Polymer-Based Colorimetric and "Turn Off" Fluorescence Sensor Incorporating Benzo[2,1,3]thiadiazole Moiety for Hg²⁺ Detection

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ABSTRACT: A conjugated polymer was synthesized by the polymerization of 4,7-dibromobenzo[2,1,3]thiadiazole (**M-1**) with tri{1,4diethynyl-2,5-bis(2-(2-methoxyethoxy)-ethoxy)}-benzene (**M-2**) via Pd-catalyzed Sonogashira reaction. The polymer shows strong orange fluorescence. The responsive optical properties of the polymer on various metal ions were investigated through photoluminescence and UV-vis absorption measurements. The polymer displays highly sensitive and selective on-off Hg²⁺ fluorescence quenching property in tetrahydrofuran solution in comparison with the other cations including Mg²⁺, Zn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Ag⁺,

INTRODUCTION In recent years, the pollution of heavy metal ions, especially mercury ion, has attracted considerable research interest owing to its deleterious effects on human health and natural ecosystems.¹ In particular, mercury can easily accumulate in vital organs and tissues through the food chain and result in cellular irreversible dysfunction, which leads to severe human health problems even at low concentrations.² The exposure to mercury can cause brain damages, serious cognitive and motion disorders, and central nervous and endocrine system defects because mercury could easily pass through biological membranes.³ Furthermore, the environmental contamination resulting from mercury ion is arousing increasing attention throughout the world.⁴ As a consequence, there is sufficient impetus aiming at designing a highly specific, sensitive, simple, and versatile mercury sensor in biological and environmental fields.⁵

To date, a variety of fluorescent sensors have been developed to signal the presence of mercury ions, such as cyclams,⁶ rhodamine,⁷ calix[4]crown,⁸ calixarene,⁹ naphthalimide,¹⁰ and their derivatives. However, most of them are based on small molecules, and there are only a few recent polymers that concern mercury ion detection.¹¹ The sensing mechanisms for sensor design involve photoinduced charge transfer (PCT),¹² photoinduced electron transfer,¹³ fluorescence resonance energy transfer,¹⁴ and chelation-enhanced quenching.¹⁵ Conjugated polymers (CPs) are fluorescent Cd²⁺, and Pb²⁺. More importantly, the fluorescent color of the polymer sensor disappears after addition of Hg²⁺, which could be easily detected by naked eyes. The results indicate that this kind of polymer sensor incorporating benzo[2,1,3]thiadiazole moiety as a ligand can be used as a novel colorimetric and fluorometric sensor for Hg²⁺ detection. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 517–522, 2012

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macromolecules with π -conjugated backbones. They have been widely used as the optical platforms for chemical and biological sensing.¹⁶ When compared with small molecular fluorophores, CPs are superior in terms of high extinction coefficient and efficient interchain/intrachain exciton migration, because of their π -electron delocalized backbone structures.¹⁷ To the best of our knowledge, most of the CP-based sensors for Hg²⁺ are only on the strength of fluorescence signals. From the design point of view, it is of particular importance for developing a new generation of CPs for naked-eye detection of mercury(II) in real time.

Additionally, some sensors for Hg^{2+} are often based on the coordination of multiple nitrogen atoms with the metal ion or strong Hg-S binding.¹⁸ In this contribution, we designed a novel benzo[2,1,3]thiadiazole (BDT)-containing CP with high selectivity and sensitivity for Hg^{2+} . In our condition, "on-off" type changes were observed only for Hg^{2+} of colorimetry and fluorometry. These findings open a way to develop highly effective transitional-metal-sensitive chemosensors by incorporating the benzothiadiazole group in the polymer main-chain backbone.

