An Imidazole-Functionalized Polyfluorene Derivative as Sensitive Fluorescent Probe for Metal Ions and Cyanide

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Received June 10, 2008; Revised Manuscript Received August 9, 2008

ABSTRACT: To develop sensitive and selective CN^- chemosensors, a new imidazole-functionalized polyfluorene (**P1**) was designed and obtained conveniently, the fluorescence of which could be completely quenched by Cu^{2+} ions at the concentration as low as 0.20 ppm in diluted solutions. By utilizing the much higher stability constant of the complex of CN^- and Cu^{2+}, the quenched fluorescence of the solution of **P1** by Cu^{2+} ions could recover upon the addition of trace CN^- anions, with the detection limit down to 0.31 ppm, making **P1** a novel, sensitive and selective cyanide probe.

Introduction

The development of fluorescent chemosensors capable of sensing target guests *via* changes in fluorescent signals is a field of great interest, due to their high sensitivity and potential applications in chemistry and biology.[1] Among the reported fluorescent chemosensors, conjugated polymer-based fluorescent (CPF) chemosensors attracted much attention in these years, since "molecular wire effect" in conjugated polymers usually greatly enhanced the sensitivity of the polymer-based chemosensors because of the enhanced electronic communication among them.[2] So far, in contrast to lots of good CPF chemosensors for the detection of positively charged or neutral species, those for anions are still scarce, although many anions are involved in chemical, biological and environmental processes of particular relevance.[3] For example, cyanide, which is widely used industrially in gold mining, electroplating, metallurgy, the synthesis of nylon and other synthetic fibers and resins, is probably one of the most toxic anions and could be found in many foods and plants.[4,5] Although it is difficult to give an exact lethal dosage or exposure limit, recent studies have shown that the lethal cyanide concentration in the blood of fire victims is ca. 20 μM.[6] Thus, the cyanide chemosensors should give response to the presence of cyanide from a few to ~20 μM.

Generally, the cyanide anion is strongly nucleopilic and can form stable complexes with many stable transition metals. According to this property, relying on the formation of cyanide complexes with some metal ion containing compounds, such as Zn(II)−porphyrin, Ru(II)−pridine, boron derivatives, *etc*., some cyanide chemosensors were developed.[7] Considering that there were many conjugated polymers bearing some acceptor groups such as bipyridyl, terpyridyl, and quinoline segments, could trap and form complexes with metal ions, to report the presence of some special metal ions,[8] we wonder that the addition of some cyanide anion to the complexes of conjugated polymers and metal ions might give out some detectable signals. From this point, we prepared an imidazole-functionalized polyacetylene (**PA**, Chart S1, Supporting Information), which could sense copper ions selectively and sensitively based on the fluorescence "turn-off". After the addition of some cyanide anions, interestingly, the quenched fluorescence of polyacetylene by Cu^{2+} could turn on, making it a novel sensitive and selective cyanide probe, with the detection limit of 70 μM (much higher than the lethal cyanide concentration in the blood of fire victims, 20 μM).[9] This result confirmed that it is possible to probe anions by utilizing the CPF metal ion chemosensors.

To further check the above idea and explore more CPF chemosensors for cyanide anions with higher sensitivity, recently, partially based on our work on conjugated polymers,[10] we designed a new imidazole-functionalized polyfluorene derivative (**P1**, Scheme 1), since polyfluorenes are perhaps the most studied conjugated polymers with very high quantum yields in solutions. Really, the fluorescence of **P1** could be quenched by Cu^{2+} completely and efficiently (the detection limit is 0.2 ppm), and the resultant **P1**/Cu^{2+} complex could selectively report the presence of cyanide anion with much improved sensitivity (down to 0.31 ppm or 12 μM, < 20 μM). Interestingly, **P1** also exhibited different quenching behavior by formic acid in different organic solvent. Herein, we would like to report the synthesis, characterization and optical properties of **P1** in detail.

