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Hg²⁺ detection by aniline-based conjugated copolymers with high selectivity

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ABSTRACT

Conjugated polymers (**P1**, **P1L** and **P2–P5**) constructed by alkynyl-substituted aniline and substituted arene analogs could be synthesized through Pd-catalyzed Sonogashira coupling. The responsive optical properties of poly(2-ethynyl aniline) (**P1** and **P1L** for different molecular weights, **P1L** with longer chains on average) toward various metal ions (including Ni²⁺, Ag⁺, Cu²⁺, Zn²⁺, Fe³⁺, Fe²⁺, Mn²⁺, Na⁺, Ca²⁺, Pb²⁺, K⁺, Cr³⁺, Al³⁺, Cd²⁺, Pt²⁺, Au³⁺ and Tl³⁺) were investigated. Hg²⁺ exhibited the most pronounced fluorescence response of both **P1** and **P1L** without interference from those coexistent ions due to aniline in the polymer backbone as the metal binding ligand, while other metal ions does not cause obvious change of fluorescence. Compared with **P1**, **P1L** exhibits better sensitivity toward Hg²⁺. Introducing pyridyl, thienyl or phenyl groups into the polymer backbone would weaken the quenching responses to Hg²⁺ compared with **P1**. The results indicated **P1** and **P1L** could be used as a selective fluorescence sensor toward Hg²⁺.

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1. Introduction

Conjugated polymers as fluorescence sensors have gained increasing attention due to their high sensitivity and ease of measurement. The high sensitivity of the conjugated polymers originates from the sensory signal amplification which is attributed to energy migration along the polymer backbone upon excitation. An additional advantage of polymer-based fluorescence sensors is that the structure and sequence of the conjugated polymers can be systematically modified to suit diverse targets by the introduction of different functional groups (based on their steric and electronic properties) at well-defined molecular levels [1,2]. The research on polymer-based fluorescence sensors for the detection of heavy and transition metal ions is emerging as an area of current interest in the recent years [3–5]. Among them, mercury and its derivatives are dangerous and widespread global pollutants which have caused serious environmental and health problems [6-9]. Many fluorescence sensors for mercury detection have been reported. Most of them are based on small molecules [3,10], while polymer-based chemosensors are very few [11-25]. Therefore, the development of highly selective and sensitive polymer-based chemosensors for mercury detection is still attractive. In this paper, we report the

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synthesis of aniline-based conjugated polymers (**P1**, **P1L** and **P2–P5**) (Scheme 1) used as fluorescence sensors for the detection of transition metal ions. Compared with other cations, such as Ni²⁺, Ag⁺, Cu²⁺, Zn²⁺, Fe³⁺, Fe²⁺, Mn²⁺, Na⁺, Ca²⁺, Pb²⁺, K⁺, Cr³⁺, Al³⁺, Cd²⁺, Pt²⁺, Au³⁺ and Tl³⁺, Hg²⁺ exhibits the most pronounced effect upon the fluorescence property of **P1**. Additionally, **P1L** with larger molecular weight exhibit better sensitivity toward Hg²⁺ compared with **P1**. The results indicate that poly(2-ethynyl aniline) (**P1** and **P1L**) could be used as a selective fluorescence sensor for Hg²⁺ detection.

2. Experimental part

2.1. Materials and measurements

NMR spectra were obtained using a Bruker DRX-500 NMR spectrometer with chemical shifts reported as ppm (TMS as the internal standard). Fluorescence spectra were obtained from a RF-5301PC spectrometer. Mass spectra were determined on a Micromass GCT machine. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) with Waters-244 HPLC pump with THF as the solvent and polystyrene as the relative standard. All reagents were of analytical grade. All perchlorates were purchased from Alfa Aesar. PtCl₂ (98%) was purchased from Alfa Aesar. TlCl₃·4H₂O (98%) was purchased from Sigma–Aldrich. All compounds were prepared according to the literature [16,26].





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Scheme 1. Synthesis procedures of the polymer sensors.

2.2. General procedure for the synthesis of aniline-based conjugated polymers (**P1**, **P1L** and **P2–P5**, **P1** as an example) (Scheme 1)