EXPERIMENTAL

Measurements and Materials

NMR spectra were obtained using a 300-Bruker spectrometer with 300 MHz for $^{1}\mathrm{H}$ NMR and 75 MHz for $^{13}\mathrm{C}$ NMR. They

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were reported as parts per million (ppm) from the internal standard TMS. FTIR spectra were taken on a Nexus 870 FTIR spectrometer. UV-vis spectra were obtained from a Perkin-Elmer Lambda 25 spectrometer. Fluorescence spectra were obtained from a RF-5301PC spectrometer. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer Pyris-1 instrument under N2 atmosphere. MS was determined on a Micromass GCT. Elemental analyses of C, H, and N were performed on an Elementary Vario MICRO analyzer. Molecular weight was determined by GPC with Waters-244 HPLC pump, and tetrahydrofuran (THF) was used as a solvent and relative to polystyrene standards. All solvents and reagents were commercially available A.R. grade. 4,7-Dibromobenzo[2,1,3]thiadiazole (M-1) was synthesized according to the literature.¹⁹ 1,4-Diiodo-2,5-bis(2-(2-methoxyethoxy) ethoxy)benzene (1) and 1,4-diethynyl-2,5-bis(2-(2-methoxyethoxy)ethoxy)benzene (2) were synthesized according to the literature.²⁰

Synthesis of M-2

A mixture of 1,4-diiodo-2,5-bis(2-(2-methoxy)ethoxy)benzene (1) (0.566 g, 1.0 mmol), Pd(PPh₃)₄ (23 mg, 0.02 mmol), CuI (5.71 mg, 0.03 mmol), and ethynyltrimethylsilane (0.14 mL, 1.0 mmol) was dissolved in 15 mL THF and 10 mL Et₃N.²¹ The reaction mixture was stirred at room temperature for 6 h under N₂ atmosphere. After cooled to room temperature, the solution was extracted with CH₂Cl₂, washed with water, dried over MgSO₄, and evaporated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate, 4:1) to give **3** as yellow oil.

¹H NMR (300 MHz, CDCl₃): δ 7.31 (s, 1H), 6.90 (s, 1H), 4.13 (m, 4H), 3.89 (m, 4H), 3.79 (m, 4H), 3.58 (m, 4H), 3.41 (s, 3H), 3.40 (s, 3H), 0.26 (s, 9H); ¹³C NMR (75 MHz, CDCl₃): δ 154.6, 151.8, 124.3, 116.9, 113.6, 100.5, 99.5, 87.8, 71.9, 70.9, 70.9, 69.9, 69.8, 69.6, 69.5, 59.0, 58.9, 0.1. FTIR (KBr, cm⁻¹): 2,857, 2,154, 1,482, 1,371, 1,249, 1,216, 1,110, 1,058, 935, 854. MS (FAB): m/z 559 (M⁺ + 23). Anal. calcd for C₂₁H₃₃IO₆Si: C, 47.02; H, 6.20. Found: C, 47.04; H, 6.34.

A mixture of **2** (362 mg, 1 mmol), **3** (1.07 g, 2 mmol), Pd(PPh₃)₄ (23 mg, 0.02 mmol), and CuI (5.71 mg, 0.03 mmol) was dissolved in 15 mL THF and 10 mL Et₃N. The reaction mixture was stirred at 40 °C for 24 h under N₂ atmosphere. After the solution was cooled to room temperature, NaOH solution (0.5 g in 5 mL MeOH) was added into the above solution. The mixture was stirred for 2 h at room temperature, and then the solvent was removed under reduced pressure. The residue was extracted with CH_2Cl_2 (2 × 50 mL) and washed with saturated brine twice. The combined organic layers were dried over anhydrous MgSO₄. After the solvent was removed under reduced pressure, the crude product was purified on silica column by using ethyl acetate as the eluent to afford **M-2** (0.75 g, 72.5%) as a light yellow crystal.

¹H NMR (300 MHz, CDCl3): δ 7.05 (s, 4H), 7.03 (s, 2H), 4.18–4.25 (m, 12H), 3.89–3.93 (m, 12H), 3.75–3.81 (m, 12H), 3.50–3.60 (m, 12H), 3.40 (s, 6H), 3.36 (s, 6H), 3.35 (s, 6H),

3.35 (s, 2H); ¹³C NMR (75 MHz, CDCl3): δ 154.1, 153.4, 153.2, 118.6, 117.7, 117.3, 114.9, 114.3, 112.9, 91.2, 91.1, 82.6, 79.6, 71.9, 71.9, 70.9, 70.9, 69.6, 69.5, 69.5, 69.5, 69.4, 69.4, 59.0, 58.9, 58.9. FTIR (KBr, cm⁻¹): 3237, 2877, 1508, 1425, 1274, 1214, 1105, 1051, 952, 860, 698. MS (FAB): m/z 1057 (M⁺ + 23); Anal. calcd for C₅₆H₇₄O₁₈: C, 64.97; H, 7.21. Found: C, 64.78; H, 7.24.

