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A New Disubstituted Polyacetylene Bearing Pyridine Moieties: Convenient Synthesis and Sensitive Chemosensor toward Sulfide Anion with High Selectivity

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Supporting Information

ABSTRACT: To develop sensitive and selective S^{2-} chemosensors, a new disubstituted polyacetylene (P2) bearing pyridine moieties in the side chains was prepared conveniently through a postfunctional method, the strong green fluorescence of which could be completely quenched by Cu²⁺ ions at the concentration as low as 2.0×10^{-6} mol/L in diluted solutions. Based on the displacement strategy, by utilizing the much higher stability constant of the complex of S²⁻ and Cu²⁺, the quenched fluorescence of the solution of P2 by Cu²⁺ ions could recover upon the addition of trace S²⁻ anions, with the detection limit down to 5.0×10^{-7} mol/L. Moreover, no interference were observed from other anions, including SO₃²⁻, HSO₃⁻, SO₄²⁻, ClO₄⁻, I⁻, Br⁻, Cl⁻, F⁻, IO₃⁻, HPO₄²⁻, PO₄³⁻, C₂O₄²⁻, S₂O₃²⁻, CO₃²⁻, AcO⁻, CN⁻, and P₂O₇⁴⁻, making P2 a novel, sensitive, and selective sulfide probe.



■ INTRODUCTION

Conjugated polymer-based fluorescent (CPF) chemosensors, which could detect different analytes involved in chemical, biological, and environmental processes of particular relevance, have attracted much attention in these years, since the "molecular wire effect" in conjugated polymers usually greatly enhanced the sensitivity of the polymer-based chemosensors because of the enhanced electronic communication among them.¹ Thanks to the enthusiastic efforts of scientists, many kinds of CPF chemosensors were designed to probe different analytes, including metal ions, anions, explosives, small organic molecules, and biomolecules. Generally, the popular design strategy for CPF chemosensors was to introduce some acceptor groups, such as bipyridyl, terpyridyl, and quinoline segments, to the polymer main or side chain, which could trap or interact with the target analytes and give out the fluorescent signal.²

As a typical type of conjugated polymers, polyacetylenes (PA), which demonstrated various functionalities upon structural modification on their side chains, were promising candidates, such as liquid crystals, polymeric light-emitting diodes, helical polymers, gas separation membranes, organic—inorganic hybrids, and non-linear optical and magnetic materials, for the practical applications.³ However, there were very few reports concerning the properties of disubstituted PAs as chemosensors, although their stability and strong luminescence could ensure them good candidates as polymer chemosensors.⁴ The reason might be partially the difficulties encountered in their synthesis, since it was still a big challenge to prepare disubstituted PAs containing the abovementioned acceptors, as well as groups such as amide, amine, hydroxyl, cyano, thio, etc.⁵ Fortunately, partially based on our previous work on functional polymers obtained through the

Chart 1



postfunctional polymeric reactions, we have successfully obtained some new functional PAs inaccessible from their corresponding monomers through the direct polymerization process, by the utilization of polymer reactions.⁶ Some of which were confirmed to be good chemosensors. For example, as shown in Chart 1, the strong fluorescence of the imidazole-functionalized polyacetylenes, **PS1** and **PS2**, could be completely quenched by copper ions selectively.^{6d,e} Interestingly, the quenched fluorescence could turn on upon the addition of trace cyanide, making them novel sensitive cyanide chemosensors. In comparison with **PS1**, the structure of **PS2** was much perfect, thanks to the relative higher reactivity of bromine atoms than that of chlorine ones in the nucleophilic substitution reactions for the preparation of **PS1**

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Scheme 1



and **PS2**. This strategy for cyanide sensors, first reported by us,^{6d} was further applied for the development of other cyanide sensors by us and other scientists.⁷

On the other hand, sulfide anion is one of the toxic anions, which could irritate mucous membranes and even cause unconsciousness and respiratory paralysis upon continuous and high concentration exposure of sulfide anion. Once being protonated, it becomes even more toxic. Actually, sulfide anion is widely used in industrial settings and produced as a byproduct in a large scale. Also, it can be formed in several ways in the biosystem, for example, the microbial reduction of sulfate by anaerobic bacteria, and the conversion from the sulfur-containing amino acids in meat proteins.8 Thus, the detection of sulfide anion has become very important from industrial, environmental, and biological points of view. A variety of detection techniques have been developed for the determination of sulfide anion, in which fluorimetry has received considerable attention due to its high sensitivity and easy detection. 9^{-12} However, the successful cases were still scarce, and to the best of our knowledge, it seemed that there were no reports concerning the CPF chemosensors toward sufide anions.

