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Graphical Abstract:

Polymer-based sensor incorporating thiazole ligand moiety exhibited "turn-off" fluorescence response on both Hg^{2+} and Ag^+ . The color change of this polymer solution could be clearly observed by the naked eyes upon the addition of Hg^{2+} (green to colorless) and Ag^+ (green to yellow).



Polymer-based Fluorescence Sensor incorporating Thiazole Moiety

for Direct and Visual Detection of Hg²⁺ and Ag⁺

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ABSTRACT: A thiazole-based conjugated polymer was synthesized by the polymerization reaction of 4,7-dibromo-2-methylbenzo[*d*]thiazole with 1,4-diethynyl-2,5-bis(octyloxy)benzene via Pd-catalyzed Sonogashira coupling reaction. The conjugated polymer emits bright green fluorescence and exhibits "turn-off" fluorescent quenching responses towards both Hg^{2+} and Ag^+ over other cations, such as Li⁺, K⁺, Ca²⁺, Mg²⁺, Ba²⁺, Zn²⁺, Cd²⁺, Co²⁺, Ni²⁺, Pb²⁺, Cu²⁺, Al³⁺ and Fe³⁺. More importantly, the color change of this polymer solution could be clearly observed by the naked eyes upon the addition of Hg^{2+} (green to colorless) and Ag+ (green to yellow), indicating that this thiazole-based conjugated polymer material could be used as a colormetric sensor for directly visual detection of Hg^{2+} and Ag⁺.

Keywords: Fluorescence sensor; Conjugated polymer; Hg²⁺ and Ag⁺; Benzo[*d*]thiazole

1. Introduction

In the past decades, conjugated polymers have attracted much attention on organic light– emitting diodes, molecular sensors and solar cells since these polymer-based materials with tunable optical and electronic properties can be greatly improved by careful combination of designed monomers at well-defined molecular level.^[11] Conjugated polymers as fluorescent sensors have been widely utilized as popular probes for chemical, biological, and medical applications. Polymer-based fluorescent chemosensors for direct recognition of various metal ions have several advantages over small molecule sensors, such as enhancements associated with electronic interaction between receptors and analytes within the π -electronic polymer backbone.^[2] The high selectivity and sensitivity of conjugated polymers on various metal ions originates from the sensory signal amplification due to energy migration along the polymer backbone upon light excitations.

Recently, the research on the polymer-based fluorescence sensor for metal ions detection is emerging as an area of current interest.^[3] Among them, Ag⁺ and Hg²⁺ as heavy metal ions have attracted considerable research interest, because researchers are interested in detecting these two ions due to their poisonous pollutants for health and environment. It is well known that mercury, one of the most toxic heavy metal elements, can lead to the dysfunction of cells and consequently cause a wide range of diseases even at a low concentration, such as digestive, nephrogenic and especially neurological disorders on account of its high affinity for thiol groups of proteins and enzymes.^[4] Meanwhile, Ag⁺ also plays an essential role in imaging industry, electronic and photographic product. Although its toxicity is surpassed only by mercury, Ag⁺ has been also ranked as the highest toxicity class.^[5] Many fluorescence sensors for Ag^+ or Hg^{2+} detection have been reported. But most of them are based on small molecules, and the polymer-based fluorescence chemosensors are very few.^[6] Therefore, the development of highly selective and sensitive polymer-based chemosensors for directly visual recognition of Ag^+ and Hg^{2+} is still greatly attractive.

There have been some reports on thiazole-based derivatives as fluorescence sensors for the detection of transition metals, but very few thiazole-based conjugated polymers were used as fluorescence sensors for directly visual detection of Hg^{2+} and Ag^{+} .^[7] In this paper, we designed and synthesized conjugated polymer incorporating thiazole moiety in the polymer main chain backbone *via* Sonogashira reaction. This thiazole-based polymer can exhibit "turn-off" fluorescence response behavior only towards Hg^{2+} and Ag^{+} . Interestingly, upon the addition of Hg^{2+} and Ag^{+} , the color of polymer solution could be clearly observed from bright green to pale green by the naked eyes for direct detection of Hg^{2+} and Ag^{+} at a low concentration under a commercially available UV lamp.

