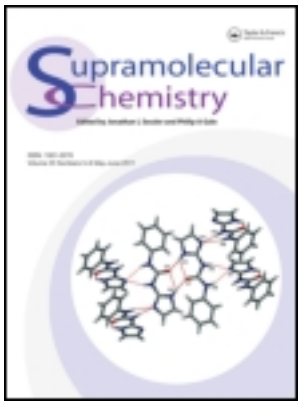

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A highly selective fluorescence chemosensor for Pb(II) in neutral buffer aqueous solution

Jing Cao [a b], Hai Yan Deng [a], Chen Hui Wang [a], Yao Xiao [a], Ming Ren [a] & You Wei Zhang [a]
[a] College of Chemistry, Xiangtan University, Xiangtan, Hunan, 411105, P.R. China
[b] Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan, Hunan, 411105, P.R. China

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A highly selective fluorescence chemosensor for Pb(II) in neutral buffer aqueous solution

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[a]*College of Chemistry, Xiangtan University, Xiangtan, Hunan 411105, P.R. China;* [b]*Key Laboratory of Enviromentally Friendly Chemistry and Application of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan, Hunan 411105, P.R. China*

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A 3,4-dimethylthieno[2,3-b]thiophene-based fluorogenic probe bearing benzo[d]-thiazole-2-thio unit (sodium 3,4-bis ((benzo[d]thiazol-2-ylthio)methyl) thieno [2, 3-b]thio-phene-2, 5-dicarboxylate) was developed as a novel fluorescent chemosensor with high selectivity towards Pb(II) over other cations tested. The new probe exhibited good water solubility and only sensed Pb(II) among metal ions examined in neutral 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid buffer solution. The selectivity and sensitivity of fluorogenic probe to Pb(II) were discussed on the basis of experimental results.

Keywords: fluorescence chemosensor; neutral aqueous solution; Pb(II); thieno[2,3-b]thiophene; benzo[d]thiazole-2-thio unit

Introduction

The selective binding of chemical species upon molecular recognition can lead to large perturbation in the host environment, particularly when the guest is ionic. Since fluoroionophore can provide chemical information on the ion concentration, they are important subjects in metal ion analysis (*1–3*). The development of selective chemosensors for the recognition, detection and measurement of transition and heavy metal ions draws particular interest as these ions play important roles in living systems and have an extremely toxic impact on the environment (*4–8*). Among them Pb(II) is considered as one of the most toxic cations for the environment because it is widely distributed in air, water and soil. In addition, a wide variety of symptoms, such as memory loss, irritability, anaemia, muscle paralysis and mental retardation, have been attributed to lead poisoning, which suggest that Pb(II) affects multiple targets *in vivo* (*9*). However, fluorescent chemosensors for heavy metal ions (*10*), particularly for lead (*11, 12*), have remained rare up to now because these metal ions are known to quench fluorescence emission via enhanced spin–orbital coupling (*13*), energy or electron transfer (*14*). Fluorescence quenching is not only disadvantageous for a high signal output during detection but is also undesirable for analytical purposes (*15*). Thus, it is important that the recognition of Pb(II) by the chemosensor does not quench the fluorescence. Furthermore, it is imperative to quantitatively monitor the existence of Pb(II) *in vitro* and *in vivo*. For these purposes, the fluorescent chemosensor for Pb(II) is needed to be water soluble at physiological pH.

Herein, we report a novel fluorescent chemosensor sodium 3,4-bis ((benzo[d]thiazol-2-ylthio)methyl) thieno [2, 3-b]thio-phene-2, 5-dicarboxylate (SBTD) of thieno[2,3-b]thiophene with benzo[d]thiazole-2-thio unit, here the introduction of carboxylate anions is of advantage to increase the solubility in water. SBTD can signal Pb(II) selectively and display large fluorescence enhancement in 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer solution compared with other metal ions examined. The synthetic route for fluorescent chemosensor SBTD is depicted in Scheme 1.

