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p-Dimethylaminobenzaldehyde thiosemicarbazone: A simple novel selective and sensitive fluorescent sensor for mercury(II) in aqueous solution

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Abstract

A novel and simple fluorophore, *p*-dimethylaminobenzaldehyde thiosemicarbazone (DMABTS), was prepared in order to find available fluorescent chemosensor for mercuric ion in aquesous solution. DMABTS emitted fluorescence at 448 nm in aqueous solution and its fluorescence intensity was completely quenched upon interaction with Hg^{2+} ions, which should be attributed to the 1:1 complex formation between DMABTS and Hg^{2+}. The binding constant of the complex was determined as 7.48×10^6 mol l^{-1}. The linear range of quantitative detection of 0 to 5.77×10^{-6} mol l^{-1} and the detection limit of 7.7×10^{-7} mol l^{-1} for Hg^{2+} in the 6.3×10^{-6} mol l^{-1} DMABTS aqueous solution were obtained from a calibration curve. The coexistence of several transition metal ions and anions did interfere the fluorometric titration of Hg^{2+} ion by less than 4% in the emission change.
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Keywords: Sensor; Mercury(II); Fluorescence; Thiosemicarbazone

1. Introduction

Due to the toxicity and environmental impacts of Hg^{2+}, its sensitively and selectively monitoring became increasingly demanding [1–5]. Many laboratory methods such as absorption spectrometry, atomic fluorescence, mass spectrometry, potentiometry or biochemical sensor have been established [6–11]. Fluorescence signaling has been the choice due to its intrinsic high detection sensitivity and its ease to couple with long distance digital transmission of signal. Considerable efforts have been devoted to the design of new fluoroionophores for Hg^{2+} and many receptors signaling Hg^{2+} in fluorescent quenching mode or enhancing mode have been reported [12–15]. However, many of these molecules have some limitations in terms of actual applicability such as the lack of water solubility, requiring the use of organic or aqueous organic solvent mixtures, cross-sensitivities toward other metal ions, difficult to synthesize. One major challenge involves creating Hg^{2+} sensor functioned in water with high selectivity and sensitivity for Hg^{2+} against a background of competing analytes. Therefore, novel easily-prepared and water-soluble fluorphores with high selectivity and sensitivity of chemosensing Hg^{2+} became our targets. Here we designed and prepared a molecule, *p*-dimethylaminobenzaldehyde thiosemicarbazone (DMABTS) shown in Scheme 1, conceiving it give highly selective fluorescent response toward Hg^{2+} in aqueous solution.

The molecular architecture of this simple fluorescent chemosensor was based on the thiosemicarbazone, which was the widely used ionophore chelated with Hg^{2+} [16–18] and has been employed for constructing ionophore as sensor for Hg^{2+} by ion-selective electrode [19]. The use of the *p*-dimethylaminobenze moiety was in terms of the suitability and performance as a fluorophore. In this donor-acceptor ensem-

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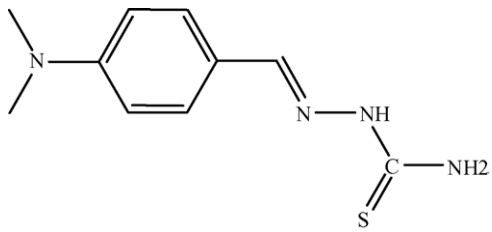


Scheme 1. The structure of the designed molecule (DMABTS).

bly, the fluorescence of dimethylaminobenzene group acting as donor would be sensitively affected when the acceptor recognition unit interacted with a metal ion [20,21]. The experimental results showed that DMABTS worked successfully as sensor for Hg^{2+} in aqueous solution.

2. Experimental

All the reagents were used as received from Shanghai Chemicals Group Company. The inorganic salts were of the highest purity available and existed in their nitrates or sulfates. Twice deionized water was further distilled in the presence of $KMnO_4$.

DMABTS was prepared by a simple one-step reaction of *p*-dimethylaminobenzaldehyde with thiosemibazide in acidic solution of ethanol and water [16]. A mixture of *p*-dimethylaminobenzaldehyde with thiosemibazide in ethanol with 10% acetic acid solution was refluxed for 2 h, then cooled to room temperature. The pale yellow precipitates were collected and washed with cold ethanol. The product was purified by recrystallization from ethanol and was identified by melting point (213–214 °C), ESI-MS: m/z 223 ($M+H^+$, Ethanol), ^1H NMR (DMSO-d_6, TMS, 500 MHz): δ (ppm) 11.179 (HN, s), 7.999 (CH, s), 7.932 – 7.571 (C_6H_4, 4H, m), 6.707 (NH_2, s), 2.957 (Me_2N, 6H, s) ,and elemental analysis, found: C, 54.34%; H, 6.35%; N, 25.03%, calcd.: C, 54.03%; H, 6.35%; N, 25.20%. (NMR data were acquired on a Varian Unity 500 MHz NMR spectrometer. ESI-MS data were obtained on a Bruker ESQUIRE-3000plus LC-MS/MS spectrometer and elemental analysis was obtained on a CE Instruments EA 1110.)

