

A Novel Polymer Chemodosimeter for the Detection of Mercury Ions: Synthesis and Fluorescence “Turn-On” Responses of Fluorene-Based Conjugated Polymer with Reactive Pendent *N,N*-Diethyl-2-(4-phenoxy)-Thioacetamide

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ABSTRACT: A novel conjugating polyfluorene bearing *N,N*-diethyl-2-(4-phenoxy)-thioacetamide as side chain was designed for the detection of Hg(II) ions. It was synthesized through postfunctionalization of acetamide-based polyfluorene derivative. Upon the addition of Hg(II) ions, the thioacetamide groups of this polymer side chains were specifically reacted with Hg(II) ions, leading to this chemodosimeter with higher selectivity for Hg(II) over other metal ions tested under the same conditions. In addition, on the basis of the effect of

fluorescent signal amplifications originated from electron transmission along the backbone, this designed conjugated polyfluorene with pendent reactive thioacetamide reached ultra high sensitivity for the detection of mercury ions. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2055–2061, 2012

Key words: polymer synthesis; reactive conjugated polyfluorene; turn-on fluorescent chemodosimeter; mercury ions detection

INTRODUCTION

Mercury pollution occurs through various natural and anthropogenic sources, including coal and gold mining, solid waste incineration, wood pulping, fossil fuel combustion, and chemical manufacturing.¹ Owing to its high toxicity and easy accumulation in organisms, mercury could cause irreversible damages to central nervous and endocrine system. Therefore, the design of new chemical tools and tactics for the detection of mercury has received increasing attention in recent years.

Traditional techniques for mercury screening, including atomic absorption/emission, spectroscopy, and inductively coupled plasma mass spectrometry etc., often require expensive instruments and/or complex sample preparations. Recently, many examples based on the fluorescence sensors of small molecules,^{2–5} polymers,^{6–10} biomolecules,^{11–15} and nanoparticles^{16–18} have been developed for the detection of mercury due to their high sensitivity and easy

measurement. Although some degree of success has been achieved, there are still many examples of Hg(II) detectors used in organic solution or in aqueous/organic solvent mixtures.^{19–21}

An advantage of conjugated polymers (CPs) over small molecule sensors is the signal amplification originated from electron transport along the polymer backbones.²² Therefore, in recent years, fluorescent CPs have been used for the detection of Hg(II) ions. However, most CPs-based sensors for Hg(II) ions employ the properties of heavy metal ions to quench fluorophore emission,^{23–25} namely fluorescence “turn-off” effect.^{8,26,27} Zhao and Zhong²⁸ prepared cholate/methionine foldamer appended with a dansyl fluorophore for the Hg(II) detection. The Hg(II) ions were coordinated to the methionine thioether moieties and quenched dansyl emission. A detection limit of 20 nM was obtained, but “turn-off” response to Ag(I) was also observed in Zhao's system. Amino acid-functionalized polyfluorene (PFA) as a water soluble Hg(II) chemosensor was reported by Qin's groups.⁸ PFA showed excellent selectivity for Hg(II) and its limit of detection in high concentrated buffer solution could be as low as 10 nM.

A few of fluorescence “turn-on” chemosensors based on the effect of the coordination between metal ions and N atoms of ethylenediamino, trimethylamino and so on, were presented in the

Additional Supporting Information may be found in the online version of this article.

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literature.^{20,21,29,30} The electron-donating ability of N atoms was weakened when the fluorophores were coordinated with metal ions, leading to the enhancement of fluorescence emission. *N,N,N'*-trimethylethylenediamine (tmeda) as receptor on a poly[*p*-(phenyleneethylene)-*alt*-(thienyleneethynylene)] (PPETE) fluorescent conjugated polymer backbone was synthesized by Fan's groups.²¹ On the addition of Hg(II), fluorescence enhancement of tmeda-PPETE occurred with detection limit of 1 μM . However, the "turn-on" effect was also observed on titrating aqueous solution of Zn(II) and Ca(II) into this polymer solution.

Both the "turn-off" and coordination-based "turn-on" sensors are prone to be disturbed by the environmental interference in real analytical systems. Up to now, the detection limit of most chemosensors for mercury ions did not reach the maximum level (10 nM) of the drinking water allowed by the US environmental protection agency (EPA).