To a flame-dried 50 mL Schlenk flask, 2 (0.167 g, 0.559 mmol), 1 (0.149 g, 0.562 mmol), (PPh₃)₂PdCl₂ (50.0 mg, 0.071 mmol), CuI (50.0 mg, 0.260 mmol), and anhydrous tetrahydrofuran (5 mL) were added under a slow stream of nitrogen. A saturated ethanol solution of KOH (1 mL) was then added. Piperidine (7 mL) was introduced to the reaction via syringe. The reaction was stirred and held at 30 °C for 48 h. The solution was poured into a mixture of chloroform (75 mL) and water (100 mL). The organic layer was washed three times with water (100 mL) followed by NH₄OH (30%, mass content, 150 mL). The aqueous layer was washed twice with chloroform (20 mL). The organic layers were combined. To the resultant organic layer, methanol (400 mL) was added to precipitate the polymer. Suction filtration afforded a brown polymer (P1). P1: Yield: 82%. M_w = 6394, $M_{\rm n} = 1353$, PDI = 4.6.¹H NMR (500 MHz, d_6 -DMSO): 7.28 (s, 2H), 5.52 (s, 2H), 2.19 (s, 3H). P1L was synthesized by increasing the reaction time to 72 h at 60 °C. P2–P5 were synthesized in a similar fashion with the corresponding reagents.

P1L: Yield: 87%. $M_w = 7149$, $M_n = 2359$, PDI = 3.0. **P2**: Yield: 76%. $M_w = 5438$, $M_n = 2753$, PDI = 1.9. ¹H NMR (500 MHz, d_6 -DMSO): 7.23–7.93 (m, 5H), 5.50 (m, 2H), 2.13–2.20 (m, 3H).

P3: Yield: 80%. M_w = 3948, M_n = 1079, PDI = 3.6. ¹H NMR (500 MHz, CDCl₃): 7.01–7.23 (m, 4H), 4.87 (s, 2H), 2.22 (s, 3H). **P4**: Yield: 73%. M_w = 2630, M_n = 1213, PDI = 2.1. ¹H NMR (500 MHz, d_6 -DMSO): 7.15–7.49 (m, 4H), 5.66 (s, 2H), 3.82–3.92 (m, 6H), 2.19 (s, 3H).

P5: Yield: 71.2%. $M_W = 1934$, $M_n = 758$, PDI = 2.5. ¹H NMR (500 MHz, CDCl₃): 7.19 (s, 2H) 7.03 (s, 2H), 3.91–4.09 (m, 4H), 2.23 (s, 3H), 1.89–1.54 (m, 8H), 0.98–1.05 (m, 12H).

2.3. Metal ion titration

Each metal ion titration experiment was started with a DMSO solution (3.0 mL) of **P1, P1L, P2, P3, P4** and **P5** with a known concentration (3.0×10^{-5} M). Mercury perchlorate salt and other perchlorate salts (1.0×10^{-2} M, aqueous solution) were used for the



Fig. 1. UV–vis absorption spectra of a DMSO solution of P1 $(1 \times 10^{-5} \text{ M}, \text{ with respect to the receptor unit) after the addition of Hg²⁺: [Hg²⁺] = (1, 2, 3, 4, 5) × 10⁻⁴ M.$

titration. PdCl₂ was dissolved by DMSO $(1.0 \times 10^{-2} \text{ M})$. TlCl₃·4H₂O was dissolved in an aqueous solution $(1 \times 10^{-2} \text{ M})$. Titration experiments were performed by adding aliquots of a solution of the selected metal salt to the DMSO solution of **P1**, **P1L**, **P2**, **P3**, **P4** and **P5**.

3. Results and discussion

3.1. Synthesis and features of the conjugated polymers (P1, P1L and P2–P5)

The synthesis procedures of the monomers **2**, **3** and the conjugated polymer are outlined in Scheme 1. In this paper, a typical Sonogashira reaction condition was applied to the synthesis of the polymers [16,26]. The polymerization could be carried out under mild reaction conditions in THF in the presence of a catalytic amount of Pd(PPh₃)₂Cl₂ (10% mol) and Cul (5% mol) with a moderate yield of 71.2%–87%.

3.2. The selective and sensitive recognition of the polymer sensor on Hg^{2+}

Ion-responsive properties of **P1** are investigated by UV–vis absorption spectroscopy. **P1** exhibits a strong absorption band at 395 nm, which is associated with π – π * transition of the conjugated segment (Fig. 1). The maximum absorption wavelengths (λ_{max}) of π -conjugated polymers are dictated by both the degree of conjugation and conjugation length.

The change of the absorption spectrum in the case of addition of Hg^{2+} is presented in Fig. 1. Most notably, the maximum absorption band experienced a shift toward the shorter wavelength. The isosbestic point with an "out of focus" impression (around 361 and 432 nm, respectively) implied the interaction of Hg^{2+} with the chelating site of **P1**.



Fig. 3. Fluorescence quenching efficiencies $(1 - F/F_0)$ of P1 $(3.0 \times 10^{-5} \text{ M})$ in the presence of various main group and transition metal ions $(5.3 \times 10^{-5} \text{ M})$ for each metal ion). F and F_0 are taken as the fluorescence intensity of P1 at the maximum emission wavelength (458.5 nm). Excitation wavelength: 411 nm.