Results and discussion

The absorption spectra of SBTD in HEPES buffer solution showed a main absorption band with λ_{max} of 265 nm and shoulder peaks around 300 nm (Figure 1). The emission spectrum of SBTD in HEPES buffer solution was recorded following excitation at 320 nm. Emission intensity of SBTD was found to be low; weak emission band with maxima at 366 nm was observed (Figure 2).

The selectivity of SBTD chemosensor for metal ions (50 equiv, respectively) was determined in HEPES buffer solution by fluorescent spectra (Figure 3). We found that the fluorescence of SBTD nearly had no significant effect in the presence of Ba(II), K(I), Sr(II), Li(I), Hg(II), Mn(II), Cd(II), Zn(II), Co(II), Ni(II) and Mg(II) ions. As shown in Figure 4, Cu(II) or Cr(III) also caused a similar but smaller fluorescence change to Pb(II) (Figure 4). Studies showed a remarkable increase in fluorescence intensities of SBTD without spectra shift in the presence of Pb(II). However, the maxima absorption band underwent bathochromic shift upon the addition of Pb(II) (Figure 5). The formation of this new

*Corresponding author. Email: caojing8088@xtu.edu.cn

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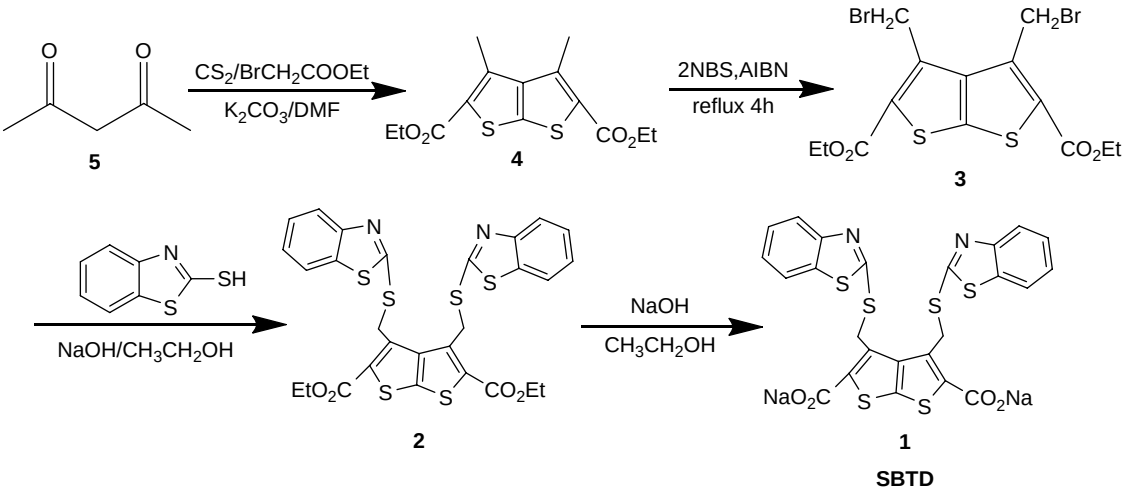

Scheme 1. The synthetic route for fluorescent chemosensor SBTD.

charge transfer band with an isosbestic point at 280 nm suggested that the SBTD and SBTD bound to Pb(II) ions exist in equilibrium.

SBTD showed good selectivity for Pb(II) ion, and then we investigated the sensitivity of SBTD towards Pb(II) ion in HEPES buffer solutions in details. The gradual increase in its fluorescent intensities could be obviously observed with the concentration changes of Pb(II) ion from 0 to 10^{-3} M, especially at the higher concentration of Pb(II) ion ($10^{-4} - 10^{-3}$ M). There was 39-fold increase in fluorescent intensity when the concentration of Pb(II) reached to 10^{-3} M (Figure 6).