Materials and Instrumentations

N,*N*-Dimethylformamide (DMF) was dried over and distilled from CaH_2 under an atmosphere of dry nitrogen. Tetrahydrofuran (THF) was dried over and distilled from K−Na alloy under an atmosphere of dry nitrogen. **P0** was synthesized according to our previous work.[10a]

^1H 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−visible 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 a Waters HPLC system equipped with a 2690D separation module and a 2410 refractive index detector. Polystyrene standards were used as calibration standards for GPC. DMF 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 cm^3/min for thermogravimetric analysis (TGA). The thermal transitions of the polymers were investigated using a METTLER differential scanning calorimeter DSC822e under nitrogen at a scanning rate of 10 °C/min.

Synthesis of P1. P0 (133 mg), imidazole (41.0 mg, 0.6 mmol) were dissolved in dry THF (2 mL) and DMF (1 mL) in the presence of potassium hydroxide (34.0 mg, 0.6 mmol) as an acid acceptor with potassium iodide as a catalyst. After stirred at 80 °C for 60 h,

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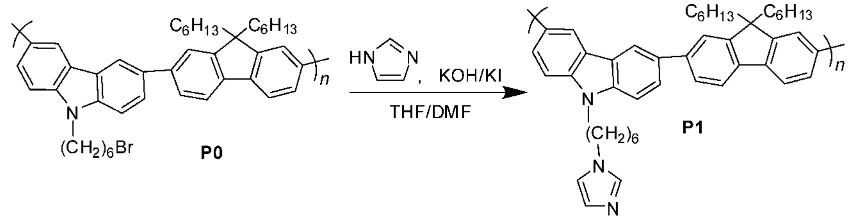
10.1021/ma8013096 CCC: $40.75

Scheme 1



the mixture was poured into a lot of water. The obtained solid was dissolved in THF, and dropped into methanol (100 mL), then the yellow precipitant was collected and washed with acetone, and dried in a vaccum desiccator (125 mg, 96.2%). $M_w = 18\,700$, $M_w/M_n = 1.26$ (GPC, polystyrene calibration). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.6−1.0 ($-CH_3$), 1.0−1.3 ($-CH_2-$), 1.4−1.6 ($-CH_2-$), 1.6−1.8 ($-CH_2-$), 1.8−2.2 ($-CH_2-$), 3.8−4.0 ($-CH_2-N-$), 4.4 ($-NCH_2-$), 6.9 (ArH), 7.0 (ArH), 7.4−7.6 (ArH), 7.6−7.9 (ArH), 8.5 (ArH). UV−vis (THF, 5.0×10^{-6} mol/L): λ_{max} (nm) 347.

Fluorescence Intensity Changes of P1 with Different Metal Ions. A solution of **P1** (5.0×10^{-6} mol/L) was prepared in THF. The solutions of metal ions (1×10^{-3} mol/L) were prepared in distilled water. A solution of **P1** (3.0 mL) was placed in a quartz cell (10.0 mm width) and the Fluorescence spectrum was recorded. Different ion solutions were introduced (9.6 μL) and the changes of the fluorescence intensity were recorded at room temperature each time (excitation wavelength: 355 nm).

Fluorescence Titration of P1 with Different Metal Ions. A solution of **P1** (5.0×10^{-6} mol/L) was prepared in THF. The solutions of metal ions were prepared in distilled water. A solution of **P1** (3.0 mL) was placed in a quartz cell (10.0 mm width) and the fluorescence spectrum was recorded. The ion solution was introduced in portions and fluorescence intensity changes were recorded at room temperature each time (excitation wavelength: 355 nm).

Fluorescence Intensity Changes of P1 by Cu^{2+} in the Presence of Other Metal Ions. Fluorescence intensity changes of **P1** (5.0×10^{-6} mol/L) were recorded before and after additions of 9.6 μL of the solutions of metal ions (Na^+, K^+, Ca^{2+}, Ba^{2+}, Fe^{2+}, Mn^{2+}, Cd^{2+}, Pb^{2+}, Mg^{2+}; the concentrations of the metal ions were 1×10^{-3} mol/L) to the solution of **P1**. Then 9.6 μL of the solution of Cu^{2+} (1×10^{-3} mol/L) was added and fluorescence intensity changes were recorded. In addition, the fluorescence intensity changes of **P1** before and after the addition of H_2O (90 μL) was also recorded (Excitation wavelength: 355 nm).