The fluorescence response behaviors of the polymer on various main group and transition metal ions have been investigated. Fig. 2 and Fig. S2 show the change of the fluorescence spectra of **P1** (3.0 \times 10⁻⁵ M in DMSO) upon the addition of Hg²⁺ (aqueous solution). As is evident from Fig. 2, the maximum fluorescence band of the polymer appears at 458.5 nm with the excitation at 411 nm. Obvious fluorescence quenching could be observed upon the addition of Hg²⁺. Hg²⁺ leads to an intense decrease (97.3%) of fluorescence intensity for **P1**. The lowest concentration of Hg²⁺ to cause an effective fluorescence quenching of **P1** was measured to be 4.5 \times 10⁻⁷ M (3 σ method).

Beyond Hg²⁺, the fluorescence response properties of **P1** toward other metal ions were also examined (Fig. 3 and Fig. S3). The fluorescence intensities of **P1** are almost not affected by the addition of Ni²⁺, Ag⁺, Cu²⁺, Zn²⁺, Fe³⁺, Fe²⁺, Mn²⁺, Na⁺, Ca²⁺, Pb²⁺, K⁺, Cr³⁺, Al³⁺, Cd²⁺, Pt²⁺, Au³⁺ and Tl³⁺, respectively. Normally, an excellent fluorescence sensor with highly sensitive and selective features needs to meet one of the essential requirements that minor or no interference from other metal ions should occur. In this paper, we further investigated the utility of P1 as an ion-selective fluorescence sensor for Hg²⁺. Herein, the fluorescence responses of **P1** $(3.0 \times 10^{-5} \text{ M})$ to a mixture of Hg²⁺ $(5.3 \times 10^{-5} \text{ M})$ and other metal ions (5.3 \times 10⁻⁵ M for each metal ion) were recorded as Fig. 4 and Fig. S4. In the coexisting metal experiment, while an intense fluorescence quenching was caused by the addition of Hg^{2+} no matter other metal ions (Ni²⁺, Ag⁺, Cu²⁺, Zn²⁺, Fe³⁺, Fe²⁺, Mn²⁺, Na⁺, Ca²⁺, Pb²⁺, K⁺, Cr³⁺ and Al³⁺ included) existed or not, no obvious interference was observed in the presence of mixed metal ions without Hg^{2+} . The existence of Cd^{2+} , Pt^{2+} , Au^{3+} and Tl^{3+} affected the fluorescence intensity a little. These results indicated P1 is specifically sensitive toward Hg²⁺ but not other metal ions. Thus the polymer



Fig. 2. A: Emission spectra of a DMSO solution of P1 $(3.0 \times 10^{-5} \text{ M})$ after the addition of Hg²⁺. [Hg²⁺] = $(0, 0.01, 0.02, 0.03, 0.13, 0.23, 0.33, 1.33, 2.33, 3.33, 4.33, 5.33) \times 10^{-5} \text{ M}$. Excitation wavelength: 411 nm. B: The change of fluorescence intensity of P1 when the concentration of Hg²⁺ added changed (data correspond to Fig. 2A).



Fig. 4. Metal ion specificity: emission spectra of a DMSO solution of P1 $(3.0 \times 10^{-5} \text{ M}, \text{solution A})$ without metal ion (red); Hg²⁺ added to solution A (blue); Ni²⁺, Ag⁺, Cu²⁺, Zn²⁺, Fe³⁺, Fe³⁺, Fe²⁺, Mn²⁺, Na⁺, Ca²⁺, Pb²⁺, K⁺, Cr³⁺, Al³⁺, Cd²⁺, Pt²⁺, Au³⁺ and Tl³⁺ added to solution A (green); Ni²⁺, Ag⁺, Cu²⁺, Zn²⁺, Fe³⁺, Fe²⁺, Mn²⁺, Na⁺, Ca²⁺, Pb²⁺, K⁺, Cr³⁺, Al³⁺, Cd²⁺, Pt²⁺, Au³⁺, Tl³⁺ and Hg²⁺ added to solution A (cyan). The concentration of each metal ion added is 5.3×10^{-5} M. Excitation wavelength: 411 nm. (For interpretation of this article.)

could be used as a sole Hg^{2+} probe with high selectivity. The sensitivity toward Hg^{2+} could be attributed to several factors, the large radius of the Hg^{2+} ion (compared with many other metal ions) and coordination diversification of Hg^{2+} , its soft acid property, the binding ability of aniline unit and strong Hg-N binding [17]. Because of its $5d^{10}6s^2$ electronic configuration and lack of ligand field stabilization energy, Hg^{2+} can accommodate a range of coordination numbers and geometries. Two-coordinate linear and four coordinate tetrahedral species are common. Hg^{2+} is a soft acid and the use of soft donor atoms (e.g. nitrogen, sulfur and phosphorus) in a chelating unit will generally increase its affinity and selectivity for Hg^{2+} [3].