The equilibrium constant for the formation of [PbL] from the interaction of L and Pb(II) was calculated for 1.12×10^5 from the plot $I_0/[I - I_0]$ vs. 1/[Pb(II)] using the Benesi–Hildebrand equation (*16*) (linearly dependent coefficient: $R^2 = 0.9365$, Figure 7). For the binding site of SBTD with Pb(II), a pocket model seems to be reasonable. In the structure of SBTD, there is a nice binding pocket composed of two benzylic sulphur atoms and two additional sulphur atoms on the benzothiazole moieties, which is probably a binding site for Pb(II). But there are two ways to form 'pocket', that is, 'pocket' could be formed not only within a molecule but also between two molecules. 'Pocket' within a SBTD molecule gave 1:1 binding for Pb(II), and Pb(II) with 'Pocket' between two SBTD molecules would form 1:2 binding (Figure 8). Of course, 1:1 binding is the main binding stoichiometry in dilute solution. Based on the above binding model, it gives a satisfactory explanation why the Benesi–Hildebrand analysis of SBDT is parabolic instead of a straight line and linearly dependent coefficient we obtained is not good ($0.9365 \ll 0.99$).

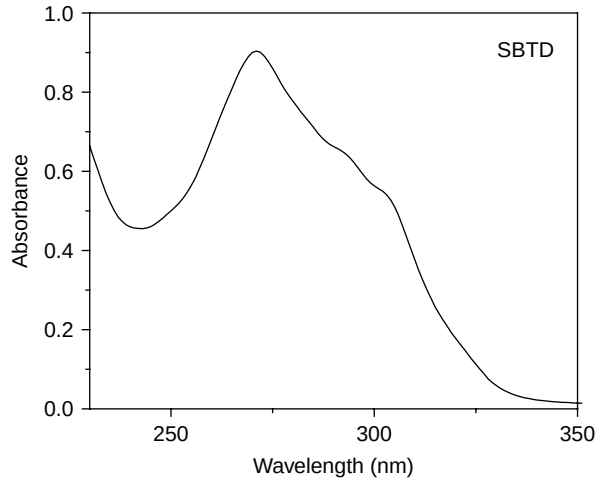

Figure 1. The UV–vis spectra of SBTD (2.0×10^{-5} M) in HEPES buffer solution (50 mmol/l, pH 7).

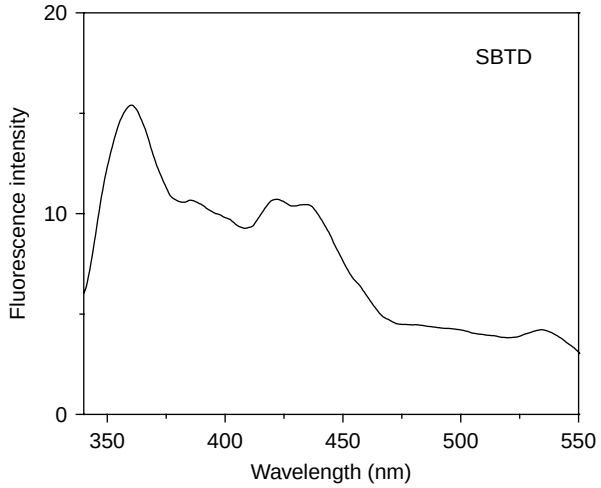

Figure 2. Fluorescence spectral variation of SBTD (2.0×10^{-6} M) in HEPES buffer solution (50 mmol/l, pH 7) excited at 320 nm.

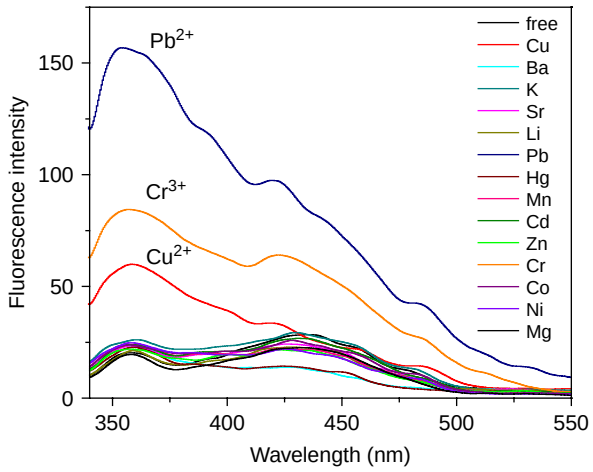

Figure 3. The selectivity of SBTD chemosensor for various metal cations (50 equiv).

