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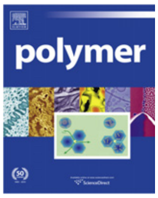

A highly selective fluorescent sensor for Hg^{2+} based on the water-soluble poly(*p*-phenyleneethynylene)

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ABSTRACT

The conjugated polymer **P-1** could be synthesized by the polymerization of 4,7-diethynyl-benzo[2,1,3] thiadiazole (**M-1**) and 1,4-bis[3′-(*N*,*N*-diethylamino)-1′-oxapropyl]-2,5-diiodobenzene (**M-2**) *via* Pd-catalyzed Sonogashira reaction. The water-soluble conjugated polyelectrolyte **P-2** could be obtained by the reaction of **P-1** with ethyl bromide. Both **P-1** and **P-2** can emit orange fluorescence. The responsive optical properties of **P-1** and **P-2** on Hg^{2+} were investigated by fluorescence spectra. Hg^{2+} can lead to nearly complete fluorescence quenching of **P-1**. On the contrary, Hg^{2+} can show the most pronounced fluorescence enhancement response of **P-2** in aqueous solution without interference from those coexistent ions, such as K^+, Mg^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Ag^+, Cd^{2+}, Cu^{2+}, Fe^{3+} and Zn^{2+}. The results also exhibit that this kind of water-soluble conjugated polyelectrolyte can be used as a highly sensitive and selective fluorescence sensor for Hg^{2+} detection in water.

1. Introduction

In the past few years, water-soluble conjugated polyelectrolytes (CPEs), when modified with hydrophilic and functional pendant substituents with fine structural control on the conjugated main chain, have showed great potential applications in many fields [1–6]. Fluorescence-based CPEs have many features. For example, they can interact electrostatically with other charged species showing an intrinsic tendency to organize into supramolecular architectures [7–9]. They also have extraordinarily high sensitivity to fluorescence quenchers [10,11]. The latter property of CPEs has been successfully exploited as novel chemo or biosensors [12–21]. CPEs used as chemosensors for metal ion detection have several advantages over small molecule sensors, such as fluorescent enhancement associated with electronic interaction between receptors and analytes within the conjugated π-electronic polymer backbone. Swager et al. reported that the delocalizable π-electronic conjugated “molecular wire” polymer can greatly amplify the fluorescence response signal due to facile energy migration along the polymer backbone upon light excitations. As a result, a single CP can provide enhanced optical response relative to one of its monomer units [22,23]. It is well-known that heavy-metal ion pollution has posed severe risk to human health and the environment. Among them, mercury and its derivatives are widespread global pollutants, and have caused serious environmental and health problems [24–27]. Mercury(II) ion has no optical spectroscopic signal because of its closed-shell d^{10} ($5d^{10}6s^2$) electronic configuration, which limits the kinds of methods that can be applied to its study and detection. Optical detection, following changes in solution fluorescence arising from a Hg(II)-induced perturbation of a chromophore, is well suited for monitoring Hg(II) in either environmental or biological system. These problems have promoted the development of methods for the quick and simple detection of mercury in aqueous solutions including biological fluids.

Many fluorescent sensors for mercury detection have been reported, but most of them are based on small molecules [28–30], only a few are polymer-based [21,31–37]. Moreover, most of them can only work in organic solvents which prevent their potential application in environment and biological systems. Although heavy-metal ions are relatively easy to chelate and detect in organic solvents, they are rather difficult to recognize directly in aqueous environments due to their strong hydrations. Therefore, development of highly selective chemosensors for Hg(II) detection in aqueous solution with minor or no interference from other metal ions is very important.

Some of these desired attributes are easy to address in the design of a sensor. The affinity and selectivity can both be tuned through modifications of the Hg(II) binding unit. In this regard, principles of Hg(II) coordination chemistry should be considered in

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selecting a Hg(II)-responsive moiety for incorporation into the probe. Because of its $5d^{10}6s^2$ electronic configuration and lack of ligand field stabilization energy, Hg(II) can accommodate a range of coordination numbers and geometries. Two-coordinate linear and four-coordinate tetrahedral species are common. Hg(II) is a soft acid and the use of soft donor atoms, including thiols and thioethers, in a chelating unit will generally increase its affinity and selectivity for Hg(II). Other donor atoms well suited for Hg(II) coordination include nitrogen and phosphorus. Some probes for Hg^{2+} are often based on the coordination of multiple nitrogen atoms with the metal ion or strong Hg-S binding [38]. In this paper, a neutral polymer **P-1** incorporating benzo[2,1,3]thiadiazole (**BT**) group and tertiary amine units was designed and synthesized by Pd-catalyzed Sonogashira reaction. Quaternization after polymerization was chosen to produce a novel water-soluble ammonium functionalized poly(*p*-phenyleneethynylene) (**P-2**). Most of fluorescence sensors based on small organic molecules or conjugated polymer for Hg^{2+} detection exhibit fluorescence quenching effect [38–40]. Although a few small molecule sensors work in "turn-on" mode [41–49], to our knowledge, very few examples based on polymer chemosensors for Hg^{2+} detection show a fluorescence enhancement result [31–33,36]. In this paper, the fluorescence response of **P-2** toward different metal ions is investigated. Compared with other cations, such as K^+, Mg^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Ag^+, Cd^{2+}, Cu^{2+}, Fe^{3+} and Zn^{2+}, Hg^{2+} can cause pronounced fluorescence enhancement response of **P-2** in water.