Crystals of the compound suitable for X-ray diffraction were grown and collected. Reflection data were collected on a Bruker SMART APEX 2000 CCD diffractometer operating with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and ω–φ scans mode in the range of $1.39 < \theta < 25°$. The structure was solved by direct method and refined by full-matrix least-squares techniques against F^2 using SHELX-97 package [22]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed in calculated positions and refined with a common isotropic thermal parameter.

Corrected fluorescence spectra were taken on a Hitachi F-4500 fluorescence spectrophotometer with excitation and emission slits of 5.0/5.0 nm, and absorption spectra were scanned on a Shimadzu UV224012PC absorption spectrophotometer. All experiments were conducted in aqueous solution at room temperature of ca. 20 °C.

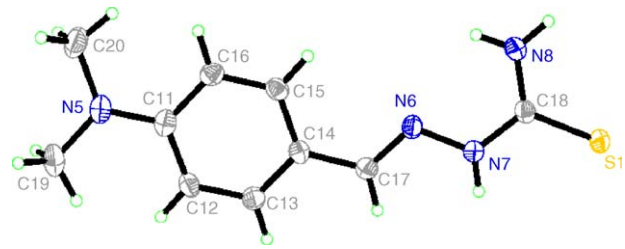


Fig. 1. An ORTEP plot of the molecule with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn in the circles with arbitrary radium.

3. Results and discussion

DMABTS was studied by X-Ray crystallographic first. The crystal structure analysis showed that the compound, $C_{10}H_{14}N_4S$, crystallizes in triclinic, space group P_{-1} with $a = 8.3810\,(13)$ Å , $b = 9.3142\,(15)$ Å , $c = 15.5105\,(25)$ Å , $\alpha = 73.259\ (2)°$, $\beta = 79.626\ (2)°$, $\gamma = 82.543\ (3)°$, $V = 1136.6\,(3)$ Å ^{3}, $Z = 4$, $M_r = 222.31$, $D_c = 1.299$ g/cm^3, $\mu = 0.258$ mm^{-1}, $F(0\,0\,0) = 472$, $R = 0.0541$, $wR = 0.1431$. The molecule structure was shown in Fig. 1. It should be pointed out that DMABTS is in a planar structure in the solid state. All non-hydrogen atoms locate at the least-squares plane with the mean deviation from the plane 0.028Å . CCDC number: 270203.

The spectroscopic character of DMABTS was investigated as shown in Table 1. Although DMABTS is the electron donor/acceptor para-substituted benzene [20], it only emits single fluorescence arising from the locally excited state around 420 nm in different solvents. The fluorescence spectrum of DMABTS in pure water was characterized as the maximum excitation and emission wavelengths found to be 353 and 448 nm, respectively. The large red shift of the absorption wavelength to around 355 nm of substituted benzene demonstrates that in DMABTS molecule the benzene is conjugated with Schiff base and this can be proved by its planar structure found in the crystal structure determination. From Fig. 2 it can be found that the fluorescence intensity did almost not varied with pH within the pH range of 4.6–10.0 in water solution. In this pH range, we studied the effect of several transition metal ions on the fluorescence intensity of DMABTS in aqueous solution.

In 0.01 mol l^{-1} acetic acid/sodium acetate buffer solution, the free fluoroionophore DMABTS (6.3×10^{-6} mol l^{-1}) showed an intense fluorescence around 448 nm ($\lambda_{ex} = 353$ nm). Upon interaction with metal ions of Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+} ions

Table 1
Spectroscopic parameter of DMABTS[a]

Solvent	ET_{30}	λ_1 (nm)	Φ_f	λ_2 (nm)	ε (mol^{-1} l cm^{-1})
Diox	36.0	408	0.012	355	3.8×10^4
THF	37.4	419	0.012	356	2.9×10^4
MeCN	46.0	421	0.014	356	4.7×10^4
EtOH	51.9	414	0.032	355	5.1×10^4
Water	63.1	448	0.035	353	4.2×10^4

[a] λ_1, emission wavelength; λ_2, absorption wavelength; Φ_f, quantum yield; ε, molar absorption coefficient.