Synthesis of Polymer Sensor

A mixture of **M-1** (29.4 mg, 0.1 mmol), **M-2** (103.5 mg, 0.1 mmol), Pd(PPh₃)₄ (4.6 mg, 0.004 mmol), and Cul (1.2 mg, 0.006 mmol) was dissolved in 6 mL THF and 6 mL Et₃N. The solution was stirred at reflux for 2 days under N₂ atmosphere. The mixture was cooled to room temperature and then was filtered through a short silica gel column in methanol (30 mL) to precipitate the polymer. The resulting polymer was filtered and washed with methanol several times. Further purification could be conducted by dissolving the polymer in THF to precipitate in methanol again. The polymer was dried in vacuum to give 64.2 mg as a red brown solid in 55.1% yield. GPC results: $M_{\rm w} = 11,380$, $M_{\rm n} = 7630$, PDI = 1.49.

¹H NMR (300 MHz, CDCl₃): δ = 7.88–7.57 (m, 2H), 7.22–7.04 (m, 6H), 4.30–4.16 (m, 12H), 4.04–3.94 (m, 12H), 3.87–3.73 (m, 12H), 3.64–3.53 (m, 12H), 3.44–3.37 (m, 18H); FTIR (KBr, cm⁻¹): 3,451, 2,871, 2,370, 2,195, 1,635, 1,503, 1,459, 1,419, 1,358, 1,274, 1,212, 1,108, 1,054, 941, 848, 733, 509. Anal. calcd for (C₆₂H₇₄N₂O₁₈S)_n: C, 63.73; H, 6.34; N, 2.31. Found: C, 63.71; H, 6.38; N, 2.22.

Metal Ion Titration

Each metal ion titration experiment was started with a 3.0 mL polymer in THF solution with a known concentration (1.0×10^{-5} mol L⁻¹ corresponding to BDT unit). Mercury perchlorate salt and other various metal salts (nitrate, 1.0×10^{-2} mol L⁻¹, CH₃CN) were used for the titration. Polymermetal complexes were produced by adding aliquots of a solution of the selected metal salt to a THF solution of the polymer sensor. All measurements were monitored for 2 h after addition of the metal salt to the polymer solution.

RESULTS AND DISCUSSION

Synthesis and Feature of the CP Sensor

The synthesis procedures of the monomers **M-1**, **M-2** and the polymer sensor are outlined in Scheme 1. The monomer **M-1** was synthesized from the starting product BDT.¹⁹ The compound **2** was obtained by a five-step reaction from the starting material hydroquinone.²⁰ The monomer **M-2** was synthesized from compounds **2** and **3** via Pd-catalyzed Sonogashira reaction.²¹ **M-1** and **M-2** could serve as the monomers for the synthesis of the target polymer sensor. Herein, a typical Sonogashira reaction was applied to the synthesis of the polymer sensor.²² The polymerization was easily carried out in the presence of a catalytic amount of Pd(PPh₃)₄ and CuI with Et₃N under N₂. M_{w} , M_{n} , and PDI of the polymer were determined by gel permeation chromatography using polystyrene standards in THF, and the value of them are 11,380, 7630, and 1.49, respectively. The GPC result of the



SCHEME 1 Synthesis procedures of M-2 and polymer sensor.

polymer sensor shows the moderate molecular weight. The polymer is an air-stable solid with red brown color and shows good solubility in common organic solvents, such as THF, CHCl₃, and CH₂Cl₂, which can be attributed to the nonplanarity of the twisted polymer backbone and the flexible ether chain group substituents. The polymer has a little solubility in pure water. Moreover, the BDT moieties can orient a well-defined spatial arrangement in the main-chain backbone of the polymer sensor and act as a ligand to form the corresponding polymer– Hg^{2+} complex with due to the BDTbinding site including sulfur atom. In addition, the vinylene bridge linker can provide an improved electron-transporting property of the polymer sensor and also reduce the steric hindrance between BDT and phenyl groups, which leads to a beneficial influence on the stability of the resulting polymer sensor. According to thermal analysis of the polymer (Fig. 1), it has a high thermal stability with no weight loss up to 350 °C. An apparently one-step degradation was observed at temperatures ranging from 350 to 650 °C. The polymer shows a total weight loss of about 58% upon heating to 700 °C. Therefore, the resulting polymer has a desirable thermal property for practical applications as a fluorescence sensor.