2. Experimental part

2.1. Materials

All solvents and reagents were commercially available and analytical-reagent-grade. (*R*)-2,2′-Binaphthol and benzo [2,1,3] thiadiazole were purchased from Aldrich and directly used without purification. THF and Et_3N were purified by distillation from sodium in the presence of benzophenone. CH_3CN were distilled from P_2O_5.

2.2. Measurements

NMR spectra were obtained using a 300-Bruker spectrometer 300 MHz for ^1H NMR and 75 MHz for ^{13}C NMR and reported as parts per million (ppm) from the internal standard TMS. FT-IR spectra were taken on a Nexus 870 FT-IR spectrometer. Fluorescence spectra were obtained from a RF-5301PC spectrometer. Specific rotation was determined with a Ruololph Research Analyfical Autopol I. MS was determined on a Micromass GCT. C, H, N and S of elemental analyses were performed on an Elementar Vario MICRO analyzer. Molecular weight was determined by GPC with Waters-244 HPLC pump and THF was used as solvent and relative to polystyrene standards.

2.3. Preparation of 4,7-diethynyl-benzo[2,1,3]thiadiazole (**M-1**) (Scheme 1)

Compound **M-1** was prepared according to a reported method [50,51]. A mixture of 4,7-dibromobenzo-thiadiazole (2.21 g, 7.5 mmol), $Pd(PPh_3)_4$ (175 mg, 0.15 mmol), CuI (55 mg, 0.30 mmol) and trimethylsilyl acetylene (3.0 mL, 22.5 mmol) was dissolved in 80 mL Et_3N. The reaction mixture was stirred at 75 °C for 5 h under a N_2 atmosphere. The solution was then cooled to room temperature and the solvent was removed under reduced pressure, the residue was extracted with CH_2Cl_2. The organic layer was washed with cool water (25 mL × 3) and aqueous 1.2 mol L^{-1} HCl (30 mL), dried over anhydrous Na_2SO_4, and evaporated in vacuum to dryness. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) (10:1, v/v) to give 4,7-bis(trimethylsilylethynyl)-2,1,3-benzothiadiazole (460 mg, 98%) as a pale yellow powder. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.35 (s, 18H), 7.72(s, 2H). A mixture of 4,7-bis(trimethylsilylethynyl)-2,1,3-benzothiadiazole (900 mg, 2.7 mmol) in 1 mol L^{-1} KOH methanol solution (75 mL) was stirred at room temperature for 1 h. The completion of the reaction was determined by TLC. The reaction mixture was poured into water (25 mL) and extracted with $CHCl_3$ (3 × 35 mL). The combined organic layers were evaporated in vacuo to dryness after dried over anhydrous Na_2SO_4 to give **M-1** (435 mg, 2.36 mmol) as yellow powder. ^1H NMR (300 MHz, $CDCl_3$): δ 3.70 (s, 2H), 7.76 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.4, 132.2, 115.1, 82.3, 81.4. TOF-MS (40:800): *m*/*z*: 183.9 [M^+].

2.4. Preparation of 1,4-bis[3′-(N,N-diethylamino)-1′-oxapropyl]-2,5-diiodobenzene (**M-2**). (Scheme 1)

A 250 mL round-bottom flask with magnetic stirring bar was charged with anhydrous potassium carbonate (4.8 g, 0.035 mol), 1,4-diiodo-2,5-hydroquinone (1.25 g, 3.45 mmol), 2-chloro-diethylamine hydrochloride (1.2 g 7.0 mmol) and 150 mL of acetone. The mixture was then refluxed for 3 days. The precipitate mixture was filtered away and the filtrate was rotary evaporated. The residue was poured into water and extracted with ether three times, and the combined organics were washed with 10% aqueous sodium hydroxide, water, and brine. The solution was dried over magnesium sulfate, filtered and stripped of solvent by rotary evaporation to yield crude solid. The crude product was recrystallized from hexane to afford colorless crystals (1.8 g yield: 93%). Mp: 76–78 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.19 (s, 2 H), 4.02 (t, 4 H, $J = 6.4$ Hz), 2.93 (t, 4 H, $J = 6.4$ Hz), 2.67 (q, 8 H, $J = 6.4$ Hz), 1.10 (t, 12 H, $J = 6.8$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.4, 122.7, 86.0, 69.2, 51.4, 47.9, 12.2.

2.5. Preparation of **P-1** (Scheme 1)

A mixture of **M-2** (1.12 g, 2 mmol), **M-1** (0.37 g, 2 mmol), 5 mol% $Pd(PPh_3)_4$ (0.12 g, 0.1 mmol) and 20 mol% CuI (0.08 g, 0.4 mmol) was dissolved in the mixed solvents of 10 mL THF and 5 mL Et_3N. The solution was stirred at reflux for 3 days under N_2. The mixture was cooled to room temperature, and then was filtered through a short silica gel column in methanol (30 mL) to precipitate out the polymer. The resulting polymer was filtered and washed with methanol several times. Further purification could be conducted by dissolving the polymer **P-1** in THF to precipitate in methanol again. The polymer was dried in vacuum to give 400 mg as a red solid **P-1** in 40.1% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 7.77 (s, 2 H), 7.53 (s, 2 H), 4.19 (br, 4 H), 3.05 (br, 4 H), 2.68 (br, 8 H), 1.10 (br, 12 H). FT-IR (KBr, cm^{-1}): 3443, 2198, 1634, 1557, 1459, 1272, 1208, 1035. Anal. calcd for $C_{28}H_{32}N_4O_2S$: C, 68.68; H, 6.79; N, 11.44; O, 6.54; S, 6.55. Found: C, 65.73; H, 6.45; N, 10.84; S, 6.33.