Considering the good chemosensors for cyanide we reported previously,^{6d,e,7a,b,f-h} according to the displacement strategy, especially the above-mentioned polyacetylenes, PS1 and PS2, we were wondering if it was possible to design CPF chemosensors for sulfide anions. Deeply thinking about the sensing mechanism of PS1 and PS2, the key point was that cyanide could form very stable complex with copper ions and snatched the copper ions from the complex of Cu²⁺ and its corresponding Cu^{2+} chemosensor. Then, there should be some Cu^{2+} chemosensors, which could not be utilized as cyanide chemosensors as we did previously, due to the much higher stability constants of their corresponding complexes formed with copper ions. If it was the case, perhaps, other anions rather than cyanide, with even stronger affinity toward copper ions, could snatch the copper ions from these complexes, accompanying with the detectable optical signals. As we knew, the solubility product constant of CuS ($K_{sp} = 6.3 \times 10^{-36}$) is much lower than that of cyanide one (3.2 × 10⁻²⁰); thus, there might be some Cu²⁺ chemosensors, which could be utilized as new sulfide chemosensors according to the displacement strategy. Therefore, we tried to link some strong ligand of copper ions to polyacetylene

and investigated the sensing behavior of the resultant functional polyacetylenes. As the first attempt, the di(2-picolyl)amine moieties were used as the acceptor group, which were successfully bonded to the polyacetylene main chain through the nucleophilic substitution reactions, to yield the corresponding functional polyacetylene, **P2** (Scheme 1). The preliminary results realized the above idea: the detection limit of **P2** for sulfide anion could be as low as 5.0×10^{-7} mol/L, nearly without any interference from other anions. Herein, we would like to report the synthesis, characterization, and optical properties of **P2** in detail.

EXPERIMENTAL SECTION

Materials and Instrumentation. N_iN -Dimethylformamide (DMF) was dried over and distilled from CaH₂ under an atmosphere of dry nitrogen. Toluene was dried over and distilled from K–Na alloy under an atmosphere of dry nitrogen. Absolute ethanol was dried over and distilled from sodium. Tetrahydrofuran (THF) was dried over and distilled from K–Na alloy under an atmosphere of dry nitrogen.

¹H and ¹³C NMR spectroscopy study was conducted with a Varian Mercury300 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. The Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer-2 spectrometer in the region of 3000–400 cm⁻¹ on NaCl pellets. UV–vis spectra were obtained using a Shimadzu UV-2550 spectrometer. Photoluminescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer. Gel permeation chromatography (GPC) was used to determine the molecular weights of polymers. GPC analysis was performed on an Agilent 1100 series HPLC system and a G1362A refractive index detector. Polystyrene standards were used as calibration standards for GPC. THF was used as an eluent, and the flow rate was 1.0 mL/min. Thermal analysis was performed on NETZSCH STA449C thermal analyzer at a heating rate of 10 °C/min in nitrogen at a flow rate of 50 cm³/min for thermogravimetric analysis (TGA).

Synthesis of 4-(3-Bromopropyloxy)iodobenzene (**3**). To a 500 mL round-bottomed flask were added 4-iodophenol (4.4 g, 20 mmol), 1,3-dibromopropane (20.2 g, 100 mmol), potassium hydroxide (5.5 g, 98 mmol), potassium iodide (0.3 g, 1.8 mmol), and acetone (200 mL). The mixture was refluxed for 24 h. The solid was removed by filtration, and the solvent was evaporated. The crude product was purified on a silica gel column using hexane as eluent. White solid of 4-(3-bromopropyloxy)-iodobenzene was obtained (4.83 g, 73.4%). ¹H NMR (300 MHz, CDCl₃),

 δ (TMS, ppm): 7.57 (d, *J* = 9.0 Hz, 2H, ArH), 6.70 (d, *J* = 9.0 Hz, 2H), 4.05 (t, *J* = 6.0 Hz, 2H), 3.60 (t, *J* = 6.6 Hz, 2H), 2.31 (m, *J* = 6.6 Hz, 2H).