UV-Vis Titration of the Polymer on Hg²⁺

As shown in Figure 2(a), the UV-vis spectra of the polymer $(1.0 \times 10^{-5} \text{ mol L}^{-1}$ in THF) display a broad absorption band at 449 nm and a weak absorption band at 250 nm before titration. As the increasing concentration of Hg²⁺ (0, 3.0, 5.0, 7.0, 9.0, 11.0, 13.0, 15.0, 17.0, and 19.0 \times 10^{-5} mol L⁻¹), the absorbance situated at 250 nm shows a gradual enhancement, which is regarded as the absorption band of benzene group. On the contrary, the intensities of absorption peak at 449 nm appear gradual decrease and blue shift as high as 45 nm. No change was observed for the absorption spectrum of the polymer sensor upon addition of about 19 equiv of Hg²⁺ [Fig. 2(b)]. The UV-vis absorption response changes of the polymer to Hg²⁺ can be attributed to the reduction of the π -conjugated system induced by the coordination of the S atom of BDT with the Hg^{2+.23} Furthermore, almost no the absorption response of the polymer sensor was observed for other metal ions (Supporting Information Fig. S1). As is evident from Figure 2(c), only Hg^{2+} can lead to a prominent absorption change in absorption spectra of the polymer sensor, which may be attributed to the poor coordination ability of the polymer sensor with these metal ions.²⁴ We also found that distinct color change of the polymer sensor can be observed from orange to colorless upon Hg^{2+} addition [Fig. 2(d)], indicating that the polymer sensor can be used as a colorimetric chemosensor for Hg^{2+} detection with high selectivity.

The Selective and Sensitive Response of the Polymer Sensor on Hg^{2+}

The fluorescence titration of the polymer $(1.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$ to Hg^{2+} was conducted in THF solution. As shown in Figure 3(a), the polymer sensor exhibits strong fluorescence centered at 570 nm. However, treatments with Hg^{2+} (0, 3.0, 5.0, 7.0, 9.0, 11.0, 13.0, 15.0, 17.0, 19.0, and 21.0×10^{-5} mol L^{-1}) induce a prominent change in the fluorescence spectra [Fig. 3(a)]. The large fluorescence turn-off response behavior can be observed. More importantly, the bright



FIGURE 1 TGA curves of the conjugated polymer sensor.



FIGURE 2 (a) UV-vis spectral changes of the polymer upon the addition of increasing amounts of Hg^{2+} . (b) Absorbance at 449 nm of the polymer sensor solution as a function of Hg^{2+} concentration. (c) Absorption response of the polymer sensor upon addition of various metal ions. (d) Visual color of the polymer sensor with the addition of different transition-metal ions: from left to right: free ion, Hg^{2+} , Ag^+ , Cd^{2+} , Co^{2+} , Cu^{2+} , Mg^{2+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} .

yellow color of the polymer fluorescence gradually disappears after addition of Hg²⁺, which could be easily detected by naked eyes [inset in Fig. 3(a)]. The addition of Hg^{2+} led to about 98% fluorescence quenching for the polymer sensor at a concentration of 21:1 molar ratio. It was also found that the photoluminescence (PL) quenching ratios (I/I_0) were proportional to the concentration of Hg^{2+} ranging from 0 to 19.0×10^{-5} mol L⁻¹ [Fig. 3(b)]. In this range of concentration, the curve could be best described by the equation F = 1.0982-5373 [Hg²⁺], R = -0.99, N = 10 (Supporting Information Fig. S2). According to the equation and the standard deviation of the blank, it was found that the polymer sensor has a detection limit of 1.0×10^{-7} mol L⁻¹ for Hg²⁺. This is sufficiently low for the submillimolar concentration range of Hg²⁺ detection in many chemical systems.²⁵ The value of the Stern-Volmer fluorescence quenching constant ($K_{\rm sv}$) for Hg²⁺ is as high as 2.16 \times 10⁵. This quenching effect could be attributed to the intramolecular PCT between the CP backbone and the BDT-Hg²⁺ complex.