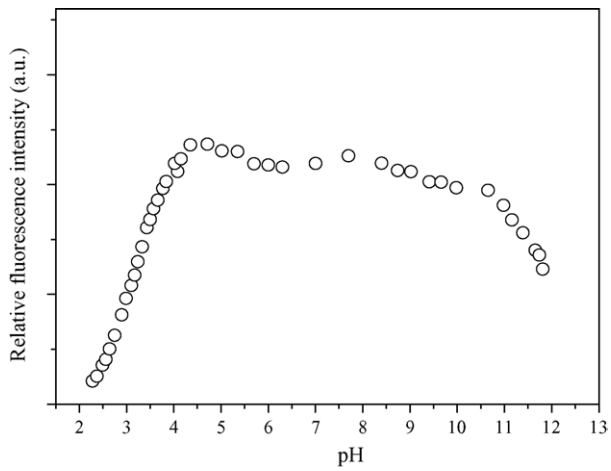


Fig. 2. The fluorescence intensity of DMABTS in different pH solution.

(in nitrate and sulphate), the emissions of DMABTS centered at 448 nm remained nearly unchanged as shown in Fig. 3(a). However, one-fold of Hg^{2+} ions acted as the most effective quencher and the quenching efficiency was found to be larger than 99%.

From Fig. 3(a) it could be seen that the fluorescence of DMABTS was quenched by Hg^{2+} substantially higher than those of other metal ions of similar electronic structure. The more experiments showed that DMABTS response to Hg^{2+} was almost unaffected by the background of 10-folds even to 100-folds of the transition metal ions except Cu^{2+}. Cu^{2+} ions of 10-folds showed some quenching effect of 20% in pH 7.0 buffer solution. But, this quenching effect could be well improved to less than 4% by changing the acidity of solution to pH 5.0. In Fig. 3(b), it can be seen that anions such as Cl^-, NO_3^- and SO_4^{2-}, $H_2PO_4^-$ had no influence on the fluorescence of DMABTS in the absence and presence of Hg^{2+} in aqueous solution.

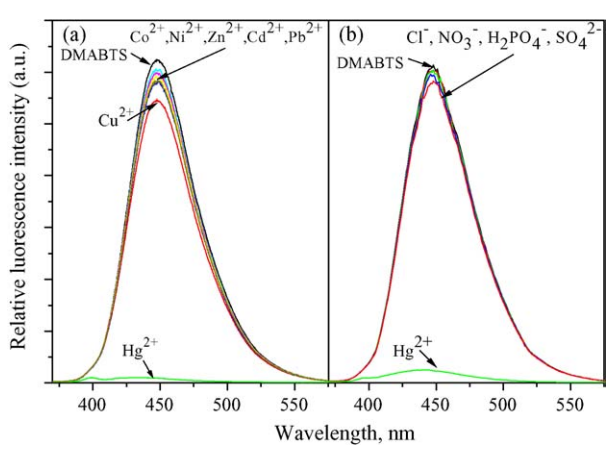


Fig. 3. (a) Fluorescence spectra of free DMABTS (λ_{ex} = 353 nm) and DMABTS in the presence of 20 equiv. of Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+} and 1 equiv. of Hg^{2+} in 0.01 mol l^{-1} acetic acid/sodium acetate buffer solution. [DMABTS] = 6.3×10^{-6} mol l^{-1}. (b) Fluorescence spectra of free DMABTS and DMABTS in the presence of 100 equiv. of Cl^-, NO_3^-, $H_2PO_4^-$, SO_4^{2-} and 1 equiv. of Hg^{2+} in 0.01 mol l^{-1} acetic acid/sodium acetate buffer solution. [DMABTS] = 6.3×10^{-6} mol l^{-1}.

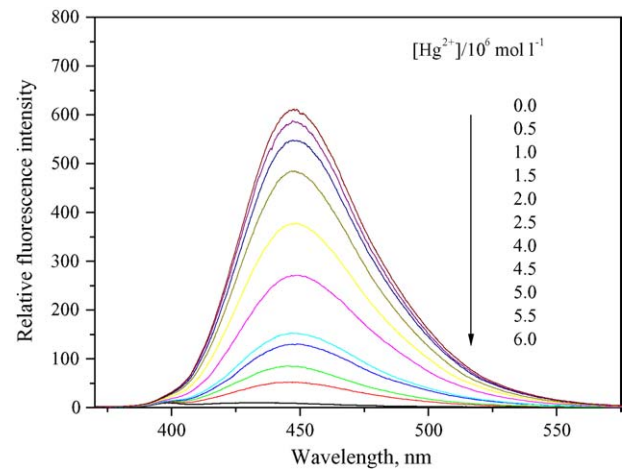


Fig. 4. Fluorescence spectra of DMABTS (6.3×10^{-6} mol l^{-1}) in 0.01 M acetic acid/sodium acetate buffer solution (pH = 5.0) upon the addition of Hg^{2+} ions [λ_{ex} = 353 nm].