Fluorescence Intensity Changes of P1 + Cu^{2+} with CN^-. A solution of **P1** (5.0×10^{-6} mol/L) was prepared in THF. The solution of NaCN (1×10^{-3} mol/L) was prepared in distilled water. A solution of **P1** (3.0 mL) was placed in a quartz cell (10.0 mm width) and the fluorescence spectrum was recorded. After the solution of Cu^{2+} (1×10^{-3} mol/L, 9.6 μL) was added to quench the fluorescence, the solution of NaCN (6.0×10^{-4} mol/L) was introduced in portions (total volume: 10, 20, 30, 40, 50, 60 μL) and the fluorescence intensity changes were recorded at room temperature each time (excitation wavelength: 355 nm).

Fluorescence Intensity Changes of P1 + Cu^{2+} with CN^- and Other Anions. A solution of **P1** (5.0×10^{-6} mol/L) was prepared in THF. The solutions of anions (1×10^{-3} mol/L) were prepared in distilled water. A solution of **P1** (3.0 mL) was placed in a quartz cell (10.0 mm width) and the fluorescence spectrum was recorded. Then different anions (36 μL) solution was introduced respectively, and fluorescence intensity changes were recorded at room temperature each time (excitation wavelength: 355 nm).

Fluorescence Intensity Changes of P1 with H^+. A solution of **P1** (5.0×10^{-6} mol/L) was prepared in THF. The solutions of hydrochloric acid (HCl) were prepared in distilled water. A solution of **P1** (3.0 mL) was placed in a quartz cell (10.0 mm width) and the fluorescence spectrum was recorded. Then different concentrations of H^+ solutions (1.0×10^{-3} and 1.0×10^{-2} mol/L) were introduced in portions (total volume: 3, 15, 30, 36, 40, 57 μL), and fluorescence intensity changes were recorded at room temperature each time (excitation wavelength: 355 nm).

Fluorescence Intensity Changes of P1 + H^+ with OH^-. A solution of **P1** (5.0×10^{-6} mol/L) was prepared in THF. The solutions of NaOH were prepared in distilled water. A solution of **P1** (3.0 mL) was placed in a quartz cell (10.0 mm width) and the fluorescence spectrum was recorded. After H^+ was added to quench the fluorescence, OH^- (1.0×10^{-1} mol/L) was then added in portions to turn on the fluorescence. The fluorescence intensity changes were recorded at room temperature each time (excitation wavelength: 355 nm).

Results and Discussion

Synthesis. The synthetic route was demonstrated in Scheme 1. **P0** was prepared as reported previously,[10a] then **P1** was obtained conveniently from the reaction between imidazole and **P0** under mild conditions in high yield (96.2%). In comparison with other polyfluorene derivatives bearing imidazole moieties,[11] **P1** was yielded by a post functional method through polymer reaction. As shown in Scheme 1, the imidazole moieties were introduced to the side chain of polymer directly by substituting the bromine atoms in polymer, thus the imidazole-containing monomer did not need to be prepared any longer, and **P1** could be purified simply by precipitation, but not column chromatography as the synthesis of imidazole-containing monomers reported in the literature.[11] Not like in the case of **PA** (the chlorine atoms could not be substituted by imidazole moieties completely),[9] the conversion of the bromine atoms in **P0** to the imidazole moieties in **P1** was as high as 100% (we would discuss this point later), indicating that the bromine atoms here were more active than the chlorine ones. Thus, **P0** could be used as a good polymeric reactive intermediate, and other acceptor groups with active hydrogen atoms could be linked to the polyfluorene main chain conveniently under similar reaction conditions for **P1**, to give other new CPF chemosensors. Further work was currently underway in our laboratory.