1-Phenyl-2-[4-(63-bromopropyloxy)phenyl]acetylene (**4**). To a Schlenk tube were added copper(I) iodide (15 mg, 0.04 mmol), dichlorobis-(triphenylphosphine)palladium (50 mg, 0.04 mmol), triphenylphosphine (15 mg, 0.04 mmol), and 4-(3-bromopropyloxy)iodobenzene (2.6 g, 7.7 mmol) in a glovebox. Triethylamine (150 mL) and phenylacetylene (1.0 g, 9.8 mmol) were then injected. The resultant mixture was stirred at room temperature overnight. The solid was removed by filtration, and the solvent was evaporated. The crude product was purified on a silica gel column using hexane as eluent. White solid of 4 was obtained (2.8 g, 84.1%). ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.49 (m, *J* = 3.0 Hz, 4H), 7.33 (m, *J* = 3.9 Hz, 3H), 6.88 (d, *J* = 8.4 Hz, 2H), 4.05 (t, *J* = 5.7 Hz, 2H), 3.60 (t, *J* = 6.3 Hz, 2H), 2.31 (m, *J* = 6.0 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃), δ (TMS, ppm): 158.6, 133.0, 131.4, 128.3, 127.9, 123.4, 115.4, 114.4, 89.2, 88.1, 67.1, 32.7, 2.5.

Poly[1-phenyl-2-[4-(3-bromopropyloxy)phenyl]acetylene] (P1). Into a baked 20 mL Schlenk tube with a stopcock in the side arm was added 4 (1.0 g). The tube was evacuated under vacuum and then flushed with dry nitrogen three times through the side arm. Freshly distilled toluene (6 mL) was injected into the tube to dissolve the monomer. The catalyst solution was prepared in another tube by dissolving tungsten(VI) chloride (47.7 mg) and tetraphenyltin (51.6 mg) in toluene (6 mL). The two tubes were aged at 80 °C for 1 h, and the monomer solution was transferred to the catalyst solution using a hypodermic syringe. The reaction mixture was stirred at 80 °C for 48 h. The solution was then cooled to room temperature, diluted with 15 mL of chloroform, and added dropwise to 150 mL of methanol through a cotton filter under stirring. The precipitate was allowed to stand overnight and was then filtered. The polymer was washed with methanol and dried in a vacuum oven to a constant weight (0.74 g, 74%). $M_{\rm w}$ = 18600, $M_{\rm w}/M_{\rm n}$ = 1.70. IR (thin film), v (cm⁻¹): 3064 (Ar-H stretching), 2954, 2870 (CH₂ stretching). ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 6.88–6.30 (br, ArH), 6.36–6.00 (br, ArH), 4.20-3.90 (br, OCH₂), 3.46-3.22 (br, CH₂Br), 1.75-1.42 (br, CH₂). ^{13}C NMR (75 MHz, CDCl₃), δ (TMS, ppm): 149.3, 148.8, 137.2, 130.9, 128.5, 127.3, 125.1, 123.0, 122.3, 108.0, 98.46, 68.8, 60.2, 24.2.

Di(2-picolyl)amine (DPA). A modified literature procedure was used.¹³ To a suspension of 2-pyridinecarboxaldehyde (1.04 g, 9.67 mmol) in absolute ethanol (20 mL) was added a solution of 2-(aminomethyl)pyridine (1.05 g, 9.71 mmol) in absolute ethanol (20 mL) dropwise at 0 °C. After 4 h, the solution was cooled to 0 °C and sodium borohydride (0.726 g, 19.2 mmol) was added in small portions. After the reaction was stirred for 12 h at room temperature, aqueous hydrochloric acid (24 mL, 0.5 M) was added slowly and stirred for 1 h. An aqueous solution of sodium hydroxide (2 M) was then added until a pH value of 11 was reached. The mixture was extracted with methylene dichloride (15 mL \times 6), dried over sodium sulfate, and then filtered. The crude product was purified on a silica gel column using THF/PE (1:1) as eluent. Pure di(2picolyl)amine (DPA) was yielded as a brown oil (0.87 g, 45.1%). ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 8.55 (d, J = 4.8 Hz, 2H), 7.64 (d, J = 7.8 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 5.1 Hz, 2H), 3.98 (s, 4H), 2.51 (s, 1H). ¹³C NMR (75 MHz, CDCl₃), δ (TMS, ppm): 159.8, 149.5, 136.8, 122.6, 122.2, 54.9.