3.3. Effect of molecular weight

In order to investigate the effect of molecular weight on the quenching properties of poly(2-ethynyl aniline), **P1L** was synthesized through increasing reaction time (72 h) at raised temperature (60 °C). The yielded polymer exhibit a larger molecular weight and lower polydispersity compared with **P1**.

As expected, **P1L** also displayed pronounced fluorescence quenching toward Hg^{2+} (Fig. 5), analogous to **P1**. Hg^{2+} leads to a decrease of fluorescence intensity (97.2%) for **P1L**, while the addition of other metal ions (Fig. 6) has weak influence on the fluorescence intensity of **P1L**. The coexisting metal experiment (Fig. S5) indicated that the fluorescence quenching response of **P1L** could not be easily affected by other disturbing metal ions. A detection limit of **P1L** toward Hg^{2+} was measured to be



Fig. 6. Fluorescence quenching efficiencies $(1 - F/F_0)$ of P1L $(3.0 \times 10^{-5} \text{ M})$ in the presence of various main group and transition metal ions $(5.3 \times 10^{-5} \text{ M})$ for each metal ion). F and F₀ are taken as the fluorescence intensity of P1L at the maximum emission wavelength. Excitation wavelength: 411 nm.

 1.8×10^{-7} M (3 σ method), about 40% of that of **P1**. These results indicated that polymers with the same backbone exhibit analogous fluorescence quenching properties and selectivity toward various metal ions. Additionally, better sensitivity toward metal ion might be obtained for polymer of longer backbones. This may derive from the more efficient energy migration along the longer polymer backbone upon the addition of metal ions [1,2]. The Hg²⁺ center coordinated with the polymer backbone provided an efficient quenching site for the whole polymer.

3.4. Effect of different polymer backbones

To gain further insight into the sensing mechanism, **P2–P5** with distinct chemical structures (e.g., side chain bulkiness, heteroatom binding site) are examined. Polymers **P2–P5** exhibit similar responses to Hg^{2+} in the absorption spectra (Figs. S6–S13). Fluorescence quenching responses of **P2–P5** to Hg^{2+} were also observed (Fig. 7) which might derive from the analogous chain unit. But, compared with **P1**, the quenching responses were much weaker. From **P2** to **P5**, the quenching intensity decreased gradually as a result of the decreased coordination ability with Hg^{2+} (aniline > pyridine > thiophene > alkoxy substituted benzene).

4. Conclusion

In conclusion, aniline-based conjugated polymers (**P1**, **P1L** and **P2–P5**) were synthesized through Pd-catalyzed Sonogashira coupling. **P1** and **P1L** exhibited intense fluorescence quenching response to Hg^{2+} . The polymer was also proved to possess excellent sensitivity and selectivity toward Hg^{2+} . The detection limit of **P1** and **P1L** to Hg^{2+} was measured to be 4.5×10^{-7} M and 1.8×10^{-7} M, respectively (3σ method). Weaker quenching responses of **P2–P5** to



Fig. 5. A: Emission spectra of a DMSO solution of P1L $(3.0 \times 10^{-5} \text{ M})$ after the addition of Hg²⁺. [Hg²⁺] = $(0, 0.01, 0.02, 0.03, 0.13, 0.23, 0.33, 1.33, 2.33, 4.33, 5.33) \times 10^{-5} \text{ M}$. Excitation wavelength: 411 nm. B: The change of fluorescence intensity of P1L when the concentration of Hg²⁺ added changed (data correspond to Fig. 5A).



Fig. 7. Fluorescence quenching degrees $(1 - F/F_0)$ of a DMSO solution of **P1–P5** $(3.0 \times 10^{-5} \text{ M})$ in the presence of Hg²⁺ $(5.33 \times 10^{-5} \text{ M})$. F and F₀ are taken as the fluorescence intensity at the maximum emission wavelength for each individual polymer.

Hg²⁺ compared with **P1** might derive from the weaker coordination capability of chain unit. Compared with the alkynyl-substituted aniline monomer, the polymer synthesized exhibit stronger fluorescent emissions due to its long conjugated π -systems, and the quenching effect caused by interaction with Hg²⁺ is obvious. Another benefit is that polymer-based detection scheme shows better selectivity for Hg²⁺ over other metal ions compared with small molecular aniline derivative based detection methods. Since the sensitivity of this polymer could be further improved by increasing the molecular weight of the polymer, aniline-based conjugated polymers (**P1** and **P1L**) is a promising metal ion sensor.

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Appendix. Supplementary information

Supplementary data related to this article can be found online at doi:10.1016/j.polymer.2011.04.017.

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