Structural Characterization. P1 was characterized by spectroscopic methods, and gave satisfactory spectral data (see Experimental Section, Supporting Information for detailed analysis data). In the ^{1}H NMR spectra of the polymers **P0** and **P1** (Figure 1), the chemical shifts were consistent with the proposed polymer structure as demonstrated in Scheme 1. It was easily seen that the absorption peak of methylene groups linked with bromine atoms in **P0**, disappeared completely after

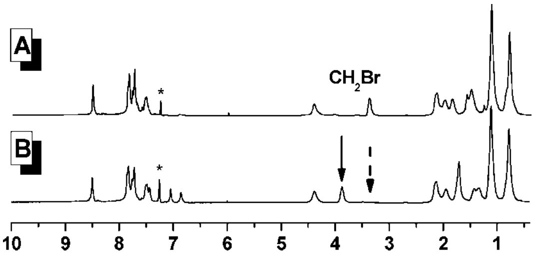


Figure 1. ^{1}H NMR spectra of (A) **P0** and **P1** (B) in chloroform-*d*. The solvent peaks were marked with asterisks (*).

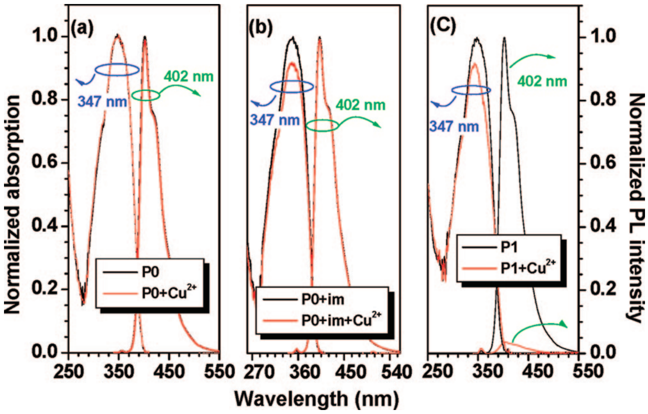


Figure 2. The UV−vis absorption and fluorescence spectra of **P0** (a), the mixture of **P0** and imidazole (im) (b) and **P1** (c) in THF before and after the addition of Cu^{2+}. The polymer concentration was 5.0 × 10^{-6} mol/L. Excitation wavelength (nm): 355.

the reaction of **P0** with imidazole, and a new peak appeared at about 3.8 ppm, which should be ascribed to the methylene groups bonded to imidazole moieties in **P1**, indicating that all the bromine atoms were converted to imidazole moieties during the substitution reaction completely.

Similar to **P0**, **P1** was soluble in common polar organic solvents such as chloroform, THF, DMF, and DMSO, and insoluble in alcohol. This point was not like the case of **PA**, which could not dissolve in the common organic solvents except alcohol, indicating the different role of imidazole moieties in the two polymers, **PA** and **P1**. The UV−vis absorption spectra of polymers were shown in Figure 2, the maximum absorption wavelength of **P1** was the same as that of **P0**, even unchanged in the case of the **P0**-imidazole mixture. **P1** was thermally stable, its TGA thermograms was shown in Figure S2, Supporting Information, with the 5% weight loss temperature at about 402 °C. The glass transition temperature (T_g) of **P1** was investigated to be about 148 °C.

Fluorescence Properties. Generally, polyfluorene derivatives emitted blue light upon excitation with high quantum yields. As demonstrated in Figure 2, both of **P0** and **P1** exhibited strong luminescence in diluted solutions with the maximum emission wavelength at 402 nm. The **P0**−imidazole mixture nearly showed the same emission behavior. The phenomena indicated that the presence of imidazole moieties did not affect the electronic properties of the conjugated polymers, no matter as free small molecules or being bonded to the polymer backbone. However, after the addition of a little amount of Cu^{2+}, the things became different. Although, similar to that of **P0**, the emission spectrum of **P0**−imidazole mixture remained nearly unchanged, the intensity of its absorption spectrum decreased. As to **P1**, the strong luminescent emission was completely quenched by the added Cu^{2+} ions. These results indicated that after being linked to the polymer main chain, the imidazole 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, **P1** could be utilized as polymer chemosensor for metal ions.