Also, there are some examples based on the fluorescence resonance energy transfer (FRET) from chromic repeat units to an energy/electron acceptor along the backbone of the CPs. Fang and his co-workers⁷ reported a series of cationic porphyrin-containing conjugated polyfluoreneethynylenes (PFEs) for mercury ions detection with a detection limit of 0.1 μM . The incorporation of porphyrin into the PFE backbone offered intramolecular energy transfer from fluoreneethynylene segments to the porphyrin units. The poly[*p*-(phenyleneethylene)-*alt*-(thienyleneethynylene)] bearing covalently linked thienylene moieties and rhodamine was synthesized and used for Hg(II)-selective FRET type fluorescence probe with a detection limit of 1 μM .¹⁰

Ren and Xu¹⁴ demonstrated a FRET system for the detection of mercury ions by using a combination of oligonucleotides, DNA intercalators and conjugated polymers. This system was the most sensitive mercury sensor whose detection limit was 0.27 nM. However, the complex system was inconvenient for the real-time event analysis and detection.

Thus, it is still a considerable challenge to design sensitive and selective fluorescent chemosensor with "turn-on" response for Hg(II) ions not requiring small molecule ligands, DNA intercalators or quantum dots.

Compared to the relatively well-developed fluorescent chemosensors, fluorescent chemodosimeters have recently emerged as a research area of significant importance.³¹⁻³³ Chemodosimeters are used to detect an analyte through a highly selective and usually irreversible chemical reaction between the dosimeter molecule and the targeted analyte. This leads to an observable signal that has an accumulative effect and hence is directly related to the concentration of the analyte. Interestingly, chemodosim-

eters provide an ideal way to design fluorescence "turn-on" probes for the quenching of the heavy metal ions.³⁴

Because of the strong thiophilic affinity of Hg(II) ions, fluorescent changes based on mercury-promoted desulfurization reactions can be used to design Hg(II) ions chemodosimeters.³¹ In fact, the use of mercury ion desulfurization reaction of small molecules chemodosimeters has been reported since 1990s.^{35,36} Chae and Czarni³⁵ reported a redox-active 9-[(Methylamion)thio-carbonyl] anthracene as Hg(II) ions sensor, which had a increased fluorescence response with the detection limit of 10 μM . The paper on the using probes of thione moieties linked to anthracene as Hg(II) sensors was documented.³⁶ Addition of Hg(II) to the probes solution could cause fluorescence enhancement with the detection limit of 80 nM, resulting from the desulfurization reactions.