2.6. Preparation of **P-2** (Scheme 1)

In a 25 mL round-bottom flask 0.2 mmol (based on repeat unit) of neutral polymer **P-1** was added. The polymer **P-1** was dissolved in 10 mL of tetrahydrofuran. To this solution was added ethyl bromide (0.78 g, 5 mmol). The solution was stirred at 50 °C for 3 days. The resulting precipitate was collected by centrifugation, washed with tetrahydrofuran and dried to get a dark red solid **P-2** (123.4 mg, yield 88%). ^1H NMR (300 MHz, CD_3OD): δ 7.41–7.96 (m, 4 H), 4.40–4.65 (m, 4 H), 3.70–3.88 (m, 4 H), 3.60 (br, 10H), 1.40 (br, 16H). FT-IR (KBr, cm^{-1}): 3395, 2195, 1627, 1557, 1468, 1273, 1212.

2.7. Metal ion titration

Each metal ion titration experiment was started with a 3.0 mL **M-1**, **P-1**, **P-2** in $CHCl_3$ solution or aqueous solution with a known concentration (1.0×10^{-5} mol L^{-1}). Mercury perchlorate salt and other various metal salts (nitrate, 1.0×10^{-2} mol L^{-1}, CH_3CN) were used for the titration. Polymer–metal complexes were produced by adding aliquots of a solution of the selected metal salt to a $CHCl_3$ solution or aqueous solution of **M-1**, **P-1**, **P-2**. All kinds of measurements were monitored 1 h after addition of the metal salt to the polymer solutions.

3. Results and discussion

3.1. Syntheses and feature of the conjugated polymers

The synthesis procedures of the monomers and the polymers are shown in Scheme 1. Monomer **M-1**, 4,7-diethynyl-benzo[2,1,3]thiadiazole, was synthesized from benzo[2,1,3]thiadiazole by a three-step reaction according to reported literature and was kept in the dark at −4 °C before using [50,51]. Monomer **M-2**, 1,4-bis[3′-(*N*,*N*-diethylamino)-1′-oxapropyl]-2,5-diiodobenzene, was synthesized by a three-step reaction from the starting material 1,4-dimethoxybenzene [52]. In this paper, a typical Sonogashira reaction condition was applied to the synthesis of the neutral polymer **P-1** by the polymerization of **M-1** and **M-2** [53,54].

The polymerization was easily carried out in the presence of a catalytic amount of $Pd(PPh_3)_4$ and CuI with Et_3N under N_2. Conversion of the neutral polymer to the final cationic polymer was achieved by treating **P-1** with bromoethane in THF at 50 °C for 3 days. M_w, M_n and PDI of the polymer were determined by gel permeation chromatography using polystyrene standards in THF and the values of them are 6140, 2570 and 2.4, respectively. The GPC result of the polymer **P-1** shows the moderate molecular weight. **P-1** shows good solubility in several common organic solvents such as THF, $CHCl_3$ and CH_2Cl_2, but insoluble in methanol. **P-2** exhibits good solubility in both methanol and water. The water-soluble polymer **P-2** does not form the completely quaternized cationic polymer. The quaternization degree (**QD**) of **P-2** could be determined by ^1H NMR spectra. According to Huang's report, after the treatment with bromoethane, all signals corresponding to −***CH₂***N− split into two peaks, which arise from the quaternized (low field) and unquaternized components. The relative integrals of each pair of the split peaks can be used to estimate the **QD** of **P-2** [55]. The neutral polymer **P-1** exhibited two well-resolved peaks at 3.05, and 2.68 ppm corresponding to the methylene groups adjacent to the nitrogen (−***CH₂***N−) atoms (see the Supporting Information). Based on the relative integrals of each pair of the split peaks, the **QD** of **P-2** is 55%. **P-1** and **P-2** are air stable solids. Thermogravimetric analyses (**TGA**) of these polymers were carried out under a N_2 atmosphere at a heating rate of 10 °C/min. According to the thermal analysis of two polymers, **P-1** has a high thermal stability without loss weight before 220 °C (Fig. 1). **P-2** also has good thermal stability. The onset degradation temperature of **P-2** is 215 °C in nitrogen, but **P-2** loses 7% of its weight from room temperature to 62 °C due to the loss of water. **P-1** shows the apparent one-step degradation at temperature ranging from 220 to 750 °C. **P-2** exhibits the slow two-step degradation process: the first step degradation is observed at temperature ranging from 215 to 265 °C, and the second step degradation appears at temperature ranging from 505 to 700 °C. The different **TGA** curves of the