Fig. 4 illustrated the changes of fluorescence spectra of DMABTS upon the addition of Hg^{2+} ions in acetic acid/sodium acetate buffer solution of pH 5.0. The fluorescence intensity was decreased with the increasing Hg^{2+} concentration, meanwhile the spectral shape kept unchanged. A calibration curve was obtained from the plot of fluorescence intensity with the added Hg^{2+} concentration. The curve equation as shown in Fig. 5 was $F = 6.23 \times 10^2 – 1.07 \times 10^8$ C_{Hg2+}, $R = -0.993$, $N = 11$, S.D. = 27.83. The linear range of quantitative detection for Hg^{2+} was determined as 0 to 5.77×10^{-6} mol l^{-1} with a detection limits of 7.7×10^{-7} mol l^{-1} for Hg^{2+} from the curve in the used aqueous solution system.

The fluorescence quenching of DMABTS by Hg^{2+} was attributed to the 1:1 complex formation between Hg^{2+} and DMABTS. The stoichiometry of Hg^{2+}–DMABTS complex was determined by the changes in the absorption response of DMABTS in the presence of different concentrations of Hg^{2+} at its maximum absorption wavelength.

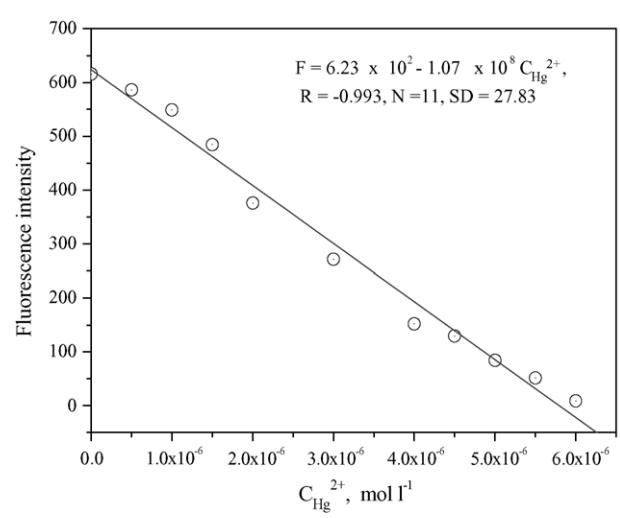


Fig. 5. Calibration curve was obtained from the plot of fluorescence intensity with the added Hg^{2+} concentration.

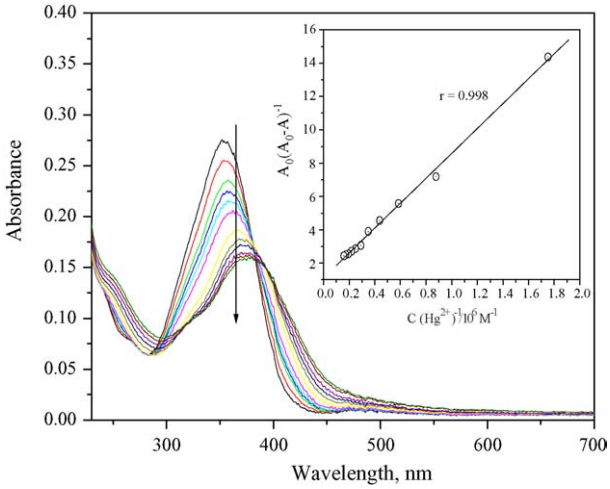
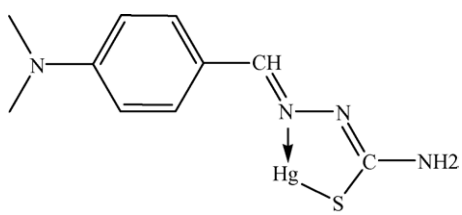


Fig. 6. Absorption spectra of DMABTS in the presence of different concentration of Hg^{2+}. $[Hg^{2+}]$ change shown in the arrow from top to bottom: 0.00, 0.57, 1.14, 1.71, 2.28, 2.86, 3.43, 4.00, 4.57, 5.14, 5.71, 6.28 in 10^{-6} (mol l^{-1}).



Scheme 2. The assumed complex formation between Hg^{2+} and DMABTS.