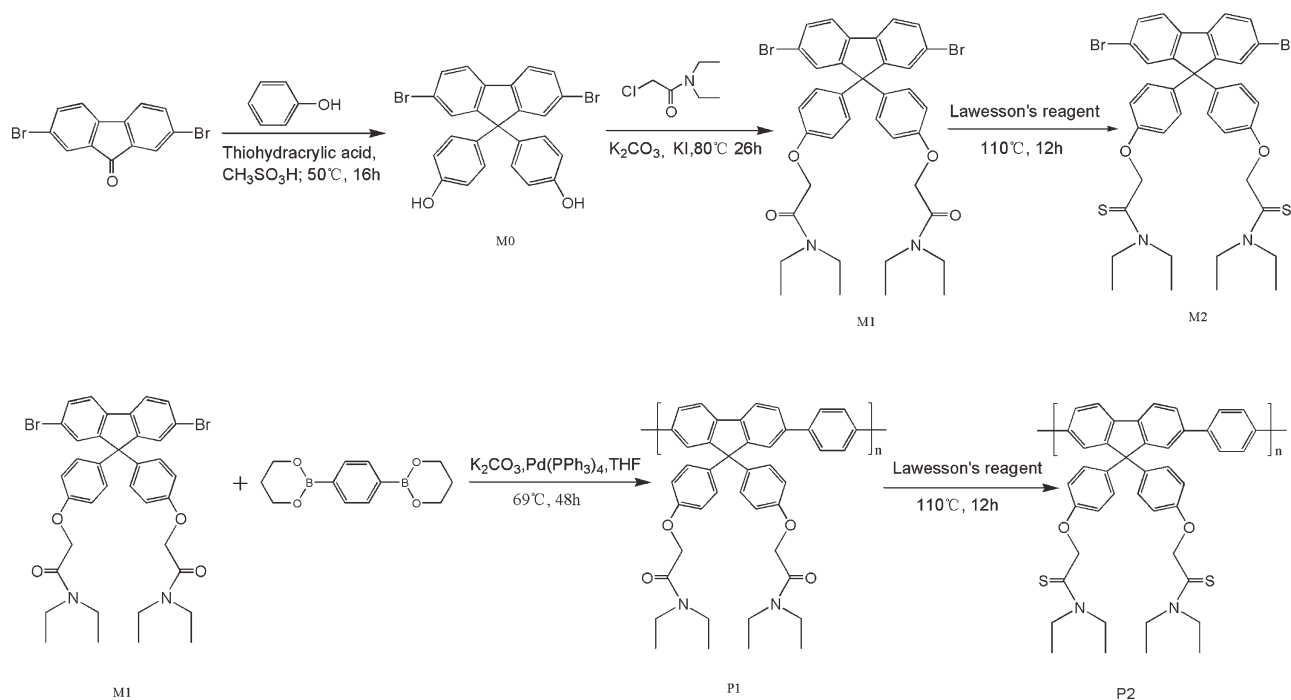
Herein we report the design and syntheses of a novel fluorene-based conjugated polymer with pendent *N,N*-diethyl-2-(4-phenoxy)-acetamide. Then, the postfunctionalization will be used to synthesize poly{9,9-bis[*N,N*-diethyl-2-(4-phenoxy)-thioacetamide]fluorene-*alt*-benzene}. As Hg(II) promoted desulfurization reactions, thioacetamide groups in the polymer side chain would be changed to acetamide. Thus, the sulfur-based photoinduced electron transfer (PET) quenching could be inhibited. Furthermore, the thioacetamide groups would be reactive with Hg(II) ions and show higher selectivity for Hg(II) ions detection in the case of the coexisting with other metal ions. Because the main chain of polyfluorene contains several chromic repeat units, the energy could be transmitted along the backbone.²² Using of CPs might lead to the increase in the limit of the detection signal, namely the enhancement of sensitivity in the "turn-on" effect. To the best of our knowledge, there is little information available in literatures about using reactive groups direct linked with fluorescent CPs as mercury chemodosimeters.

EXPERIMENTAL

General information

Tetrakis-(triphenylphosphine) palladium, benzene-1,4-bis(boronic acid)-propane-1,3-diol diester were purchased from Synwitech. *N,N*-diethyl chloroacetamide was purchased from Tokyo Chemical Industry (TCI). Other materials were used directly without further purification unless otherwise stated. The 2,7-dibromo-9,9-bis(4-phenol) fluorene (M0) was prepared according to the literature.³⁷

The ¹H and ¹³C NMR spectra were obtained in CDCl₃ using tetramethylsilane as an internal



Scheme 1 Schematic for the synthesis of amide-based monomer, fluorene-based CPs with pendent *N,N*-diethyl-2-(4-phenoxy)-acetamide and the post functionalization.

reference on a Bruker Avance 500 NMR spectrometer. PL spectra (at room temperature) were recorded on Hitachi F-4500 fluorescence spectrophotometer. FTIR Spectra from KBr sample pellets were acquired on a Bruker FTIR spectrometer (TENSOR 27). The thermal gravimetric analysis (TGA) was performed with a NETZSCH 209 F1 thermal analyzer at a heating rate of $10^\circ\text{C min}^{-1}$ under a nitrogen atmosphere, and the temperature ranged from 40 to 800°C . Gel permeation chromatograph (GPC) measurements were carried out at 40°C on a Waters 2410 chromatographic with refractive index detector, using THF as eluent at a flow rate of 1.0 mL min^{-1} . The GPC data were calibrated by using polystyrene (PS) standards. Column chromatography was performed with silica gel (100–200 mesh).

Synthesis and characterization

The synthetic route to the amide-based monomer, fluorene-based CPs with pendent *N,N*-diethyl-2-(4-phenoxy)-acetamide, and the postfunctionalization is presented in Scheme 1.