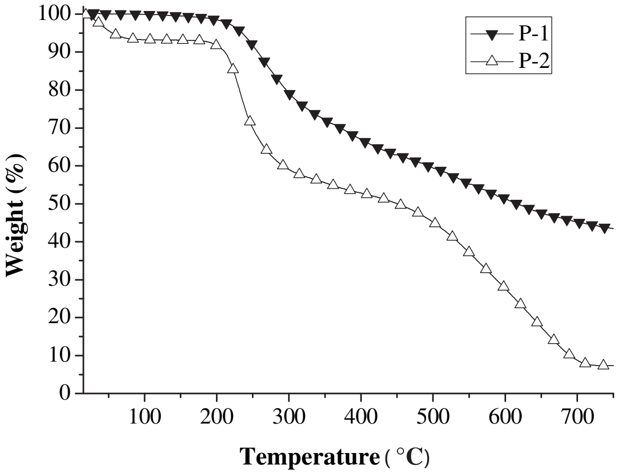
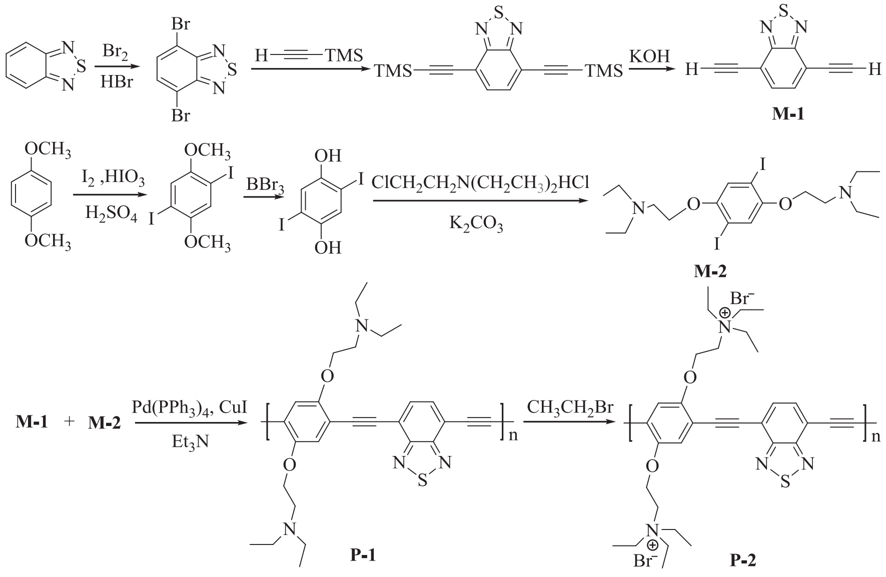


Fig. 1. **TGA** curves of the polymers **P-1** and **P-2**.



Scheme 1. Synthesis procedures of **M-1**, **M-2** and the conjugated polymers **P-1**, **P-2**.

polymers could be attributed to the different structure of the neutral polymer and the quaternized cationic polymer.

3.2. Optical properties

Fig. 2 illustrates the UV–vis absorption spectra of **M-1**, **M-2**, **P-1** and **P-2**. According to Fig. 2, UV–vis spectra of the polymers **P-1**, **P-2** are similar due to the similar repeating units of the conjugated polymer backbone. UV–vis absorption maxima λ_{max} of **M-1** appeared at 315 and 365 nm, λ_{max} of M-2 appeared at 301 nm, and the conjugated polymers **P-1** and **P-2** show the strong and broad absorption at the region from 400 to 550 nm. Especially, compared to the monomers **M-1** and **M-2**, the strongest absorption wavelengths λ_{max} of **P-1** and **P-2** display great red shifts and appear at 492 and 474 nm, respectively. A large red shift in the electronic absorptions of the conjugated polymers can be attributed to the effective π–π^* conjugated segments of the polymer main chain backbone. Fluorescence spectra of **M-1**, **M-2**, **P-1** and **P-2** are shown in Fig. 3. **P-1**, **P-2** can emit orange light under ultraviolet light (361 nm) at a concentration of 1×10^{-5} mol L^{-1}. As shown in Fig. 3, similar photoluminescence spectra are observed for **P-1** and **P-2** due to the same conjugated backbone. Fluorescence maxima λ_{max} of **M-1** and **M-2** appear at 435 and 440 nm, on the contrary, the emission wavelengths λ_{max} of **P-1**, **P-2** exhibit a large red shift located at 551 and 572 nm due to the extended π-electronic structure in the main chain backbone. The **PL** efficiency (Φ_{PL}) of **P-1** and **P-2** is 0.031 and 0.027, respectively. The low values may be due to the receptors of the polymers which contain relatively high-energy nonbonding electron pair of tertiary amino groups, and this electron pair quenches the fluorescence of the fluorophore by rapid intramolecular electron transfer (**ICT**) from the receptor to the excited fluorophore [31].

3.3. Responsive signal changes of the monomer **M-1** and **P-1** on Hg^{2+}

The effect of the fluorescence response behavior of the monomer **M-1** has been investigated in order to compare fluorescence changes of the polymer on the mercury detection with the corresponding small molecule sensor of the model compound. Fig. 4 shows the fluorescence spectra of the monomer **M-1** (1.0×10^{-5} mol L^{-1} in CHCl$_3$) upon the molar ratio addition of Hg^{2+} from 1:1 to 1:6 at a concentration of 1.0×10^{-2} mol L^{-1} in CH$_3$CN.

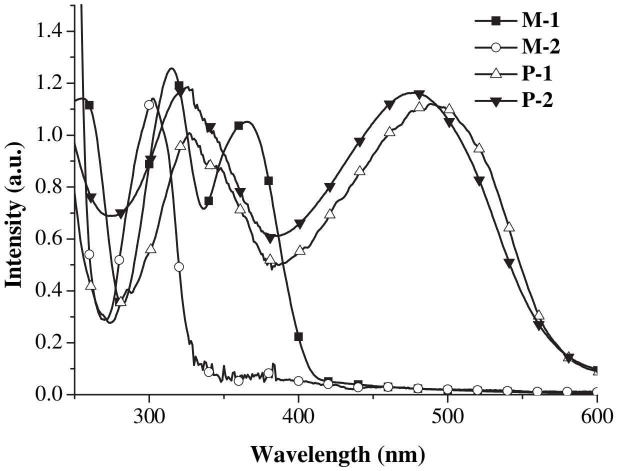


Fig. 2. UV–vis spectra of **M-1** (1.0×10^{-5} mol L^{-1}), **M-2** (1.0×10^{-5} mol L^{-1}), **P-1** (1.0×10^{-5} mol L^{-1}) in CHCl$_3$ and **P-2** (1.0×10^{-5} mol L^{-1}) in water.

