



A colorimetric chemosensor for fluoride ions based on an indigo derivative



SuJuan Wang^{a,*}, YanLei Zhao^a, ChunXia Zhao^a, Lei Liu^a, ShuangJun Yu^b

^a College of Chemistry and Environment Science, Hebei University, Baoding, PR China

^b Tangshan CaoFeidian Industrial Park of Equipment Manufacture, Tangshan, PR China

ARTICLE INFO

Article history:

Received 20 May 2013

Received in revised form 22 September 2013

Accepted 24 September 2013

Available online 24 October 2013

Keywords:

Indigo

Boron trifluoride complex

Colorimetric chemosensor

Fluoride ion

ABSTRACT

A novel indigo derivative (**1**) was synthesized and fully characterized. Its structure, confirmed by X-ray crystallography, showed that compound **1** is a planar molecule. Interestingly, compound **1** only has response to fluoride ions among six different anions (F^- , Cl^- , Br^- , I^- , AcO^- , and HSO_4^-) in an anhydrous methylene chloride solution and this response can be detected by the 'naked eyes'.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

During the past decade, highly sensitive and selective chemosensors for ions and biomolecules have attracted a lot of scientists [1–14]. Especially, sensors based on organic conjugated molecules and polymers (which can generate electrochemical and optical responses) can be easily tailored to specially sense one or two ions through simple modification. Using organic probes to detect one or two anions is more challenging because other anions might affect the response to a special anion. Among all anions, fluoride ion is very important in biosystem and can prevent dental carries and osteoporosis [15–17]. However, excess or deficient fluoride ion can not only cause pain in the legs and incomplete stress fractures but also result in accidental and suicidal deaths from acute poisoning [18,19]. Therefore, the fast and efficient detection of fluoride ions is very urgent.

Currently, the chemosensors for fluoride ion are based on naphthalene derivatives [20–24], coumarin derivatives [25,26], cyclopyrrole derivatives [27], indole compounds [28], bis(σ -fluorophenylacetyl) platinum(II) complexes [29] and organo-boron compounds [30,31]. However, a new receptor with higher sensitivity and selectivity is still required because ideal sensors not only offer the qualitative or quantitative information but also can be used for rapid visual sensing. This gap strongly encourages us to

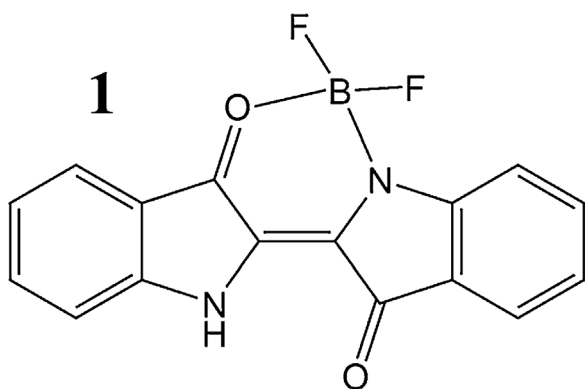
design and prepare a novel fluoride chemosensor based on a new indigo derivative.

As one family of organic natural molecules, indigos with donor ($-NH$) and acceptor ($-C=O$) structures have been widely studied in organic field effect transistors [32]. In addition, their properties could be further tuned through putting different substituted groups in the central region or the benzene rings [33–36]. For example, Melo and Voss groups have prepared a series of novel indigo derivatives and studied their physical properties in detail [37,38]. However, using these compounds to detect ions is rare. Herein, we report the synthesis and characterization of a novel BF_2 -complexed indigo compound **1** (Scheme 1) and its positive response to the fluoride anion.

2. Results and discussion

The synthetic procedure for compound **1** is shown in Scheme 2. Compound **1** was synthesized as a violet solid through a one-step reaction of indigo and $BF_3 \cdot Et_2O$ using methylene chloride as a solvent in the presence of dry Et_3N at 40 °C (Scheme 2). The as-prepared compound **1** was fully characterized through FT-IR, 1H NMR, ^{13}C NMR, and MS mass spectrometers, which were summarized in the supporting information. Thermal gravimetric analysis (TGA) indicated that compound **1** is stable up to 300 °C (see the supporting information, Figure S1). Compound **1** is soluble in common organic solvents such as methylene chloride, chloroform, tetrahydrofuran (THF), acetonitrile, *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO).

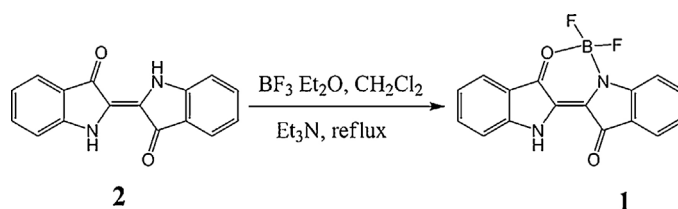
* Corresponding author. Tel.: +86 312 5079317.
E-mail address: wangsj@126.com (S. Wang).