2. Results and discussion

The synthesis procedures of the thiazole-based polymer are outlined in Scheme 1. Monomers 4,7-dibromo-2-methylbenzo[*d*]thiazole (M-1) and 1,4-diethynyl-2,5-bis(octyloxy)benzene (M-2) were synthesized according to the reported literatures.^[8,3c] The thiazole-based polymer could be synthesized by the polymerization of M-1 with M-2 *via* the Pd-catalyzed halogenoalkane-alkyne Sonogashira reaction. The polymer could be further purified by washing with MeOH and collected as brown solids. The thiazole-based polymer could be dissolved in common organic solvents (THF, toluene, CH₂Cl₂, CHCl₃) due to the flexible *n*-octyl substituents. GPC result of polymer shows moderate molecular weights. TGA of polymer was carried out under a N₂ atmosphere at a heating rate of 10 °C/min. TGA result shows that the degradayion temperature (T_d) of 5% weight loss of the polymer is 276 °C, indicating that this polymer can provide desirable thermal property for practical applications as fluorescence sensor (Figure S16).





The UV-vis absorption spectra of polymer sensor toward various anions were conducted in THF (1×10⁻⁵ mol/L) at room temperature. As shown in Figure 1a, the polymer sensor exhibits an absorption maxima at 439 nm, which is attributed to a π - π * transition of conjugated polymer backbone.^[4c] Upon the addition of Hg²⁺, the intensities of absorption peak at 439 shows obvious decrease with blue shift as high as 17 nm. But no changes were observed for the absorption spectrum of the polymer sensor beyond 10 equiv of Hg²⁺. The UV-vis absorption response behavior of the polymer on Hg²⁺ can be regarded as the reduction of the π -conjugated system induced by the coordination of thiazole ligand moiety of polymer sensor with the Hg²⁺.^[4c, 7b, 7c, 9] In addition, the strongest absorbance peak at 439 nm shows an obvious decrease upon the

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increasing concentration of Ag^+ , meanwhile, a new absorption peak centered at 508 nm turns on a gradual increase with two clear isosbestic point at 359 nm and 459nm, indicating an unusual interaction between thiazole ligand moiety of the polymer sensor with Ag^{+} .^[9] But no changes could be observed for the absorption spectrum of the polymer sensor beyond 10 equiv of Ag^+ . Furthermore, as is evident from Figure 2, almost no the absorption response behaviors of the polymer sensor were observed for other metal ions. Only Hg^{2+} and Ag^+ 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 other metal ions.^[4h] More interestingly, the color changes of polymer solution could be clearly observed from green to colorless and pale yellow by the naked eyes upon addition of Hg^{2+} and Ag^+ , respectively (inset, Figure 2), demonstrating that the polymer sensor could be effectively used as a colorimetric chemosensor for Hg^{2+} and Ag^+ detection with high selectivity and sensitivity.



Figure 1. (a) UV–vis spectral changes of the polymer $(1 \times 10^{-5} \text{ mol/L in THF})$ upon the addition of increasing amounts of Hg²⁺. (b) UV–vis spectral changes of the polymer $(1 \times 10^{-5} \text{ mol/L in THF})$ upon the addition of increasing amounts of Ag⁺. (c) Absorbance at 439 nm of the polymer sensor solution $(1 \times 10^{-5} \text{ mol/L in THF})$ as a function of Hg²⁺ concentration. (d) Absorbance at 508 nm of the polymer sensor solution $(1 \times 10^{-5} \text{ mol/L in THF})$ as a function of Ag⁺ concentration.



Figure 2. UV–vis spectral changes of the polymer $(1 \times 10^{-5} \text{ mol/L in THF})$ upon 5 equiv. of various metal ions. Inset: the solution color of the polymer before and after the addition of various metal ions.