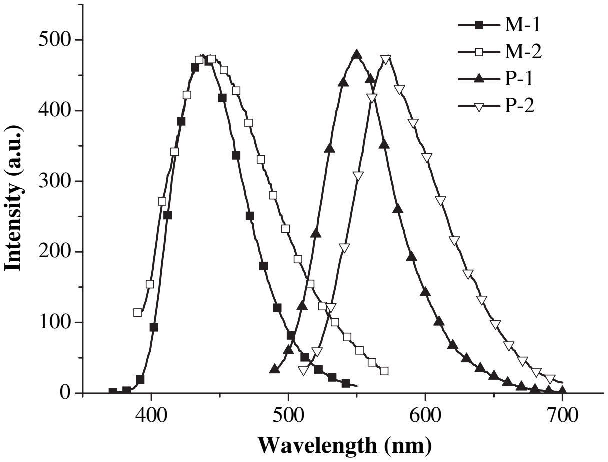


Fig. 3. Fluorescence spectra of **M-1** ($\lambda_{ex} = 362$ nm, 1.0×10^{-5} mol L^{-1}), **M-2** ($\lambda_{ex} = 290$ nm, 1.0×10^{-5} mol L^{-1}), **P-1** ($\lambda_{ex} = 480$ nm, 1.0×10^{-5} mol L^{-1}) in CHCl$_3$ and **P-2** ($\lambda_{ex} = 522$ nm, 1.0×10^{-5} mol L^{-1}) in water.

The results indicate that Hg^{2+} causes a little fluorescence quenching of **M-1** at a concentration of 6:1 molar ratio. In comparison with **M-1**, the effects of the fluorescence response behavior of **P-1** on Hg^{2+} have been investigated. Fig. 5 shows the fluorescence spectra of **P-1** (1.0×10^{-5} mol L^{-1} in CHCl$_3$) upon the addition of Hg^{2+} in CH$_3$CN solution, with the excitation at 480 nm. As is evident from Fig 5, Hg^{2+} leads to obvious fluorescence quenching of **P-1** at a concentration of 6:1 molar ratio. The quenching ratios (η) of **P-1** on Hg^{2+} can be calculated according to equation: $\eta = 1 - F/F_0$. Herein, F_0 is the fluorescent emission intensity in the absence of the quencher, and F is the fluorescent emission intensity in the presence of the quencher. As a result, the fluorescence quenching ratios of **P-1** are 34.86, 51.13, 61.67, 72.64, 76.78, and 81.73 by Hg^{2+} upon the 1:1 to 1:6 molar ratios addition of the Hg^{2+} salt solution. The quenching efficiency of **M-1** and **P-1** is related to the Stern–Volmer constant, K_{SV}, and is determined by monitoring measurable changes in the fluorescence spectra *via* the Stern–Volmer equation: $F_0/F = 1 + K_{SV}[Q]$, herein, $[Q]$ is the quencher concentration, that is metal ion concentration. Average lgK_{SV} of the polymer **P-1** and **M-1** on Hg^{2+} is 5.79 and 3.28, respectively. It could be concluded that the resulting polymer exhibits more sensitive detection than the corresponding small molecule, which should be attributed to signal

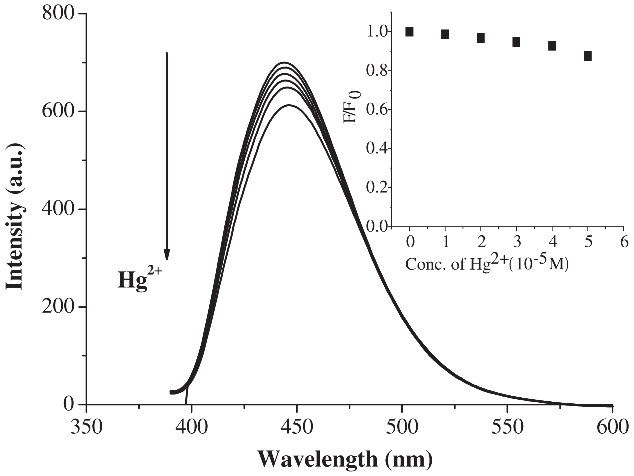


Fig. 4. Fluorescence spectra of **M-1** (1.0×10^{-5} mol L^{-1} in CHCl$_3$) with increasing amounts of Hg^{2+} in CH$_3$CN (0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0×10^{-5} mol L^{-1}) ($\lambda_{ex} = 362$ nm). Inset: fluorescence quench values (F/F_0) vs the increasing concentration of Hg^{2+}.