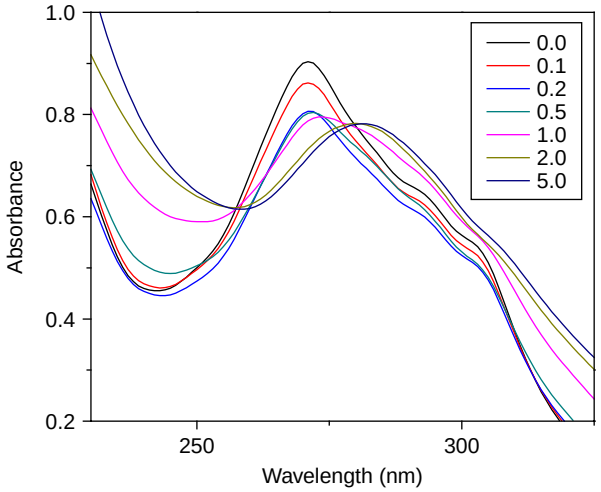

Figure 5. The UV–vis spectra of SBTD (2.0×10^{-5} M) in HEPES buffer solution (50 mmol/l, pH 7) upon the addition of different concentrations of Pb^{2+}(0–5.0 equiv).

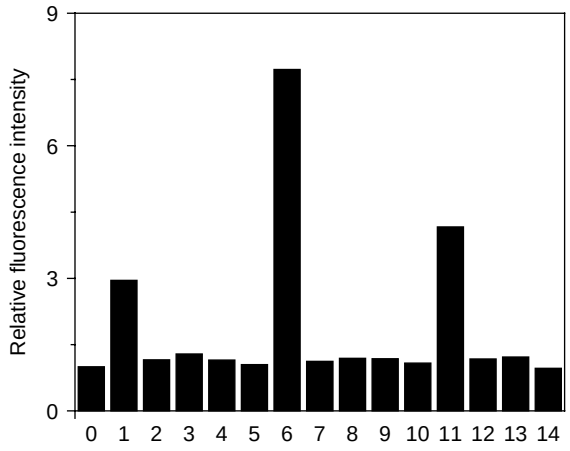

Figure 4. Fluorescence intensity changes ($(I - I_0)/I_0 \times 100\%$) of SBTD ($2.0 \times 10^{-6}$ M) in HEPES buffer aqueous solution (50 mmol/l, pH 7) at room temperature upon the addition of various metal cations (50 equiv). Excitation wavelength was at 320 nm. I_0 = fluorescence emission intensity of free SBTD. I = fluorescence emission intensity of metal ion-complexed SBTD. 0, free; 1, Cu^{2+}; 2, Ba^{2+}; 3, K^{+}; 4, Sr^{2+}; 5, Li^{+}; 6, Pb^{2+}; 7, Hg^{2+}; 8, Mn^{2+}; 9, Cd^{2+}; 10, Zn^{2+}; 11, Cr^{3+}; 12, Co^{2+}; 13, Ni^{2+}; 14, Mg^{2+}.

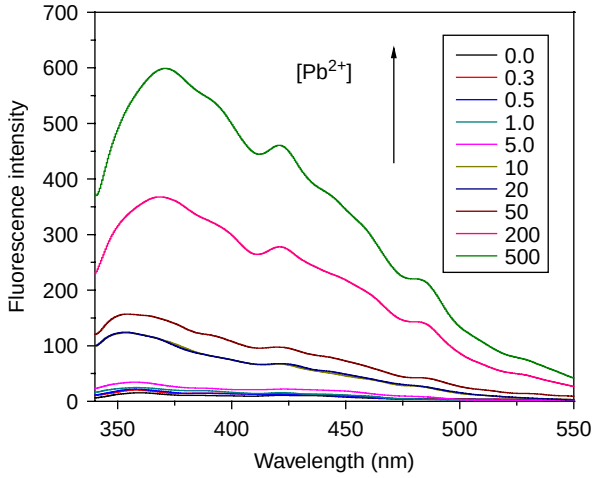

Figure 6. Fluorescence spectral variation of SBTD (2.0×10^{-6} M) upon the addition of Pb^{2+} in HEPES buffer solution (50 mmol/l, pH 7) from 0 to 500 equiv excited at 320 nm.