Scheme 1. The chemical structure of compound **1**.

To further precisely understand the structure of compound **1**, single crystal study has been demonstrated. Single crystals suitable for X-ray diffraction analysis were obtained by the slow evaporation of methylene chloride/*n*-hexane (v/v, 1:1) at room temperature. Fig. 1a shows the labeled structure of compound **1** [39]. Compound **1** has a triclinic crystal system, belonging to the space group P1 with the unit cell parameters of $a = 9.0799(18) \text{ \AA}$, $b = 9.2486(18) \text{ \AA}$, $c = 9.2486(18) \text{ \AA}$, $\alpha = 76.54(3)^\circ$, $\beta = 65.06(3)^\circ$, and $\gamma = 65.06(3)^\circ$. As shown in Fig. 1b, the packing model of compound **1** had a short interplanar distance (3.34 Å), indicating that there is strong π - π stacking interactions between neighboring molecules.

The response behavior to fluoride ion for compound **1** was analyzed in anhydrous methylene chloride, as shown as in Fig. 2. Indigo in methylene chloride/DMSO (v/v, 19:1) has single



Scheme 2. Synthetic procedure for compound **1**.

monomeric absorption peak with a maximum at 600 nm (see the supporting information, Figure S2). In contrast to the indigo molecule, the BF_3 -functionalized compound **1** ($3 \times 10^{-5} \text{ M}$) displays a broad absorption band (500–700 nm) with λ_{max} at 620–660 nm. Such a broad peak might be due to the electronic transitions being delocalized throughout the electron-donating group and the electron-withdrawing unit [40–45]. The addition of fluoride ion (0 – $6.0 \times 10^{-4} \text{ M}$) in the form of a tetrabutylammonium salt led to a decrease in the intensity of the primary peaks at 620–660 nm, with the concomitant growth of a blue-shifted band at 580 nm. It should be noted that the intensity of the band at 580 nm reached a constant value at 20 equiv. of fluoride ion at room temperature. Meanwhile, several isosbestic points at 328, 380, 504, 593, and 718 nm were observed, which not only indicated the formation of a new complex but also exhibited an obvious visible response to fluoride anions. In addition, the Job's plot experiment between compound **1** and fluoride anion with a total concentration of $1 \times 10^{-4} \text{ M}$ in anhydrous methylene chloride displays a 1:1 stoichiometric ratio (see the supporting information, Figure S3). Accordingly, the binding constant between compound **1** and fluoride ion was determined through nonlinear

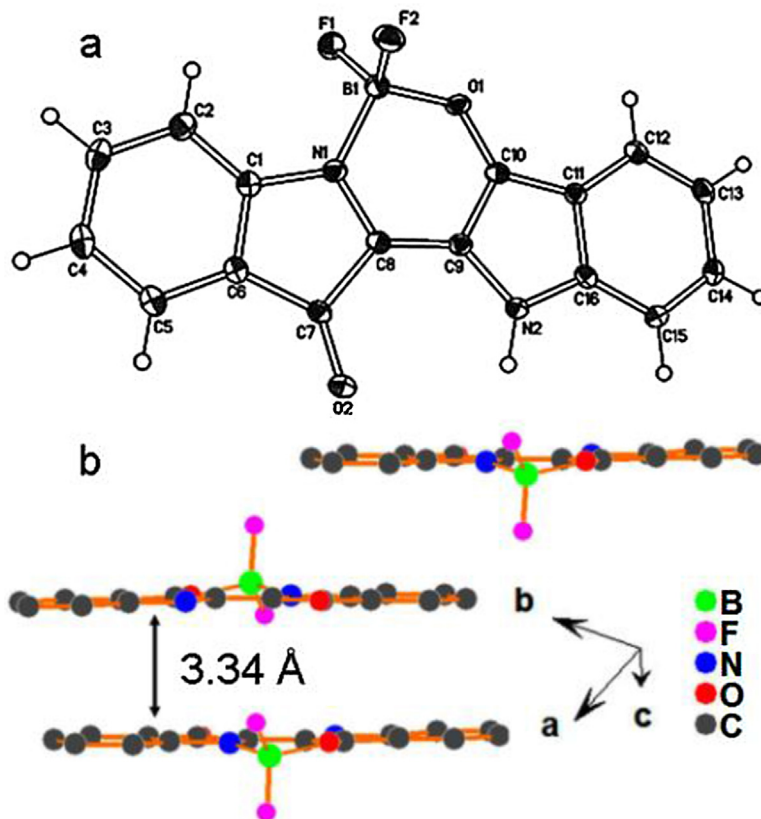


Fig. 1. (a) X-ray structure and (b) molecular packing of compound **1**. Carbon, oxygen, nitrogen, fluoride, and boron atoms are colored gray, red, blue, purple, and green, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Download English Version:

<https://daneshyari.com/en/article/1313871>

Download Persian Version:

<https://daneshyari.com/article/1313871>

[Daneshyari.com](https://daneshyari.com)