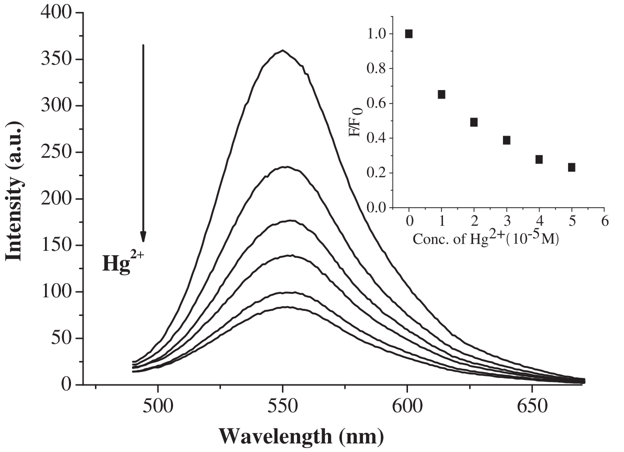


Fig. 5. Fluorescence spectra of **P-1** (1.0×10^{-5} mol L^{-1} in $CHCl_3$) with increasing amounts of Hg^{2+} (0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 $\times 10^{-5}$ mol L^{-1}) ($\lambda_{ex} = 480$ nm). Inset: Fluorescence quench values (F/F_0) vs the increasing concentration of Hg^{2+}.

amplification from electronic communication between the conjugated polymer backbone and Hg^{2+}–**P-2** complex [22,23]. Huang and his coworkers reported a kind of **PPE-BT** conjugated polymer-poly(p-phenyleneethynylene) incorporating benzo[2,1,3]thiadiazole (**BT**) moiety in the polymer main chain backbone [52]. This conjugated polymer was used as a highly selective and multi-signaling optical sensor for Hg^{2+}, which was attributed to the complex formation by coordination of Hg^{2+} to the lone-pair electrons on the sulfur atom of **BT** unit in the polymer main chain of **PPE-BT**. They thought that the fluorescence quenching effect arises from interchain p–p interactions. This interchain excited-state interaction likely has a significant charge-transfer character, which leads to pathways for rapid non-radiative decay.

*3.4. Responsive signal changes of the water-soluble polymer **P-2** on metal ions*

The effects of the fluorescence response behavior of the water-soluble conjugated polyelectrolyte **P-2** on Hg^{2+} have been investigated. Fig. 6 shows the fluorescence spectra of the polymer **P-2** (1.0×10^{-5} mol L^{-1}) in water upon the molar ratio addition of Hg^{2+} from 1:1 to 1:11 at a concentration of 1.0×10^{-2} mol L^{-1} in water. In comparison with **P-1**, The fluorescence intensities of Hg^{2+}–**P-2** complex show gradual enhancement as high as 1.2-fold, which can be concluded that this kind response change would reduce the likelihood of false positive signals. Rurack et al. reported a fluoroionophore for Hg^{2+}, Ag^{+} and Cu^{2+} that gave significant fluorescence enhancements upon complexation with these ions in CH_3CN [56]. And in water/acetonitrile mixtures, fluorescence of the metal ion complexes was significantly attenuated [44]. Herein, fluorescence enhancements of Hg^{2+}–**P-2** complex in water is not so significant due to the strong hydration of Hg^{2+}. It was also found that the addition curve keeps nearly linear correlation with the concentration mole ratio of Hg^{2+} from 1 to 10. According to Fan and Jones's report [31], **P-2** can be thought as conjugated polymer **PET** chemosensors, in which the conjugated polymer backbone as the fluorophore and diethylamino group as the receptors. In such systems, the diethylamino group receptors contain a relatively high-energy nonbonding electron pair. In the absence of analytes, this electron pair quenches the fluorescence of the fluorophore by rapid intramolecular electron transfer from the receptor to the excited fluorophore. When this electron pair is coordinated to Hg^{2+}

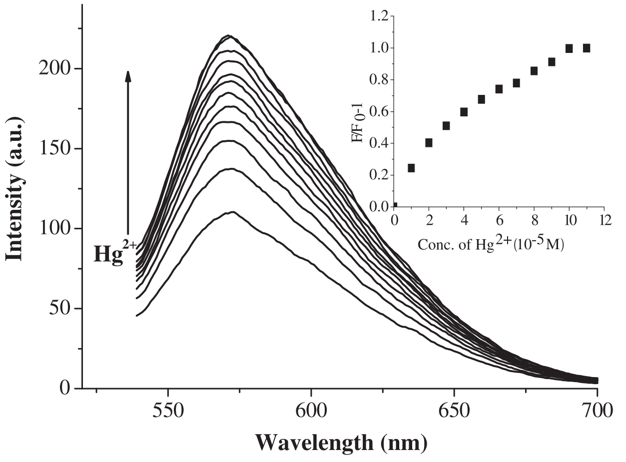


Fig. 6. Fluorescence spectra of **P-2** (1.0×10^{-5} mol L^{-1}) in water with increasing amounts of Hg^{2+} (0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0 $\times 10^{-5}$ mol L^{-1}) in water ($\lambda_{ex} = 522$ nm); Inset: Fluorescence enhancement values ($F/F_0 - 1$) vs the increasing concentration of Hg^{2+}.

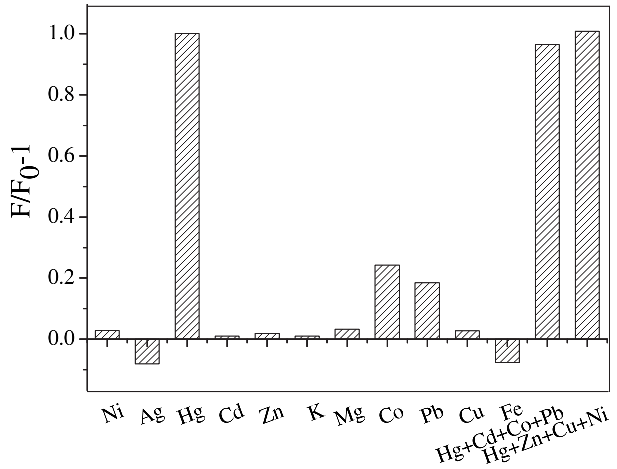


Fig. 7. Fluorescence enhancement degree of **P-2** (1.0×10^{-5} mol L^{-1}) in the presence of various metal ions (each 5.0×10^{-5} mol L^{-1}); the right two columns exhibit the fluorescence enhancement degree of **P-2** in the mixed metal ions.