Conclusion

In summary, a novel thieno[2,3-b]thiophene functionalised chemosensor SBTD exhibiting good water solubility was synthesised and characterised. The selectivity of compound SBTD to Pb(II) in HEPES buffer solution from a series of cations was evidenced as its exceptional fluorescence enhancement. The sensitivity of compound SBTD to Pb(II) was demonstrated in the neutral aqueous solution, indicating its potential application for Pb(II) diagnoses in clinics.

Experimental

Materials

Unless otherwise stated, all chemical reagents were obtained from commercial suppliers and used without further purification. All the reagents were used as received from Aladdin Reagent Company (Shanghai, China) without further purification. The inorganic salts were of the analytical purity available. All the water was twice deionised water. HEPES buffer solutions (50 mM, pH 7.0) were prepared in water. Both absorption and fluorescence titrations were carried out with a concomitant addition of small volumes of metal ion aqueous solution to neutral HEPES buffer solution of SBTD. (Metal salts:

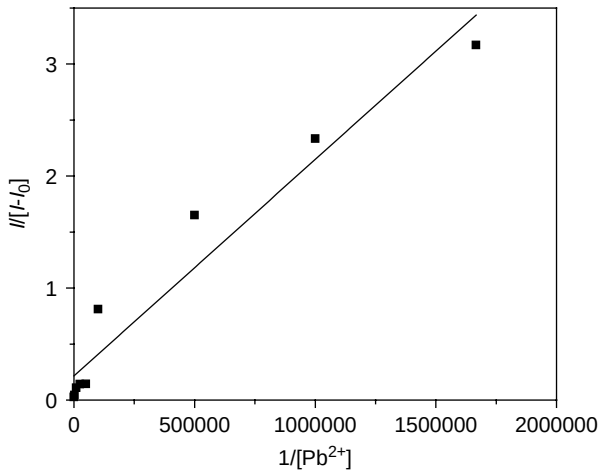

Figure 7. The Benesi–Hildebrand analysis of SBTD with different concentrations of Pb^{2+}.

$CuCl_2{\cdot}2H_2O$, $BaCl_2{\cdot}2H_2O$, KCl, $SrCl_2{\cdot}6H_2O$, $LiCl{\cdot}H_2O$, $Pb(NO_3)_2$, $HgCl_2$, $MnSO_4{\cdot}H_2O$, $CdCl_2{\cdot}2.5H_2O$, $ZnCl_2$, $CrCl_3{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $MgSO_4$.)

Instruments

^1H and ^{13}C NMR were acquired on a Bruker AVANCE 400 MHz spectrometer with chemical shifts reported in parts per million (**2** and **3** in $CDCl_3$, **1** in dimethyl sulfoxide (DMSO); tetramethylsilane as an internal standard). UV–vis spectra were scanned on a Lambda 25 spectrophotometer. Fluorescence spectra were recorded on a PerkinElmer LS55 luminescence spectrometer with a xenon lamp as the light source, 10/10 nm as excitation and emission slit and 320 nm as excitation.

Synthesis of SBTD

*Process for preparation of diethyl 3,4-dimethylthieno[2,3-b]thiophene-2,5-dicarboxylate (**4**)*

Diethyl 3,4-dimethylthieno[2,3-b]thiophene-2,5-dicarboxylate (**4**) was prepared following the already published procedures (*17*).