Synthesis of **P2**. **P1** (30 mg), DPA (70 mg, 0.35 mmol), and potassium hydroxide (140 mg, 2.5 mmol) were added to dry DMF (6 mL). After stirring at 80 °C for 2 days, the resultant mixture was filtered, and then the filtrate was added dropwise to 150 mL of water through a cotton filter under stirring. The precipitate was allowed to stand overnight and then filtered. The polymer was washed with water and dried in a vacuum oven to a constant weight to yield **P2** (0.035 g, 89%). ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 8.60–8.30 (br, ArH), 7.70–7.20 (br, ArH), 7.20–6.90 (br, ArH), 6.88–6.40 (br, ArH), 6.40–5.80 (br, ArH), 4.80–4.50 (br, OCH₂), 4.40–4.00 (br, CH₂Br),

4.00–3.50 (br, CH₂N), 2.80–2.42 (br, CH₂). ¹³C NMR (75 MHz, CDCl₃), δ (TMS, ppm): 159.6, 149.3, 148.8, 137.2, 130.9, 128.5, 127.3, 126.3, 125.1, 123.0, 122.3, 108.0, 98.46, 68.8, 67.7, 60.2, 29.5, 24.2.

Preparation of Polymer Solutions. P2 (9.3 mg) was dissolved in THF to afford the stock solution with the concentration of 2.31×10^{-3} mol L⁻¹. This stock solution was diluted with THF and water (v/v = 1/1) to 2.31×10^{-5} mol L⁻¹.

Fluorescence Titration of P2 with Cu²⁺. A solution of P2 $(2.31 \times 10^{-5} \text{ mol } \text{L}^{-1})$ was prepared in THF/H₂O (v/v = 1:1). The solution of Cu²⁺ was prepared in distilled water. A solution of P2 (3.0 mL) was placed in a quartz cell (10.0 mm width), and the fluorescence spectrum was recorded. The Cu²⁺ solution was introduced in portions, and fluorescence intensity changes were recorded at room temperature each time (excitation wavelength: 324 nm).

Fluorescence Intensity Changes of the Mixture of P1 and Di(2-picolyl)amine with Cu²⁺. A solution of the mixture of P1 and di(2-picolyl)amine $(2.31 \times 10^{-5} \text{ mol L}^{-1})$ was prepared in THF/H₂O (v/v = 1:1). The solutions of Cu²⁺ ($1 \times 10^{-3} \text{ mol/L}$) were prepared in distilled water. A solution of the mixture of P1 and di(2-picolyl)amine (3.0 mL) was placed in a quartz cell (10.0 mm width), and the fluorescence spectrum was recorded. The ion solution was introduced (9 μ L), and fluorescence intensity changes were recorded at room temperature each time (excitation wavelength: 324 nm).

Fluorescence Intensity Changes of P2 + Cu²⁺ with S^{2–}. A solution of P2 ($2.31 \times 10^{-5} \text{ mol } \text{L}^{-1}$) was prepared in THF/H₂O (v/v = 1:1). The solution of Na₂S ($1 \times 10^{-3} \text{ mol } \text{L}^{-1}$) was prepared in distilled water. A solution of P2 (3.0 mL) was placed in a quartz cell (10.0 mm width), and the fluorescence spectrum was recorded. The solution of Cu²⁺ ($1 \times 10^{-3} \text{ mol } \text{L}^{-1}$, 9 μ L) was added to quench the fluorescence. Then Na₂S solution was introduced in portions, and the fluorescence intensity changes were recorded at room temperature each time (excitation wavelength: 324 nm).

Fluorescence Titration of P2 with Other Anions. A solution of P2 ($2.31 \times 10^{-5} \text{ mol L}^{-1}$) was prepared in THF/H₂O (v/v = 1:1). The solutions of anions were prepared in distilled water. A solution of P2 (3.0 mL) was placed in a quartz cell (10.0 mm width), and the fluorescence spectrum was recorded. The solution of Cu²⁺ (1 × $10^{-3} \text{ mol L}^{-1}, 9 \,\mu\text{L}$) was added to quench the fluorescence. The other anion solution was introduced in portions, and fluorescence intensity changes were recorded at room temperature each time (excitation wavelength: 324 nm).