The fluorescence responses of the polymer sensor toward various ions were carried out in THF $(1 \times 10^{-5} \text{ mol/L corresponding to benzo[d]thiazole moiety)}$ by using the excitation wavelength at 381 nm. The polymer sensor emits strong fluorescence at 474 nm as shown in Figure 3. But obvious fluorescence quenching could be observed upon the addition of Hg²⁺, which could be attributed to the reduction of the π -conjugated system induced by the coordination of thiazole moiety of polymer sensor with Hg^{2+} . Hg^{2+} leads to about 90% fluorescence quenching for the polymer at a concentration of 3:1 molar ratio. It can be also found that the fluorescent intensity of the polymer shows a gradual decrease with the concentration mole ratio of Hg^{2+} from 0 to 3.0 (Figure 4a), and bright green fluorescence of solution almost disappears (Figure 4a inset). A curve equation in the range of Hg²⁺ concentrations from 0 to 3.0×10^{-5} mol/L is $F = 1.15 \times 10^{7} - 3.52 \times 10^{11}$ $[Hg^{2+}]$, R= -0.99563, N= 11(Figure S1). According to the equation and the standard deviation of the blank, the fluorescence detection limit of the polymer solution for Hg^{2+} was determined to be as low as 5.1×10^{-7} mol/L. Herein, we further performed the fluorescence response behaviors of the polymer on Ag^+ under the same condition as Hg^{2+} ion determination. Meanwhile, fluorescence quenching effect could be observed upon the addition of Ag⁺, which could be attributed to coordination interaction between thiazole moiety and Ag⁺. Ag⁺ leads to about 71.4% fluorescence quenching for the polymer sensor at a concentration of 1:1 molar ratio, and bright green solution turns on pale green (Figure 4b inset). It can be also found that the fluorescent intensity of the polymer shows a gradual decrease with the concentration mole ratio of Ag⁺ from 0 to 1.0. A curve equation in the range of Ag⁺ concentrations from 0.2×10^{-5} to 1.0×10^{-5} mol/L is F = $1.32 \times 10^{7} - 1.07 \times 10^{12}$ [Ag⁺], R= -0.9791, N= 9 (Figure S2). According to the equation and the standard deviation of the blank, the fluorescence detection limit of the polymer sensor for Ag⁺ could reach as low as 1.68×10^{-7} mol/L.



Figure 3. Fluorescence spectra changes of the polymer $(1 \times 10^{-5} \text{ mol/L in THF})$ upon the addition of 5 equiv. various metal ions. Inset: visible fluorescence of the polymer before and after the addition of various metal ions under a 365 nm UV lamp.

In a set of comparable experiments, we investigated the fluorescence response behaviors of the polymer sensor on other metal ions under the same conditions as Hg²⁺ and Ag⁺ ion determination. As is evident from Figure 3, almost no obvious fluorescence changes could be observed upon the addition of Li⁺, K⁺, Ca²⁺, Mg²⁺, Ba²⁺, Zn²⁺, Cd²⁺, Co²⁺, Ni²⁺, Pb²⁺, Cu²⁺, Al³⁺ and Fe³⁺, indicating that the resulting polymer sensor possesses remarkable recognition ability for Hg²⁺ and Ag⁺. In this paper, we further investigated the utility of the polymer as an ion-selective fluorescence sensor for Hg²⁺ and Ag⁺. Herein, we subjected the polymer (1×10^{-5} mol/L) to a mixture of Hg²⁺ $(2 \times 10^{-4} \text{ mol/L})$ and each of the metal ions $(2 \times 10^{-4} \text{ mol/L})$. The deviations from other metal ions' interference are less than 5% in the coexisted metal ions experiment (Figure S3). Meanwhile, we subjected the polymer $(1 \times 10^{-5} \text{ mol/L})$ to a mixture of Ag⁺ $(5 \times 10^{-5} \text{ mol/L})$ and each of the metal ions $(5 \times 10^{-5} \text{ mol/L})$ as shown in Figure S4. The deviations from other metal ions' interference are less than 5% in the coexisted metal experiment, especially for Hg²⁺. The unique selectivity and high sensitivity recognition of the polymer sensor only for Hg²⁺ and Ag⁺ can be attributed to several factors, such as the structural rigidity of the thiazole unit, the matched radius of the Hg²⁺ and Ag^+ ion, its soft acid property, and the binding ability of thiazole unit with Hg^{2+} and Ag^{+} .^[9, 4c, 10] 4h1