Synthesis of 2,7-dibromo-9,9-bis[*N,N*-diethyl-2-(4-phenoxy)-acetamido] fluorene (M1)

To a solution of M0 (5.080 g, 10 mmol), K_2CO_3 (3.450 g, 25 mmol), and KI (0.255 g, 1.5 mmol) in THF (30 mL), *N,N*-diethyl chloroacetamide (3.750 g, 25 mmol) was added. Then the mixture solution was stirred at 80°C for 26 h. After cooling to the room temperature,

the above mixture solution was concentrated by reduced pressure distillation and extracted using dichloromethane/water. The organic layer was washed with deionized water and concentrated under reduced pressure. The resultants were purified by column chromatography with hexane-ethyl acetate (1 : 1, v/v) to yield compound M1 as a white powder (4.153 g, yield: 56.5%, m.p: $302.6\text{--}304.6^\circ\text{C}$). $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 1.19(m, 6H, $-\text{CH}_2\text{CH}_3$), 3.36(m, 4H, $-\text{CH}_2\text{CH}_3$), 4.63(s, 2H, $-\text{OCH}_2\text{CO}$), 6.80–7.57(m, 7H, Ar-H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 12.8, 14.4, 40.3, 41.5, 64.4, 67.5($-\text{CH}_2\text{CO}$), 114.7, 121.6, 129.1, 130.8, 137.2, 137.8, 153.5, 157.3, 166.8(C=O).

Synthesis of 2,7-dibromo-9,9-bis[*N,N*-diethyl-2-(4-phenoxy)-thioacetamido] fluorene (M2) from M1 through modification by Lawesson's reagent

To a solution of M1 (3.672 g, 5 mmol) in dry toluene, 1,3,2,4-dithiadiphosphetane (Lawesson's reagent, 4.848 g, 12 mmol) was added, stirred at 110°C for 12 h and then allowed to cool slowly to the room temperature. The resultant was purified by column chromatography with hexane-ethyl acetate (1 : 4, v/v) to yield compound M2 as a yellow powder (2.161 g, yield: 56.4%, m.p: $271.7\text{--}273.4^\circ\text{C}$). $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 1.13(m, 6H, $-\text{CH}_2\text{CH}_3$), 3.69(q, 2H, $-\text{CH}_2\text{CH}_3$), 3.94(q, 2H, $-\text{CH}_2\text{CH}_3$), 5.01 (s, 2H, $-\text{OCH}_2\text{CS}$), 6.90–7.57(m, 7H, Ar-H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 10.8, 13.8, 47.1, 47.6, 64.4, 75.5 ($-\text{CH}_2\text{CS}$), 115.0, 121.6, 129.2, 130.9, 137.4, 137.9, 153.4, 157.1, 194.6 (C=S).

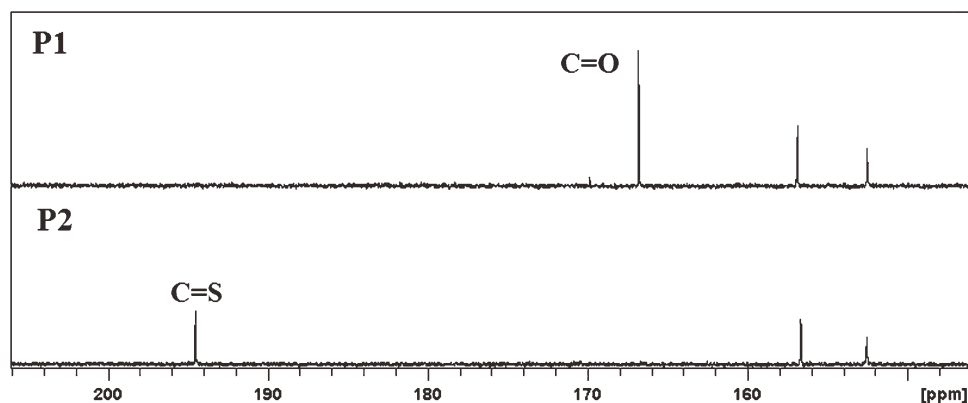


Figure 1 The difference between C=O and C=S in the ^{13}C NMR of P1 and P2.

Synthesis of poly {9,9-bis [*N,N*-diethyl-2-(4-phenoxy)-acetamide] fluorene-*alt*- benzene} (P1)

To a solution of monomer M1 (0.734 g, 1 mmol) and benzene-1,4-bis(boronic acid)- propane-1,3-diol diester (0.246 g, 1 mmol) in THF (15 mL), aqueous solution of potassium carbonate (2.0M, 10 mL) was added. The mixture was degassed for 15 min, and then Pd(PPh₃)₄ (2 mol %, 24 mg) was added under N₂ protection. The above reaction solution was stirred at 69°C for 48 h. After cooling to the room temperature, the product was purified by reprecipitating in methanol, and washed with methanol, distilled water, and methanol sequentially. Finally, P1 was afforded as brown powder by being stirred in acetone over night to remove the catalyst and other small molecules. Yield: 0.282 g, 43.4%. $\bar{M}_n = 4899$, PDI = 1.47. ^1H NMR (CDCl₃, 400 MHz) δ 1.13(m, 6H, -CH₂CH₃), 3.30(m, 4H, -CH₂CH₃), 4.57(s, 2H, -OCH₂CO), 6.77–7.81(m, 9H, Ar-H).