*Process for preparation of diethyl 3,4-bis(bromomethyl) thieno[2,3-b]thiophene-2,5-dicarboxylate (**3**)*

N-bromosuccinimide (2.85 g, 15.6 mmol) and azobisisobutyronitrile (0.0454 g, 2.7 mmol) were added to a solution of diethyl 3,4-dimethyl thieno[2,3-b]thiophene-2,5-dicarboxylate (**4**) (2.220 g, 7.1 mmol) in CCl_4 (40 ml), and the mixture was held at reflux for another 4 h. After the reaction was complete and the mixture cooled sufficiently, the crude product was filtered to remove the precipitate. The filtrate was evaporated and the residue was purified by recrystallisation from diethyl ether and petroleum ether (1:1, v/v). Compound **3** was obtained in 93% yield.

*Process for preparation of diethyl 3,4-bis((benzo[d]thiazol-2-ylthio)methyl)thieno[2,3-b]thiophene-2,5-dicarboxylate (**2**)*

A solution of diethyl 3,4-bis(bromomethyl)thieno[2,3-b]thiophene-2,5-dicarboxylate (**3**) (2.35 g, 5 mmol), benzo[d]thiazole-2-thiol (1.92 g, 11.5 mmol), potassium carbonate (1.59 g, 11.5 mmol) and potassium iodide (0.17 g, 10 mmol) in fresh dry acetone was held at reflux overnight under the protection of nitrogen. Then, the reaction mixture was poured into 200 ml of ice water. The precipitate was collected and washed three times with water. Compound **2** was obtained in 86% yield. ^1H NMR ($CDCl_3$, ppm): δ 7.11–7.59 (m, 8H), 5.56 (s, 4H), 4.35–4.40 (q, 4H), 1.34–1.35 (t, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 165.04, 161.58, 152.91, 145.49, 145.07, 136.41, 135.26, 134.30, 125.74, 124.07, 121.45, 120.64, 61.78, 29.40, 14.16. TOF-MS: *m*/*z* 641.

*Process for preparation of sodium 3,4-bis((benzo[d]thiazol-2-ylthio)methyl)thieno [2,3-b]thio-phene-2,5-dicarboxylate (**1**)*

NaOH (0.26 g, 6.6 mmol) was dissolved in water as little as possible, diethyl 3,4-bis(bromomethyl)thieno[2,3-b]thiophene-2,5-dicarboxylate (**2**) (1.93 g, 3 mmol) and ethyl alcohol (60 ml) were added. The mixture was held at reflux for 12 h. When the reaction was complete, the

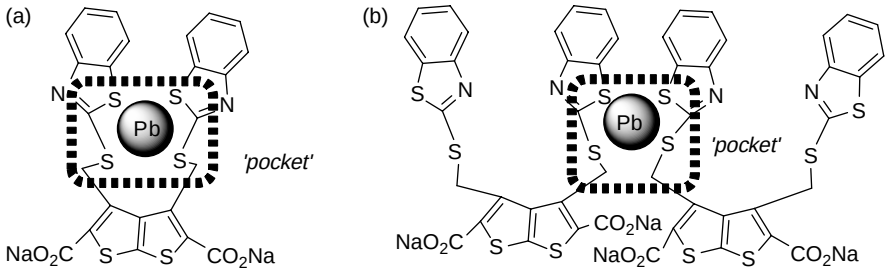

Figure 8. The possible mechanism for SBTD binding with Pb^{2+} (a) 'pocket' in a molecule; (b) 'pocket' between two molecules.

reaction mixture was filtered while it was hot. The precipitate was purified by recrystallisation from ethanol. Compound **1** was obtained in 86% yield. ^{1}H NMR (DMSO, ppm): δ 7.11–7.63 (m, 8H), 5.63 (s, 4H). ^{13}C NMR (DMSO, ppm): δ 166.86, 165.31, 152.99, 148.52, 145.73, 137.64, 134.70, 127.09, 126.22, 124.29, 121.56, 121.04, 29.60. Anal. calcd for $C_{24}H_{12}N_2O_4S_6Na_2$:C, 45.70; H, 1.92; N, 4.44; S, 30.50. Found C, 45.51; H, 2.07; N, 4.36; S, 30.69. TOF-MS: *m*/*z* 628.

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