To confirm specificity, the solution of the polymer sensor was also challenged with various metal ions under the same conditions (Supporting Information Fig. S3). The PL quenching degrees $(1 - I/I_0)$ of the polymer sensor are shown in Figure 3(c). As presented in Figure 3(c), cations, such as $\mathrm{Co}^{2+},\ \mathrm{Ni}^{2+},\ \mathrm{Ag}^+,\ \mathrm{Cd}^{2+},\ \mathrm{Cu}^{2+},\ \mathrm{Zn}^{2+},\ \mathrm{Mg}^{2+},\ \mathrm{and}\ \mathrm{Pb}^{2+},\ \mathrm{do}\ \mathrm{not}$ lead to any noticeable change in the fluorescence emission wavelength spectra, and only Hg²⁺ can exhibit strongly fluorescence quenching response, indicating that the resulting polymer sensor possesses remarkable recognition ability for Hg^{2+} . Meanwhile, one of the essential aspects for Hg^{2+} detection is minor or no interference from other metal ions. Hence, the utility of the polymer sensor as an ion-selective fluorescence sensor for Hg^{2+} was further investigated. We subjected the polymer to a mixture of Hg^{2+} (21 equiv) and each of metal ions (21 equiv) as shown in Supporting Information Figure S4. As shown in Figure 3(d), almost similar PL quenching ratio was observed. The deviations from other metals' interference are less than 2% in the presence of coexisting metal ions, which shows that the interference from these metal ions is negligible for the Hg²⁺ detection. Most importantly, although the fluorescence response was carried out by the Hg^{2+} titrations in the presence of the



FIGURE 3 (a) Fluorescence spectra of the polymer sensor in THF with increasing amounts of Hg²⁺ in CH₃CN ($\lambda_{ex} = 480$ nm). Inset showing the fluorescence before (a) and after (b) the addition of 21 equiv Hg²⁺. (b) Plot of PL quenching efficiencies (///₀) versus Hg^{2+} concentration, where I is the fluorescence intensity of the polymer sensor with the addition of Hg^{2+} , and I_0 is the fluorescence. cence intensity of the polymer sensor without Hg^{2+} . (c) Fluorescence quenching degree $(1 - ||I_0)$ of the polymer sensor in the presence of various transition-metal ions (each 21 equiv). (d) Metal specificity. Mix: the mixture of Mg²⁺, Zn²⁺, Cd²⁺, Ag⁺, Pb²⁺, Cu²⁺, Co^{2+} , and Ni^{2+} .

mixed metal ions, such as Co²⁺, Ni²⁺, Ag⁺, Cd²⁺, Cu²⁺, Zn²⁺, Mg^{2+} , and Pb^{2+} , no obvious interference was observed in the fluorescence of the polymer sensor. The unique selectivity and high sensitivity of the polymer for Hg^{2+} recognition can be attributed to several factors, such as the structural rigidity of the thiadiazole unit, the matched radius of the Hg^{2+} ion, its soft acid property, and the binding ability of BDT unit with Hg^{2+.24}

CONCLUSIONS

The polymer was synthesized through Pd-catalyzed Sonogashira reaction. The responsive properties of the polymer on various transition-metal ions were investigated by fluorescence spectra. Compared with other cations, including Mg^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Ag^+ , Cd^{2+} , and Pb^{2+} , a highly Hg^{2+} selective fluorescence quenching response and the visible colorimetric change can be observed. The results indicate that this kind of polymer sensor incorporating with BDT unit as a receptor in the CP main-chain backbone can be used as a selective fluorescence sensor for Hg^{2+} detection. This work can further expand the application of Sonogashira reaction in design and synthesis of the novel fluorescence sensor for metal ion detection.

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