Synthesis of poly {9,9-bis [*N,N*-diethyl-2-(4-phenoxy)-thioacetamide] fluorene-*alt*-benzene} (P2)

To a solution of P1 (0.098 g, 0.02 mmol) in dry toluene, Lawesson's reagent (0.120 g, 0.3 mmol) was added, stirred at 105°C for 12 h and then allowed slowly to cool to the room temperature. The resulting polymer was purified by acetone to remove the excess Lawesson's reagent. Yield: 97.2%. $\bar{M}_n = 5326$, PDI = 1.41. ^1H NMR (CDCl₃, 400 MHz) δ 1.26 (m, 6H, -CH₂CH₃), 3.67(m, 4H, -CH₂CH₃), 4.99(s, 2H, -OCH₂CS), 6.89–7.83(m, 9H, Ar-H).

RESULTS AND DISCUSSION

Through the use of the postfunctionalization, we have successfully synthesized poly{9,9-bis[*N,N*-diethyl-2-(4-phenoxy)-thioacetamide]fluorene-*alt*-benzene} (P2). The experimental results showed that P2 can not be gained directly by Suzuki coupling reaction

between 9,9-bis[*N,N*-diethyl-2-(4-phenoxy)-thioacetamide] fluorene (M2) and borate ester. It is assumed that the bond C=S of thioacetamide would be unstable in the alkaline solution, which is the necessary environment for Suzuki coupling reaction. Thioacetamide group has a tendency to be hydrolyzed during the polymerization reaction process. As Lawesson's reagent is a mild thiophilic agent, it is possible to transform the amide group to thioamide group.³⁸

The postfunctionalization from P1 to P2

To investigate postfunctionalization, the NMR and FTIR of polymers were measured (as shown in Supporting Information Fig. S1–S6).

In the ^{13}C NMR spectra, the transformation from C=O to C=S can be seen clearly (as shown in Fig. 1). The characteristic shift of C=O on acetamide of P1 is at $\delta = 166.8$ ppm. However, in the ^{13}C NMR spectrum of P2, the chemical shift at around 166 ppm disappeared. Instead, a new chemical shift appeared at $\delta = 194.5$ ppm, which is the characteristic shift of C=S³⁹.

The FTIR spectra (Supporting Information Fig. S1–S2) indicate that the strong intensity of 1668 cm⁻¹ (P1) belongs to the absorption of C=O stretching vibration,⁴⁰ but the absorption peaks at about 1668 cm⁻¹ disappeared in the IR spectrum of P2, which means C=O bonds did not exist after postfunctionalization. Thus, through the postfunctionalization, the transformation from acetamide to thioacetamide can be realized and demonstrated.

Thermal gravimetric analysis of polymers

The TGA data of P1 and P2 are shown in Table I. The TGA curves are presented in the Supporting Information Figure S7.

It is known that the stability of acetamide groups (as the side chain of P1) is better than that of

TABLE I
The Key Parameters and TGA Data of P1 and P2

Sample	\bar{M}_n	PDI	Yield (%)	PL _{max} (nm)	T_{onset}^a (°C)	T_{max}^a (°C)	Residue ^b (%)
P1	4899	1.47	43.4	417/435	312	365	52.5
P2	5325	1.41	97.2	410/433	259	300	50.2

^a T_{onset} is defined as the temperature at 5% weight loss. T_{max} is defined as the temperature at maximum weight loss rate.

^b The char residue at 800°C.

thioacetamide groups (as the side chain of P2). The results of the thermal analysis reflect the difference between side chains structures of P1 and P2, and indicate that the thermal stability of P1 and P2 is good enough to be used as chemodosimeters.