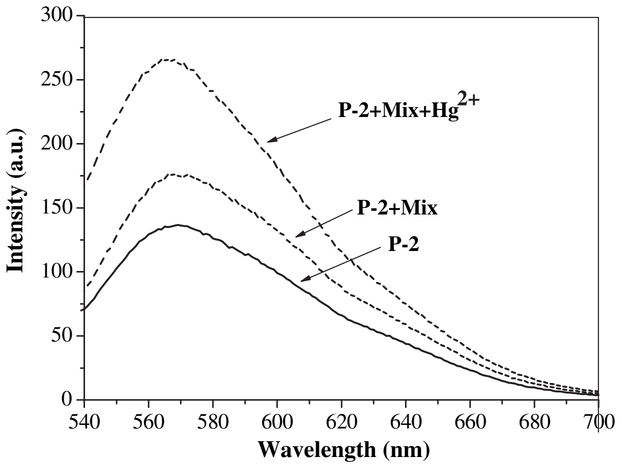


Fig. 8. Fluorescence spectra of **P-2** in water in the presence of various metal ions (K^{+}, Mg^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, Fe^{3+} and Zn^{2+}, each 5.0×10^{-5} mol L^{-1}), and further addition of Hg^{2+} ions ($[Hg^{2+}] = 1.1 \times 10^{-4}$ mol L^{-1}).

(Lewis acid cation) in solution, the HOMO of the receptor is lowered. This decreases the driving force for the PET process and can turn on the fluorescence of the fluorophore.

The fluorescence response behaviors of **P-2** on other various metal ions were also examined under the same conditions as Hg^{2+} ion determination (Fig. 7). As a result, the fluorescence enhancement degree ($F/F_0 - 1$) of the polymer **P-2** is 1.0, 3.0, 18.5, 24.3, 2.8, −8.0, 1.0, 2.7, −7.6 and 1.9% by K^+, Mg^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Ag^+, Cd^{2+}, Cu^{2+}, Fe^{3+} and Zn^{2+} upon the 1:5 molar ratio addition of a metal salt solution, respectively. The results indicate that **P-2** can exhibit excellent selectivity in sensing Hg^{2+}. For Hg^{2+} detection, one of the essential requirements is minor or no interference from other metal ions. The Hg^{2+} selective detection experiments of **P-2** in water (1.0×10^{-5} mol L^{-1}) were conducted in the presence of the mixture of K^+, Mg^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, Fe^{3+} and Zn^{2+} (Fig. 8) at 5.0×10^{-5} mol L^{-1} in water, respectively. Compared with that containing both mixture ions and Hg^{2+}, the fluorescence intensities of **P-2** do not appear obvious change. Herein, the water-soluble polymer **P-2** is specifically sensitive toward Hg^{2+}, not toward other metals, which can be attributed to strong Hg–S binding and coordination diversification of Hg^{2+} with the resulting polymer. It can be concluded that this kind water-soluble polyelectrolyte **P-2** can be used as Hg^{2+} selective probe which could hardly be affected by those coexistent ions.

4. Conclusion

A new fluorometric probe for detecting Hg^{2+} in aqueous solution based on the water-soluble conjugated polyelectrolyte **P-2**, which exhibits a very high selectivity over other interfering cations, has been developed. **P-2** was obtained by quaternization of **P-1** which was synthesized by Pd-catalyzed Sonogashira reaction. The result has shown that the water-soluble polyelectrolyte **P-2** can be used as Hg^{2+} selective probe which could hardly be affected by those coexistent ions in aqueous solution.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version of this paper at doi:10.1016/j.polymer.2010.05.038.