Figure 4. (a) Fluorescence spectra changes of the polymer $(1 \times 10^{-5} \text{ mol/L in THF})$ upon the addition of increasing amounts of Hg²⁺. Inset: visible fluorescence of the polymer before (left) and after (right) the addition of Hg²⁺ under a 365 nm UV lamp. (b) Fluorescence spectra changes of the polymer $(1 \times 10^{-5} \text{ mol/L in THF})$ upon the addition of increasing amounts of Ag⁺. Inset: visible fluorescence of the polymer before (right) and after (left) the addition of Ag⁺ under a 365 nm UV lamp. (c) Plot of PL quenching efficiencies (I/I0) versus Hg²⁺ concentration, where I is the fluorescent intensity of the polymer sensor with the addition of Hg²⁺, and I₀ is the fluorescent intensity of the polymer sensor. (d) Plot of PL quenching efficiencies (I/I₀) versus Ag⁺ concentration.

The stoichiometry for Hg^{2+} with polymer could be determined on the basis of the Benesi-Hildebrand expression: $1/(F - F_0) = 1/{K(F_{min} - F_0)[Hg^{2+}]^n} + 1/(F_{min} - F_0)$, where F_0 and Fare the fluorescent intensities in the absence and presence of Hg²⁺, respectively.^[10] Herein, F_{min} is the minimum fluorescent intensity in the presence of Hg²⁺, and K is the associated constant. Plotting the $1/(F - F_0)$ quantity against $[Hg^{2+}]^n$ (n = 1) by using the fluorescent intensity for polymer (λ_{em} = 474 nm) gave an excellent linear curve, indicating that there is a 1:1 binding mode between polymer and Hg²⁺. In addition, the associated constants calculated from the slope and intercept of the line is 2.81×10^4 M⁻¹ (Figure S5). As for Ag⁺, plotting the 1/(F - F₀) quantity against $[Ag^+]^n$ (n = 2) by using the fluorescent intensity for polymer ($\lambda_{em} = 474$ nm) gave an excellent linear curve, indicating that there is a 1:2 binding mode between polymer and Ag⁺. In addition, the associated constants calculated from the slope and intercept of the line is 3.71×10^{10} M^{-2} (Figure S6). A possible mechanism for polymer Ag⁺ and Hg²⁺ detection can be attributed to coordination interaction between S or N atoms of thiazole ligand moiety and Hg^{2+}/Ag^+ . In order to further investigate the mechanism of recognition process, ¹H NMR titration of the polymer sensor on Hg²⁺ and Ag⁺ was carried out, as shown in the ESI, Figure S14 and Figure S15. It could be clearly observed that the ¹H NMR signal of the methyl group of thiazole moiety was shifted to downfield region upon addition of Hg^{2+}/Ag^+ , indicating the electron density change of H in methyl group due to the coordination interaction between Hg^{2+} or Ag^+ and S or N atoms of thiazole ligand.

3. Conclusions

The benzo[*d*]thiazole-based polymer sensor could exhibit the most pronounced fluorescence response behaviors towards only Hg^{2+} and Ag^+ due to thiazole ligand moiety in the polymer main chain as the metal binding site. More importantly, Hg^{2+} and Ag^+ can lead to the color changes from green to colorless and yellow, respectively, which could be clearly observed by naked eyes. The results also demonstrate that this thiazole-based conjugated polymer can be used as a highly selective and sensitive fluorescence sensor for direct and visual detection of Hg^{2+} and Ag^+ .