Photophysical properties

In the fluorescence spectra of P2 shown in Figure 2(a), there are two maximum emission peaks at around 410 and 433 nm, which can be assigned to the emission of fluorene-based chromophore.³⁰ The

fluorescence intensity increased with the increasing concentration of P2 in the range of 10^{-9} to 10^{-6} M. Figure 2(b) shows that the fluorescence intensities of P2 follow a linear relationship in range of concentration from 10^{-9} to 2×10^{-7} M, which implies that there is no chain aggregation at least under the solution concentration of 2×10^{-7} M.²⁰ Therefore, 10^{-7} M of the polymer's concentration was chosen for the study of fluorescence response to mercury (II) ion or other metal ions.

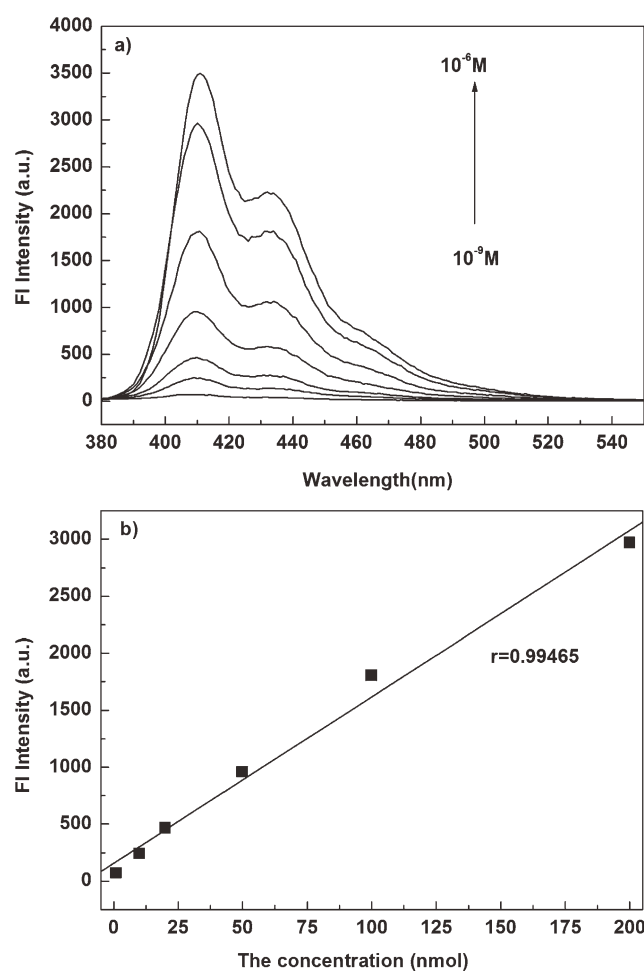


Figure 2 Fluorescent emission spectra (a), the plot of the fluorescence intensity I_{410} (b) of P2 with different concentrations in THF/H₂O (v/v = 4/1); excitation wavelength was 320 nm.

