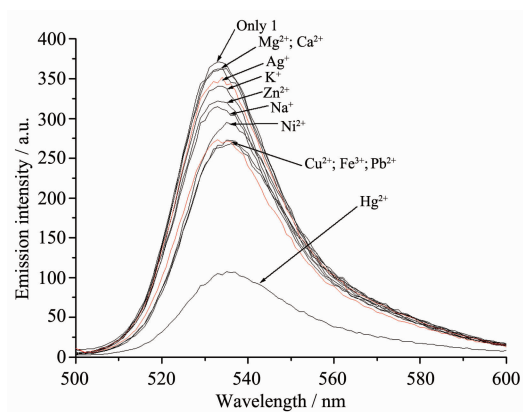


Fig.2 Fluorescence spectra of free **1** and **1** in the presence of $1.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \text{ Hg}^{2+}$, $2.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ metal cations such as Mg^{2+} , Ca^{2+} , Ag^{+} , K^{+} , Na^{+} , Ni^{2+} , Zn^{2+} , Cu^{2+} , Fe^{3+} and Pb^{2+} ($\lambda_{\text{ex}}=490 \text{ nm}$). $c_1=5.0 \mu\text{mol} \cdot \text{L}^{-1}$ in CH_3OH

quenching effects on the fluorescence intensity of **1**, but their degrees of quenching are more insignificant compared to Hg^{2+} ions and at most less than 15% and 30% in the presence of $2.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ former three kinds of metal ions and the latter ones, respectively. The observed significant fluorescence quenching of **1** by Hg^{2+} seems to be very attractive for the design of on-

off type fluorescent probes or molecular switches.

Fig.3 illustrates the changes in fluorogenic responses of **1** in the presence of varying concentrations of Hg^{2+} ions in MeOH. It is clear that the fluorescence intensity of **1** significantly decreases with increasing amount of Hg^{2+} while the position and shape of the fluorescence spectra are almost not affected (only with a slight bathochromic shift in the emission maxima), that is a typical PET type mechanism^[24]. The almost complete quenching of the fluorescence down to the base line is observed with $4.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \text{ Hg}^{2+}$ ions. In the molecular system of dye **1**, the selective binding of Hg^{2+} by the 8-benzoic acid moiety is supposed to be the result of efficient fluorescence quenching, by both the well-known quenching behavior of the complexed Hg^{2+} ions and the benzoic acid/benzoate-dependent on-off type quenching of the BDP- benzoic acid compounds. The association constant K_s for the interaction of **1** with Hg^{2+} ions was determined by the nonlinear curve-fitting procedure of the fluorescence titration data (Fig. 3), and the K_s value of the 1:1 complex formation for **1**- Hg^{2+} is $8183 \text{ mol}^{-1} \cdot \text{L}$.

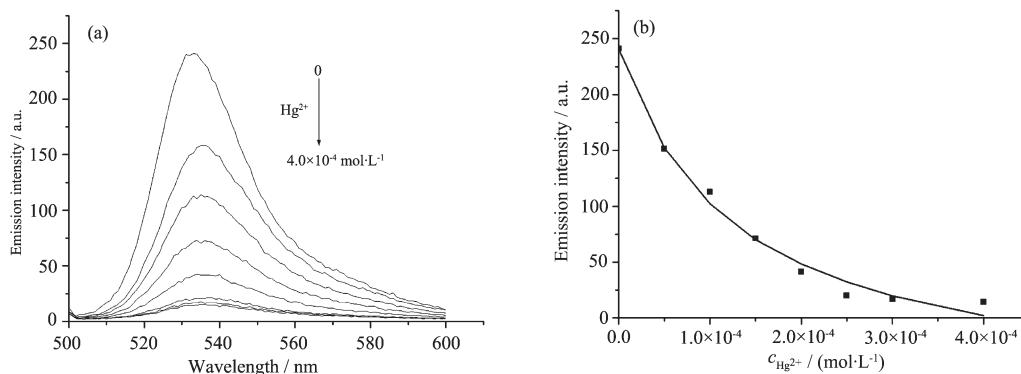


Fig.3 (a) Emission spectra of $5.0 \mu\text{mol} \cdot \text{L}^{-1}$ **1** in CH_3OH in the presence of increasing concentration Hg^{2+} ($0 \sim 4.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$); (b) The fluorescence titration curve of $5.0 \mu\text{mol} \cdot \text{L}^{-1}$ for **1** in CH_3OH as a function of $c_{\text{Hg}^{2+}}$ is obtained from Fig.3a ($\lambda_{\text{em}}=533 \text{ nm}$, $\lambda_{\text{ex}}=490 \text{ nm}$), and the solid line represents the best fits to the fluorimetric titration data of **1**

Obviously, a distinct change in the absorption spectra of **1** is observed by the addition of Hg^{2+} in MeOH. Fig.4 shows that the absorption band of **1** at 523 nm is gradually red shifted to 533 nm with an isobestic point at 536 nm in comparison to that of free dye, and the color of the solution changed from somewhat light

amber of free dye **1** into red, which can be detected with the naked eyes. The changes in the absorption spectra can be explained in terms of electrostatic interactions between the cation and the dipole moment of the dye^[20]. The dipole moment of dye **1** in the excited state is higher than that in the ground state. Therefore, when a

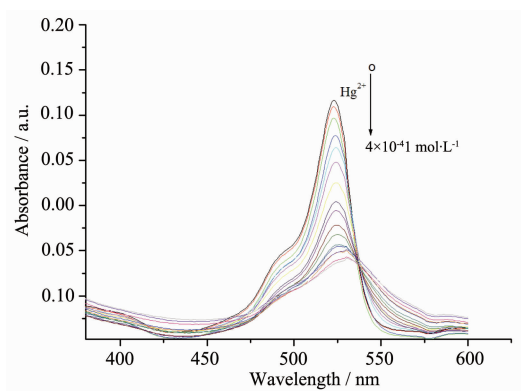


Fig.4 Effect of addition of Hg^{2+} ($0 \sim 4.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$) on the absorption spectra of **1** ($5.0 \mu\text{mol} \cdot \text{L}^{-1}$) in CH_3OH

cation is coordinated with dye **1**, the excited state is more stabilized than the ground state so that the absorption spectrum is red shifted. In addition, we also can observe that the fluorescence spectra are red shifted upon cation binding but to a lesser extent than the absorption spectra. Among the other metal ions employed (Ni^{2+} , Zn^{2+} , Cu^{2+} , Fe^{3+} and Pb^{2+} ions, etc.) a negligible absorption spectral changes are detected, again manifesting a good chromogenic selectivity of **1** toward Hg^{2+} in CH_3OH .

All the observed results indicate that compound **1** shows a selective and sensitive on-off type fluorescence signaling behavior besides a significant chromogenic behavior that makes possible “the naked-eye detection” of Hg^{2+} in CH_3OH . Therefore, **1** can be used as fluorescent and colorimetric probe for Hg^{2+} .

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