RESULTS AND DISCUSSION

Synthesis. The synthetic route to **P2** is shown in Scheme 1. First, monomer 4, which contained a bromine atom, was easily prepared from the esterification reaction followed by the Sonogashira coupling reaction in the total yield of 61.7%, according to the similar procedure reported earlier.^{6e} Then, through the direct polymerization process, this monomer was converted to the corresponding PA, **P1**, in which the bromine atoms remained for the further functionalization. During the followed nucleophilic substitution reaction, the bromine atoms in the side chain of **P1** were substituted by the di(2-picolyl)amine moieties, yielding the expected new di(2-picolyl)amine-functionalized PA, **P2**.

It should be pointed out that the preparation of **P2** was through the postfunctionalization approach. Generally, if disubstituted acetylene monomers contained polar groups or active hydrogen atoms, such as amide, amine, hydroxy, cyano, thio, azo, etc., they could not be polymerized to give the corresponding disubstituted polyacetylenes due to the deactivation of the transition-metal catalysts. Fortunately, by utilizing the polymer reactions of some disubstituted polyacetylenes bearing reactive



Figure 1. ¹H NMR spectra of (A) P1 and P2 (B) in chloroform-*d*. The solvent peaks were marked with asterisks.

groups, such as chlorine and bromine atoms, and azido moieties, some polar groups could be introduced to the side chains through the Sonogashira coupling reaction, the click chemistry reaction, the nucleophilic substitution reaction, and the hydrolysis reaction. In our previous case, in the nucleophilic substitution reaction, the bromine atoms in the side chain of polydisubstituted acetylene exhibited much higher reactivity than that of the chlorine ones. And sometimes, the bromine atoms could be converted to another functional group completely.^{6e} Thus, here, the polydisubstituted acetylene (P1) bearing bromine atoms in the side chains was designed for the preparation of P2. This time, possibly due to the bulk hindrance effect of di(2-picolyl)amine moieties and its relatively low reactivity, 75% of the bromine atoms were converted to the di(2-picolyl)amine moieties, and there were still unreacted bromine atoms remained. However, this might not affect the sensing property of the resultant P2, and we would discuss this point later. Thus, although not so perfect, the successful preparation of P2 still confirmed that the postfunctionalization strategy was a good alternative approach to yield disubstituted polyacetylenes inaccessible from their corresponding monomers through the direct polymerization reactions. The purification procedure was simple; we only needed to isolate the monomer 4 and di(2picolyl)amine by a silica gel column, and polymers P1 and P2 could be purified easily by precipitations from their solutions into methanol or water.

Structural Characterization. P1 and **P2** were characterized by spectroscopic methods and gave satisfactory spectral data (see Experimental Section and Supporting Information for detailed analysis data). In the ¹H NMR spectra of the polymers **P1** and **P2** (Figure 1), the chemical shifts were consistent with the proposed polymer structure as demonstrated in Scheme 1. After the reaction with di(2-picolyl)amine, there were some new absorption peaks appeared at about 7.04, 7.46, and 8.48 ppm in the downfield, which should be ascribed to the aromatic protons of moieties in **P2**, indicating that the bromine atoms were converted to the di(2picolyl)amine moieties successfully. Also, from the integration of these peaks, the concentration of the unit of the di(2-picolyl)amine moieties in **P2** could be calculated to be about 75%; that is, there were still about 25% of the bromine atoms in **P1** remained unreacted during the substitution reaction. Previously, the bromine atoms could be converted to other functional groups through the substitution reaction completely while reacted with imidazole.^{7e} Here, the bulk of the di(2-picolyl)amine moieties was much bigger, which should hinder the substitution reaction, directly resulting in the uncompleted conversion of the bromine atoms in **P1**.