4. Experimental section

4.1. General methods and materials

All of the solvents and reagents were commercially available and of analytical reagent grade. THF, DMF, and Et₃N were purified by distillation. NMR spectra were collected on a Bruker 400/500/600 spectrometer and are reported in parts per million (ppm) relative to TMS as an internal standard. Fluorescence spectra were recorded on a Fluoromax-4 Spectrofluorometer. Ultraviolet-visible (UV-vis) spectra were obtained using a Perkin-Elmer Lambda 35 spectrophotometer. Elemental analysis was performed on an Elementar Vario MICRO analyzer. Thermogravimetric analysis (TGA) was performed on a Perkin–Elmer Pyris-1 instrument under a N₂ atmosphere. Molecular weights were determined by gel-permeation chromatography (GPC) with a Waters 244 HPLC pump; THF was used as the solvent relative to polystyrene standards. The solvent of cation solution was water. The concentration of cation solution was 10^{-2} mol/L, and the volume of the polymer solution was 3 mL.

4.2 Synthesis of Polymer sensor

A mixture of M-1 (120.4 mg, 0.39 mmol), M-2 (150 mg, 0.39 mmol), Pd(PPh₃)₄ (45.3 mg, 0.04 mmol) and CuI (7.5 mg, 0.04 mmol) was dissolved in 16 mL DMF and 8 mL Et₃N. The solution was stirred at 70 °C for 2 d under N₂ atmosphere and cooled to room temperature, and then filtered through a short silica gel column. After the solvent was removed, the mixture was dissolved in 2 mL CH₂Cl₂, and then added into 50 mL CH₃OH to precipitate conjugated polymer. The polymer was filtered and washed with methanol several times. The thiazole-based polymer was dried in vacuum to give brown solids in 70% yield. ¹H NMR (400 MHz, CDCl₃): 7.84 (s, 1H), 7.52 (m, 1H), 7.19 (m, 1H), 7.04 (m, 1H), 4.08 (m, 4H), 2.93 (m, 3H), 1.93 (s, 4H), 1.37 (m, 8H), 1.27 (m, 12H), 0.88 (s, 6H); ¹³C NMR (150 MHz, CDCl₃): 153.87, 153.75, 153.03, 138.93, 130.87, 130.03, 129.78, 129.31, 127.41, 117.53, 117.29, 116.48, 92.55, 59.78, 69.49, 69.58, 31.90, 29.74, 29.58, 29.49, 29.35, 29.18, 26.25, 26.07, 22.72, 20.53, 17.81, 14.15; GPC: M_w =15850, M_n =10950, PDI=1.45; Anal. Calcd for C₃₄H₄₁NO₂S: C, 77.38; H, 7.83; N, 2.65, found C, 77.24; H, 7.65; N, 2.68.

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Supporting Information

Polymer-Based Fluorescence Sensor incorporating Thiazole Moiety

for Direct and Visual Detection of Hg²⁺ and Ag⁺

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Contents:

1. Synthesis procedures of monomers and polymer, and experimental section.

2. Fluorescence responsive behaviors of polymer sensor on various metal ions.

3. ¹H NMR spectra of compounds and TGA curve of polymer sensor.

1. Synthesis procedures of monomers and polymer, and experimental section.



Scheme. S1. Synthesis procedures monomers and polymer. (TMSA: Trimethyl silyl acetylene;HMDO: Hexamethyldisiloxane)

Synthesis of N-(2,5-dibromophenyl)acetamide (2)

A mixture of compound **1** (11.24 g, 40 mmol) and iron powder (22.00 g, 400 mmol) in AcOH (20 mL) was stirred at 70 °C for overnight. The mixture was washed with water and extracted with ethyl acetate after cooling to room temperature. The collected organic layers were dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure to afford 2,5-dibromoaniline. Acetyl chloride (3.32 g, 42.4 mmol) was slowly added to a solution of the foregoing 2,5-dibromoaniline in pyridine (80 mL), and the resulting mixture was heated under reflux for 1 h. The reaction mixture was poured into ice water (200 mL) after cooling to room temperature. The precipitate was collected by filtration and recrystallized from MeOH (20 mL) to give the pure product **2** as a white solid (11.20 g, 96% yield). ¹H NMR (500 MHz, CDCl₃): 8.57 (br s, 1H), 7.57 (br s, 1H), 7.37 (d, *J*=8.5 Hz, 1H), 7.10 (d, J=8.5 Hz, 1H), 2.24 (s, 3H).