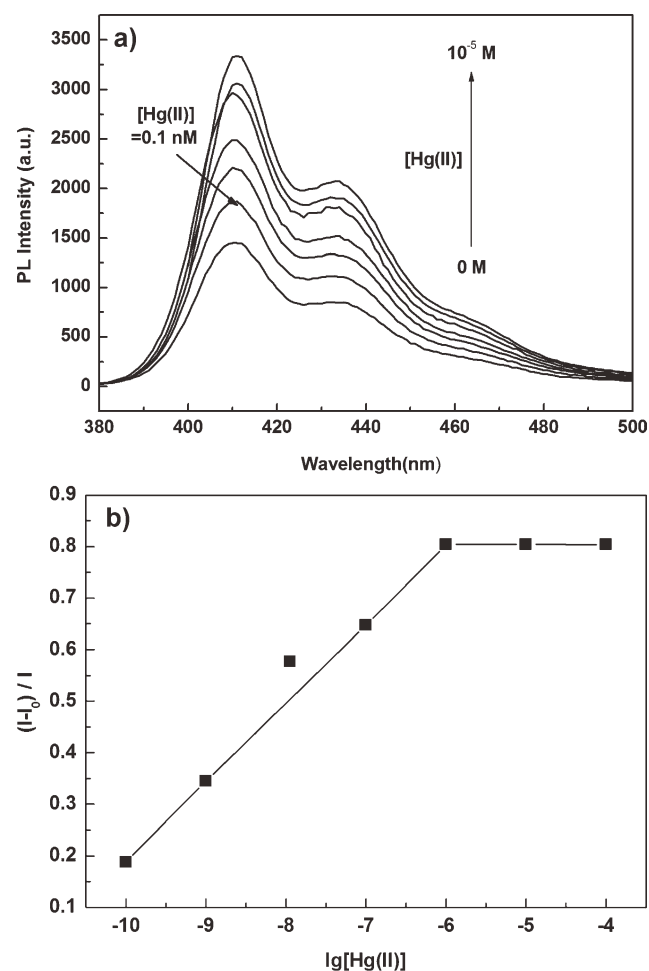
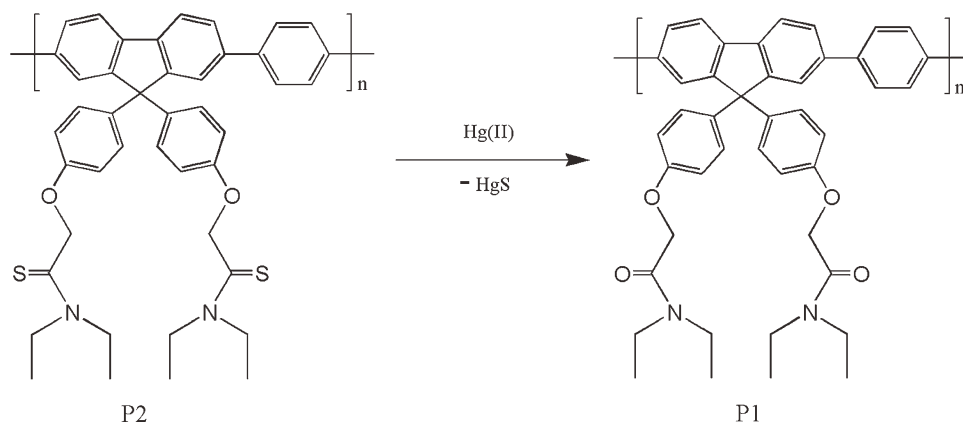


Figure 3 Fluorescent emission spectra (a), the plot of the fluorescence intensity at 410 nm (b) of P2 in the presence of different concentrations of Hg(II) ions in THF/H₂O (v/v = 4/1); [P2] = 10^{-7} M, [Hg(II)] = 10^{-10} – 10^{-4} M; excitation wavelength was 320 nm.



Scheme 2 Mechanism for desulfurization of thioacetamide groups in P2 by Hg(II) ions.

Fluorescence “turn-on” effect of P2 upon addition of Hg(II) ions

To investigate the sensitivity of the novel polymer chemodosimeter to Hg(II) ions, the “turn-on” effect of Hg(II) with their different concentrations on the fluorescence behavior of P2 were studied. The results indicate that, upon the addition of Hg(II) ions, the fluorescent emission intensity of P2 at 410 and 433 nm increased as shown in Figure 3(a). When there is no addition of Hg(II) ions, the lower quantum yields of P2 most probably resulted from the PET process caused by the lone electron pair of the oxygen atom of phenoxy segment.²⁰ As the atomic radius of sulfur is larger than oxygen, the electron withdrawing ability of sulfur is really weaker. The lone electron pair of the oxygen atom on phenoxy segment can transfer along the backbone of P2, which could cause PET process and make the fluorescence emission of P2 quenched. While Hg(II) promoted desulfurization reactions proceeded (as presented in Scheme 2),³⁹ thioaceta-

mid groups were transformed into original structures of acetamide, whose oxygen atom shows stronger electron withdrawing ability than sulfur, inhibiting the PET process and the fluorescence “turn-on” effects were triggered.

The detection concentration of this chemodosimeter for Hg(II) was also investigated. As shown in Figure 3(b), fluorescence intensity at 410 and 433 nm with increasing the concentration of the Hg(II) ions up to 10^{-5} M and then remained relatively constant. From the titration results, the detection limit of P2 for the analysis of Hg(II) ions in solution of H₂O/THF (v/v = 1 : 4) was determined to be 10^{-10} M (0.1 nM). This ultra high sensitivity of P2 to Hg(II) ions might caused by the amplifying effect of molecular wire of conjugated polymers.⁴¹

To study the selectivity of P2 to Hg(II) ions, a competition experiment with other biologically and environmentally relevant metal ions including alkali, alkaline-earth and transition-metal ions was carried out. Figure 4 shows the fluorescence “turn-on” of P2