The two polymers, P1 and P2, exhibited much different solubility in common organic solvents. For example, P1 was insoluble in alcohol, and in the purification procedure, we could remove unpolymerized monomers and some other impurities by the precipitation from its chloroform solution into methanol; however, after most of the bromine atoms in P1 were converted to the di(2-picolyl)amine moieties, the solubility of the resultant polymer P2 changed dramatically: P2 could dissolve in alcohol, in contrast to most of the reported disubstituted polyacetylenes. This disclosed that the introduction of di(2-picolyl)amine moieties to the PA backbone has brought some changes to the resultant polyacetylene. P2 was thermally stable, and its TGA thermograms are shown in Figure S1, with the 5% weight loss temperature at about 285 °C.

Fluorescence Properties. As mentioned in the Introduction, their stability and strong luminescence could ensure disubstituted polyacetylenes good candidates as polymer chemosensors. As demonstrated in Figure 2, both of P1 and P2 emitted strong luminescence in diluted solutions with the maximum emission wavelength at about 535 and 507 nm, respectively. The P1-di(2-picolyl)amine mixture nearly showed the same emission behavior as P1, indicating that the presence of di(2-picolyl)amine in the mixture did not affect the electronic properties of the conjugated polymers. However, the blue-shifted emission (28 nm) of P2 in comparison with that of P1 disclosed the minor change of the electronic properties of the conjugated polymers before and after the linkage of the di(2-picolyl)amine moieties, partially explaining the totally different sensing behavior of P2 and the mixture of P1 and di(2-picolyl)amine discussed as follows.

As shown in Figure 2, after the addition of a little amount of Cu^{2+} , the things became different. Similar to that of **P1**, the emission spectrum of the **P1**–di(2-picolyl)amine mixture remained



Figure 2. Fluorescence spectra of **P1** (A), the mixture of **P1** and di(2-picolyl)amine (DPA) (B), and **P2** (C) in THF/water (1:1) before and after the addition of Cu^{2+} . The polymer concentration was 2.31×10^{-5} mol/L. Excitation wavelength (nm): 324.



Figure 3. Emission quenching of the solution of **P2** by Cu²⁺ in THF/ H₂O (1:1). Polymer concentration: 2.31×10^{-5} mol/L. Excitation wavelength (nm): 324. The pH value was 6.32.

almost unchanged. As to **P2**, the strong luminescent emission was completely quenched by the added Cu^{2+} ions, although its absorption curve only changed a little upon the addition of copper ions (Figure S2a). These results indicated that after being linked to the polymer main chain, the di(2-picolyl)amine moieties could efficiently transfer the energy from the conjugated polymer backbone to the copper ions, leading to the quenching of the strong luminescence of the polymer. Thus, **P2** could be utilized as polymer chemosensor for metal ions. Also, the results confirmed that the receptor should be linked to the polyacetylene backbone to the metal ions, similar to those observed previously.^{6e}

To study the quenching behavior of Cu^{2+} ions in detail, we investigated the decrease in fluorescence intensity by adding successive aliquots of aqueous stock solutions of Cu^{2+} ions to the diluted solution of **P2**. As shown in Figure 3, quenching of



Figure 4. Fluorescence emission response profiles of P2. The polymer concentration: 2.31×10^{-5} mol/L. The concentration of copper ions: 2×10^{-6} mol/L, while 5×10^{-5} mol/L for other metal ions. Excitation wavelength (nm): 324. Inset photo: polymer (A); P2 + Cu²⁺ (B), P2 + Zn²⁺ (C), P2 + K⁺ (D), P2 + Mg²⁺ (E), P2 + Mn²⁺ (F), P2 + Ca²⁺ (G), P2 + Cd²⁺ (H), P2 + Ba²⁺ (I), P2 + Na⁺ (J), P2 + Li⁺ (K), P2 + Pb²⁺ (L), P2 + Ag⁺ (M), P2 + Fe²⁺ (N), P2 + Fe³⁺ (O), P2 + Co²⁺ (P), P2 + Ni²⁺ (Q), P2 + Hg²⁺ (R), P2 + Cr³⁺ (S), P2 + Al³⁺ (T).