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Synthesis of 4,7-dibromo-2-methylbenzo[*d*]thiazole (M-1)

A solution of compound **2** (2.93 g, 10 mmol) and hexamethyldisiloxane (HMDO) (2.92 g, 18 mmol) in toluene (50 mL) was added to phosphorus pentasulfide (0.72 g, 3.25 mmol) at 60 °C, and the mixture was heated under reflux for 5 h. The crude product was purified by flash chromatography on silica gel by using ethyl acetate as eluent to obtain a mixture. And then the solution of the above mixture and sodium hydroxide (3.2 g, 80 mmol) in water-EtOH (40 mL-2 mL) was added dropwise to the potassium ferricyanide (13.17 g, 40 mmol) in water (20 mL). The mixed solution was stirred at 95 °C for 2 min and cooled in an ice bath to produce the precipitate. Subsequently, the precipitate was filtered, washed with water, and concentrated in vacuo. The crude product was purified by column chromatography (petroleum ether/ethyl acetate =20/1, v/v) to obtain the product **M-1** as pale yellow powders (2.13 g, 70% yield). ¹H NMR (400 MHz, CDCl₃): 7.55 (d, J = 9.5 Hz, 1H), 7.36 (d, J = 9.5 Hz, 1H), 2.88 (s, 3H).

2. Fluorescence responsive behaviors of polymer sensor on various metal ions.



Figure S1. Calibration curve was obtained from the plot of fluorescence intensity with the added Hg^{2+} from 1:0-1:20.0 molar ratios.







Figure S3. Metal specificity: the concentration of the polymer is 1.0×10^{-5} mol·L⁻¹, Hg²⁺ and other metal ion are used at a concentration of 2.0×10^{-4} mol·L⁻¹, respectively. Mix: the mixture of Li⁺, K⁺, Ca²⁺, Mg²⁺, Ba²⁺, Zn²⁺, Cd²⁺, Co²⁺, Ni²⁺, Pb²⁺, Cu²⁺, Al³⁺ and Fe³⁺ (each 2.0×10^{-4} mol·L⁻¹).



Figure S4. Metal specificity: the concentration of the polymer is 1.0×10^{-5} mol·L⁻¹, Ag⁺ and other metal ion are used at a concentration of 5.0×10^{-5} mol·L⁻¹, respectively. Mix: the mixture of Li⁺, K⁺, Ca²⁺, Mg²⁺, Ba²⁺, Zn²⁺, Cd²⁺, Co²⁺, Ni²⁺, Pb²⁺, Cu²⁺, Al³⁺ and Fe³⁺ (each 5.0×10^{-5} mol·L⁻¹).



Figure S5. Benesi-Hildebrand plot for Hg²⁺-bound polymer.



Figure S6. Benesi-Hildebrand plot for Ag^+ -bound polymer.



Figure S7. The solution color of the polymer before and after the addition of various metal ions

3. ¹H NMR spectra of compounds and TGA curve of polymer sensor.



Figure S9. ¹H NMR of 2 (CDCl₃, 500 MHz)



Figure S11. ¹H NMR of M-2 (CDCl₃, 300 MHz)



Figure S13. ¹³C NMR of polymer sensor (CDCl₃, 150 MHz)



Figure S14. ¹H NMR titration of the polymer sensor (CDCl₃) with Hg^{2+} (0, 0.5, 1, 2 e.q.,d⁶-DMSO)



Figure S15. ^1H NMR titration of the polymer sensor (CDCl_3) with Ag^+ (0, 0.5, 1, 2 e.q.,d^6-DMSO)



Figure S16. TGA curve of polymer sensor