From Fig. 6, it could be seen that the absorption spectra of DMABTS were red-shifted and the intensities decreased with increasing of Hg^{2+} concentration, demonstrating that Hg^{2+} and DMABTS form a 1:1 complex in solution and its binding constant was calculated as 7.48×10^6 mol l^{-1} by a strict 1:1 model [13]. Therefore, the formation of 1:1 complex of Hg^{2+} with DMABTS is responsible for the fluorescence quenching. The intense fluorescence of DMABTS was quenched by approaching of Hg^{2+} ions upon the complexation [16], as shown in Scheme 2.

In summary, a fluorescence spectroscopic method for the sensor of Hg^{2+} based on the measurement the decrease of fluorescence intensity of the designed molecule DMABTS has been developed. The selectivity, sensitivity, rapidity and simplicity of the present method make the method as a novel sensor material for the detection of Hg^{2+} ions by fluorescence in buffer aqueous solution, and could be used as a good alternative to the other sensors for Hg^{2+}.

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References

[1] A. Segura-Carretero, J.M. Costa-Fernandez, R. Pererio, A. Sanz-Medel, Talanta 49 (1999) 907.
[2] X.-B. Zhang, C.-C. Guo, Z.-Z. Li, G.-L. Shen, R.-Q. Yu, Anal. Chem. 74 (2002) 821.
[3] X.-P. Yan, X.-B. Yin, D.-Q. Jiang, X.-W. He, Anal. Chem. 75 (2003) 1726.
[4] P.E. Koulouridakis, N.G. Kallithrakas-Kontos, Anal. Chem. 76 (2004) 4315.
[5] J.-H. Kim, A.-R. Hwang, S.-K. Chang, Tetrahedron Lett. 45 (2004) 7557.
[6] X.-F. Guo, X.-H. Qian, L.-H. Jia, J. Am. Chem. Soc. 126 (2004) 2272.
[7] J.Y. Yoon, N.E. Ohler, D.H. Vance, W.D. Aumiller, A.W. Czarnik, Tetrahedron Lett. 38 (1997) 3845.
[8] S.Y. Moon, N.R. Cha, Y.H. Kim, S.-K. Chang, J. Org. Chem. 69 (2004) 181.
[9] J.V. Cizdziel, S. Gerstenberger, Talanta 64 (2004) 918.
[10] E.M. Nolan, S.J. Lippard, J. Am. Chem. Soc. 125 (2003) 14270.
[11] (a) V.K. Gupta, S. Chandra, H. Lang, Talanta 66 (2005) 575;
(b) V.K. Gupta, S. Chandra, S. Agarwal, Ind. J. Chem. 42A (2003) 813;
(c) A.K. Jain, V.K. Gupta, L.P. Singh, Bull. Electrochem. 12 (1996) 418.
[12] J.-M. Liu, W.-T. Chen, Q.-H. Wang, L.-D. Li, Talanta 62 (2004) 713.
[13] A.B. Descaizo, R. Marthinez-Manez, R. Radeglia, K. Rurack, J. Sato, J. Am. Chem. Soc. 125 (2003) 3418.
[14] Q.-Y. Chen, C.-F. Chen, Tetrahedron Lett. 46 (2005) 165.
[15] M. Shamsipur, M. Hosseini, K. Alizadeh, N. Alizadeh, A. Yari, C. Caltagirone, V. Lippolis, Anal. Chim. Acta 533 (2005) 17.
[16] (a) T.S. Lobana, A. Sanchez, J.S. Casas, A. Castuneiras, J. Sordo, M.S. Garcia-Tasende, E.M. Vazquez-Lopez, J. Chem. Soc., Dalton Trans. (1997) 4289;
(b) T.S. Lobana, A. Sanchez, J.S. Casas, A. Castineiras, J. Sordo, M.S. Garcia-Tasende, Polyhedron 17 (1998) 3701.
[17] F. Basuli, S.-M. Peng, S. Bhattacharya, Inorg. Chem. 39 (2003) 39.
[18] D.X. West, A.E. Liberta, S.B. Padhye, R.C. Chilate, P.B. Sonawane, A.S. Kumbhar, R.G. Yerande, Coord. Chem. Rev. 123 (1993) 49.
[19] R.K. Mahajan, I. Kaur, T.S. Lobana, Talanta 59 (2003) 101.
[20] W. Rettig, Angew. Chem. Int. Engl. 25 (1985) 971.
[21] Z.R. Grabowski, K. Rotkiewicz, W. Rettig, Chem. Rev. 103 (2003) 3899.
[22] G.M. Sheldrick, SHELXL-97, Program for refnement of crystal structures, University of Göttingen, Germany, 1997.