photoluminescence was observed at very low level of Cu²⁺ (1.0×10^{-7} mol/L), and the fluorescent intensity decreased rapidly upon the increase of the added concentration of Cu²⁺. While the concentration of Cu²⁺ was 2.0×10^{-6} mol/L, nearly no luminescence could be seen. The quenching efficiency was nearly fit to the Stern–Volmer equation, $I_0/I = K_{sv}[A] + 1$, which related to the fluorescence intensity, *I*, at different concentrations of analyte quencher, [A], where I_0 was the intensity at [A] = 0, and K_{sv} was the Stern–Volmer constant. According to the fluorescence titration of **P2** in THF solutions with Cu²⁺, K_{sv} was determined to be 8.2×10^6 M⁻¹. As the pyridine group is apt to act as a hydrogen acceptor, we thought that perhaps **P2** could be a hydrogen acceptor and might give out some detectable signals upon the addition of acids. As shown in Figure S2b, really,



Chart 2. Schematic Representation of Cu^{2+} and S^{2-} Sensors Based on the Fluorescence "Turn-Off" and "Turn-On" of P2

the fluorescence of **P2** could be quenched by the addition of hydrochloric acid, and nearly no luminescence could be observed while the pH value of the resultant solution decreased to 0.94. This phenomenon indicated that the di(2-picolyl)amine moieties acted as hydrogen acceptor, and the energy could be transferred from the conjugated backbone to the hydrogen ions, similar as to the copper ions. Interestingly, the quenched fluorescence could be recovered after the addition of some base (Figure S2c), as observed in our previous case.^{7b} The above titration experiments of copper ions were further conducted at different pH values (Figure S2d,e), and the obtained results demonstrated that the optimized pH value was 6.32, as utilized in the experiment for Figure 3. Thus, all the following fluorescent experiments were conducted at the pH value of 6.32.

To evaluate the copper ion-selective nature of P2, the influence of other metal ions was investigated. As shown in Figure 4 and Figures S3-S21 (in Supporting Information), other metal ions nearly gave no disturbance to the selectively sensing of copper ions, except very little response from Co^{2+} . Thus, the selectivity for copper ions over other metal ions was relatively high. The competition experiments using solutions containing copper ions and all the other metal ions demonstrated that P2 could still report the presence of copper ions in the presence of other common interfering metal ions (Figure S22). As the sensing sensitivity of P2 toward Cu²⁺ was also very high, we wondered if it was possible to detect this metal ion visually at very low concentration with the aid of a normal UV lamp, but not a fluorescence spectrophotometer. As shown in the photographs of the solutions of P1 (Figure 4), after the addition of the copper ions, the strong green fluorescence of P2 was completely quenched and the corresponding bottle became dark, under UV illumination. However, upon the addition of other metal ions, no changes could be observed. Thus, the difference was very apparent and could be seen visually, even the concentration of ${
m Cu}^{2+}$ was only 2.0 imes 10^{-6} mol/L (0.13 ppm). The above obtained results were very different from those of small fluorophors bearing di(2-picolyl)amine moieties,¹⁴ which could bind with Zn²⁺ and produce fluorescence changes, indicating that the selectively sensing of metal ions by using di(2-picolyl)amine groups as receptor could be adjusted after being linked to the conjugated backbones. This is reasonable, since the various degrees of affinity of di(2-picolyl)amine groups toward metal ions should lead to different influence to the interaction between the di(2-picolyl)amine groups and the conjugated polymer backbone or other fluorophors



Figure 5. Fluorescence emission spectra of P2 before and after the addition of Cu²⁺ and turned on by S²⁻. The polymer concentration is fixed at 2.31×10^{-5} mol/L.

repoted in the literature, due to their different electronic properties.

From the obtained experimental results, we could conclude that **P2** could report the presence of trace Cu²⁺ ions based on the fluorescence "turn-off", since the di(2-picolyl)amine moieties could efficiently transfer the energy from the conjugated backbone to the copper ions, leading to the quenching of the strong luminescence of the polymer. Previously, according to the displacement strategy, we have developed some good chemosensors for cyanide, ^{6d,e,7a,b,f-h} since cyanide could snatch the copper ions from the complex of copper ions and the corresponding chemosensors. So, here, if some species, which could snatch the Cu²⁺ ions from the di(2-picolyl)amine moieties in **P2** to form more stable new complexes, were added in the **P2**/Cu²⁺ complex, the quenched luminescence of **P2** might recover. As discussed in the Introduction, the solubility product constant of CuS ($K_{sp} = 6.3 \times 10^{-36} \text{ mol}^2/\text{L}^2$) was very low; thus, the **P2**/Cu²⁺ complex might give some response to the S²⁻ anions.