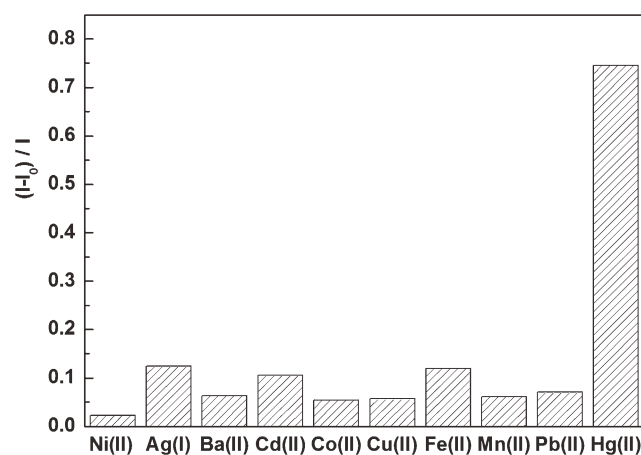


Figure 4 Relative fluorescence intensity increases at 410 nm for P2/metal ions in THF/H₂O (v/v = 4/1); [P2] = 10^{-7} M, [metal ions] = 10^{-5} M; excitation wavelength was 320 nm.

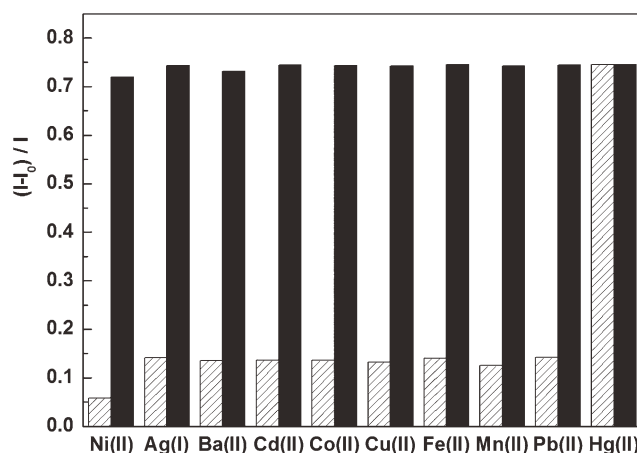


Figure 5 Relative fluorescence intensity increases at 410nm for P2/metal ions (the shadow bar) and P2/metal ions/Hg(II) ion (the black bar) in THF/H₂O (v/v = 4/1); [P2] = 10^{-7} M, [metal ions] = 10^{-4} M, [Hg(II)] = 10^{-5} M; excitation wavelength was 320 nm.

in the presence of varying metal ions. Note that there is no significant fluorescence increment of P2 on adding one of the other metal ions such as Ag(I), Ni(II), Ba(II), Cd(II), Co(II), Cu(II), Fe(II), Mn(II), or Pb(II).

For better understanding the selectivity, we carried out all the experiments in the concentration of 10^{-4} M for the compared other metal ions and 10^{-5} M for Hg(II) ions. Although the concentrations of other metal ions were 10 times as Hg(II) ions', the "turn-on" enhancements of the fluorescence intensity for the systems of Hg(II) ions together with another coexisting metal ions were not influenced (as shown in Fig. 5). The thioacetamide groups of P2 responded to Hg(II) ions specially through irreversible desulfurization reactions, which prevented other metal ions from interference in real time detection.

CONCLUSIONS

In conclusion, we designed a novel chemodosimeter polyfluorene bearing *N,N*-diethyl-2-(4-Phenoxy)-thioacetamide as side chains and prepared by Suzuki coupling reaction and postfunctionalization. The polymer's fluorescence behavior and response to mercury ions were investigated. The transformation of the thioacetamide into acetamide groups resulted in fluorescence "turn-on" response for Hg(II) ions in organic/aqueous environment.

The excellent sensitivity (0.1 nM) of P2 for Hg(II) ions is due to the significant amplification effect of conjugated polymers. The high selectivity for Hg(II) over other competing analytes is owing to desulfurization for the reactive thioacetamide groups of the fluorescent polymer. As far as we know, our polymer chemodosimeter shows lower detection limit of mercury ions far beyond the level of most other mercury ions sensors as reported in previous literatures.

Further study on modification of the structures of polyfluorene with reactive groups and distinctive selectivity for Hg(II) ions in aqueous system and biological contexts is in progress in our group.

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