References

[1] Pinto MR, Schanze KS. Synthesis 2002;9:1293–309.
[2] Jiang H, Taranekar P, Reynolds JR, Schanze KS. Angew Chem Int Ed 2009; 48:4300–16.
[3] Hoven CV, Garcia A, Bazan GC, Nguyen TQ. Adv Mater 2008;20:3793–810.
[4] Dwight SJ, Gaylord BS, Hong JW, Bazan GC. J Am Chem Soc 2004; 126:16850–9.
[5] Chen LH, Xu S, McBranch D, Whitten DJ. J Am Chem Soc 2000;122:9302–3.
[6] Izuhara D, Swager TM. J Am Chem Soc 2009;131:17724–5.
[7] Tan C, Pinto MR, Schanze KS. Chem Commun 2002;5:446–7.
[8] Tan C, Atas E, Muller JG, Pinto MR, Kleiman VD, Schanze KS. J Am Chem Soc 2004;126:13685–94.
[9] Pinto MR, Kristal BM, Schanze KS. Langmuir 2003;19:6523–33.
[10] Zhou Q, Swager TM. J Am Chem Soc 1995;117:12593–602.
[11] Chen L, McBranch DW, Wang HL, Helgeson R, Wudl F, Whitten DG. Proc Natl Acad Sci U S A 1999;96:12287–92.
[12] Harrison BS, Ramey MB, Reynolds JR, Schanze KS. J Am Chem Soc 2000;122:8561–2.
[13] Wang DL, Gong X, Heeger PS, Rininsland F, Bazan GC, Heeger AG. Proc Natl Acad Sci U S A 2002;99:49–53.
[14] Kumaraswamy S, Bergstedt T, Shi XB, Rininsland F, Kushon S, Xia WS, et al. Proc Natl Acad Sci U S A 2004;101:7511–5.
[15] Miranda OR, You CC, Phillips R, Kim IB, Ghosh PS, Bunz UHF, et al. J Am Chem Soc 2007;129:9856–7.
[16] Jones RM, Bergstedt TS, McBranch DW, Whitten DG. J Am Chem Soc 2001; 123:6726–7.
[17] Kushon SA, Ley KD, Bradford K, Jones RM, McBranch D, Whitten D. Langmuir 2002;18:7245–9.
[18] Pu KY, Liu B. Adv Funct Mater 2009;19:277–84.
[19] Pu KY, Cai L, Liu B. Macromolecules 2009;42:5933–40.
[20] Pu KY, Liu B. Macromolecules 2008;41:6636–40.
[21] Fang Z, Pu KY, Liu B. Macromolecules 2008;41:8380–7.
[22] McQuade DT, Pullen AE, Swager TM. Chem Rev 2000;100:2537–74.
[23] Thomas III SW, Joly GD, Swager TM. Chem Rev 2007;107:1339–86.
[24] Zhang Z, Wu D, Guo X, Qian X, Lu Z, Zu Q, et al. Chem Res Toxicol 2005;18:1814–20.
[25] Grandjean P, Weihe P, White RF, Debes F. Environ Res 1998;77:165–72.
[26] Boening DW. Chemosphere 2000;40:1335–51.
[27] Harris HH, Pickering IJ, George GN. Science 2003;301:1203.
[28] Nolan EM, Lippard SJ. Chem Rev 2008;108:3443–80.
[29] Kim IB, Dunkhorst A, Gilbert J, Bunz UHF. Macromolecules 2005;38:4560–2.
[30] Fan LJ, Jones WE. J Am Chem Soc 2006;128:6784–5.
[31] Fan LJ, Zhang Y, Jones WE. Macromolecules 2005;38:2844–9.
[32] Kim IB, Bunz UHF. J Am Chem Soc 2006;128:2818–9.
[33] Liu X, Tang Y, Wang L, Zhang J, Song S, Fan C, et al. Adv Mater 2007; 19:1471–4.
[34] Tang Y, He F, Yu M, Feng F, An L, Sun H, et al. Macromol Rapid Commun 2006;27:389–92.
[35] Li C, Zhou C, Zheng H, Yin X, Zou Z, Liu H, et al. J Polym Sci Part A Polym Chem 2008;46:1998–2007.
[36] Huang XB, Meng J, Dong Y, Cheng YX, Zhu CJ. J Polym Sci Part A Polym Chem 2010;48:997–1006.
[37] Zheng LF, Huang XB, Shen YG, Cheng YX. Synlett 2010;3:453–6.
[38] de Silva AP, Gunaratne HQN, Gunnlaugsson T, Huxley AJM, McCoy CP, Rademacher JT, et al. Chem Rev 1997;97:1515–66.
[39] Chen Y, Pu KY, Fan QL, Qi XL, Huang YQ, Lu XM, et al. J Polym Sci Part A Polym Chem 2009;47:5057–67.
[40] Balamurugan A, Reddy MLP, Jayakannan M. J Polym Sci Part A Polym Chem 2009;47:5144–57.
[41] Ros-Lis JY, Marcos MD, Mártinez-Máñez R, Rurack K, Soto J. Angew Chem Int Ed 2005;44:4405–7.
[42] Yang YK, Yook KJ, Tae J. J Am Chem Soc 2005;127:16760–1.
[43] Nolan EM, Lippard SJ. J Am Chem Soc 2003;125:14270–1.
[44] Prodi L, Bargossi C, Montalti M, Zaccheroni N, Su N, Bradshaw JS, et al. J Am Chem Soc 2000;122:6769–70.
[45] Tang B, Ding B, Xu K, Tong L. Chem Eur J 2009;15:3147–51.
[46] Wu JS, Hwang IC, Kim KS, Kim JS. Org Lett 2007;9:907–10.
[47] Lee MH, Wu JS, Lee JW, Jung JH, Kim JS. Org Lett 2007;9:2501–4.
[48] Ko SK, Yang YK, Tae J, Shin I. J Am Chem Soc 2006;128:14150–5.
[49] Nolan EM, Lippard SJ. J Am Chem Soc 2007;129:5910–8.
[50] Huang XB, Xu Y, Zheng LF, Meng J, Cheng YX. Polymer 2009;50:5996–6000.
[51] Neto BAD, Lopes AS, Ebeling G, Gonçalves RS, Costa VEU, Quina FH, et al. Tetrahedron 2005;61:10975–82.
[52] Liu SJ, Fang C, Zhao Q, Fan QL, Huang W. Macromol Rapid Commun 2008; 29:1212–5.
[53] Sonogashira K, Tohda Y, Hagihara N. Tetrahedron Lett 1975;16:4467–70.
[54] Chinchilla R, Nájera C. Chem Rev 2007;107:874–922.
[55] Liu B, Yu W, Lai YH, Huang W. Chem Commun; 2000:551–2.
[56] Rurack K, Kollmannsberger M, Resch-Genger U, Daub J. J Am Chem Soc 2000;122:968–9.