Really, the qualitative analysis demonstrated that the addition of sulfide anion to the $P2/Cu^{2+}$ complex turned on the fluorescence of P2 (Chart 2), verifying the above idea. The recovering behavior of the fluorescence of the complex of P2 and Cu²⁺



was studied in detail (Figure 5). The completely quenched fluorescence of P2 by Cu²⁺ turned on after the addition of sulfide anion, even at a very low concentration (2.0 \times 10⁻⁷ mol/L). Further increasing the concentration of sulfide anion led to stronger fluorescence. When the added concentration of S^{2-} was 4.5×10^{-6} mol/L (0.144 ppm), the fluorescent intensity could recover to more than 80% of the original intensity of P2 without Cu^{2+} , and this intensity was strong enough to be used as "turn-on" to probe trace S²⁻. Thus, by applying a "turn-off-turnon" circle, P2 was both selective chemosensor for Cu^{2+} and sensitive one for S^{2-} . To exclude the possibility of the fluorescent signal response of P2 toward S^{2-} directly without the presence of Cu²⁺, another control experiment was conducted: successive aliquots of aqueous solutions of S^{2-} were added to the diluted solution of P2, and the changes of the fluorescence spectra were recorded. As shown in Figure S23, no changes could be observed before and after the addition of the S^{2-} solutions; even the concentration of S^{2-} was 1.0×10^{-5} mol/L, much higher than those used in the above experiment (Figure 5). Thus, the obtained results confirmed the speculated mechanism (Chart 2) for the sensing of S^{2-} again.

To evaluate the S²⁻-selective nature of **P2**, the influence of other anions toward the complex of **P2** and Cu²⁺ was studied (Figure 6). Nearly nonluminescence could be observed upon the addition of most of anions at the concentration of 2.0×10^{-5} mol/L, such as F⁻, Cl⁻, Br⁻, ClO₄⁻, NO₂⁻, and SO₄⁻. Thus, other anions gave nearly no disturbance to the selective sensing of sulfide anion, indicating that the selectivity for S²⁻ was relatively high. Furthermore, the competition experiments using solutions containing S²⁻ and all the other anions was conducted.



Figure 7. Fluorescence emission spectra of P2 and Cu²⁺ ($3 \times 10^{-6} \text{ mol/L}$) in H₂O–THF (1:1, v/v) in the presence of different amounts of anions. The concentration of S²⁻ was $6 \times 10^{-6} \text{ mol/L}$. Excitation wavelength (nm): 324.

As shown in Figure 7, the complex $P2-Cu^{2+}$ could still report the presence of S^{2-} . Thus, this sulfide selective sensor was not affected by the presence of other common interfering anions, indicating its possible practical application for the probe of S^{2-} in the real water samples.

CONCLUSIONS

In summary, we have successfully prepared a new di(2picolyl)amine-functionalized disubstituted polyacetylene (P2) by utilizing the postfunctional strategy and studied its ability to sense metal ions and anions by the fluorescence spectra. P2 could report the presence of trace S²⁻ anions as low as 5.0×10^{-7} mol/L selectively by an indirect strategy, making it good candidate for potential application of human safeguard. The preliminary results demonstrated that:

- By utilization of the postfunctional strategy, the di(2picolyl)amine moieties could be conveniently introduced to the PA backbone, offering the resultant polymer the sensing ability to report the presence of trace copper ions. This, once again, confirmed that disubstituted polyacetylenes could be promising candidates as CPF chemosensors.
- 2. It is a good and alternative approach to develop sensitive and selective CPF anion probes by applying a "turn-off—turn-on" circle with the usage of CPF metal ion chemosensors. Or in other words, it is really possible to find many good CPF anion probes even in the present CPF metal ion chemosensors. Thus, the large amount of the reported CPF metal ion chemosensors could be possibly utilized as "new" CPF anion probes with good performance, especially those Cu²⁺ chemosensors. Specially, we could utilize the different coordination ability of different anions toward coppers to develop different chemosensors for the probe of different anions, by using the displacement strategy.

ASSOCIATED CONTENT

Supporting Information. TGA and IR spectra and PL spectra of solutions of **P2** in the presence of different metal ions.

This material is available free of charge via the Internet at http://pubs.acs.org.

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