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 **P1**. As shown in Figure 3, quenching of photoluminescence was observed at very low level of Cu^{2+} (3.0 × 10^{-8} mol/L), and the fluorescent intensity decreased rapidly upon the increase of the added concentration of Cu^{2+}. While the concentration of Cu^{2+} was 5.0 × 10^{-6} mol/L, nearly no luminescence could be seen. The quenching efficiency was

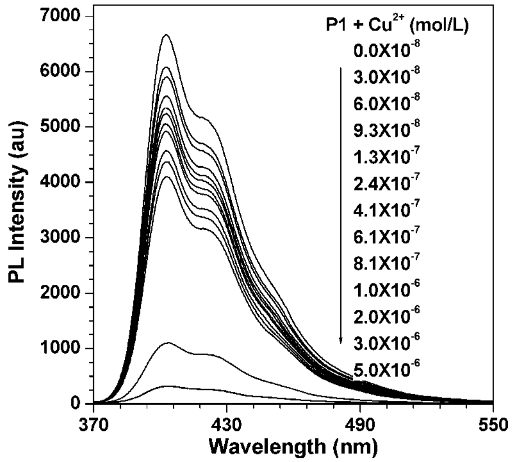


Figure 3. Emission quenching of the solution of **P1** in THF by Cu^{2+}. The polymer concentration: 5.0 × 10^{-6} mol/L. Excitation wavelength (nm): 355.

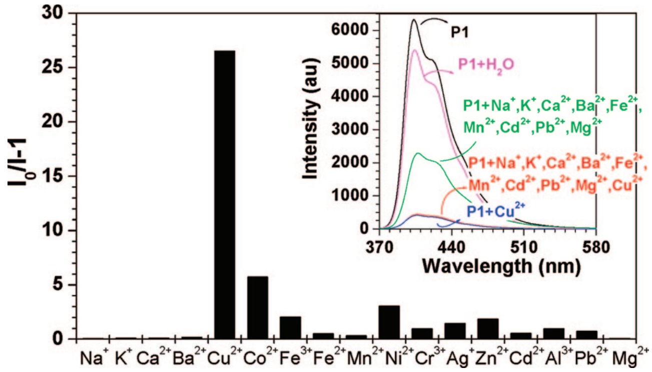
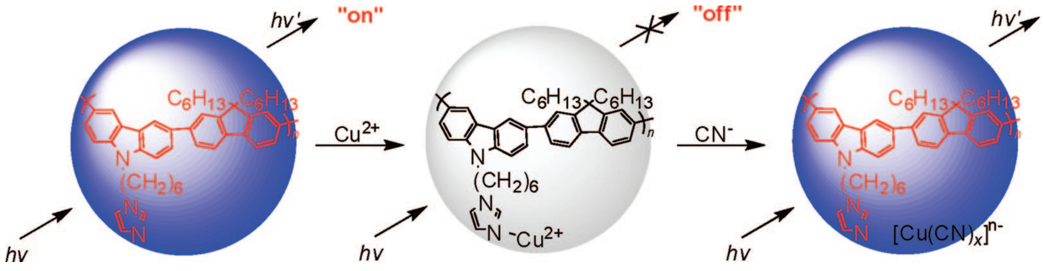


Figure 4. Fluorescence emission response profiles of **P1**. Insert: Emission quenching of the solution of **P1** in THF by Cu^{2+} (3.2 × 10^{-6} mol/L) with and without other metal ions (3.2 × 10^{-6} mol/L). The polymer concentration was 5.0 × 10^{-6} mol/L. Excitation wavelength (nm): 355.

nearly fit to the Stern−Volmer equation, $I_0/I = K_{sv}[A] + 1$, which related 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 **P1** in THF solutions with Cu^{2+}, K_{sv} was determined to be 2.1 × 10^6 M^{-1}. Considering that the introduced trace water in the added Cu^{2+} solution might affect the intensity of **P1** during the fluorescence titration experiments, we studied the influence of the added trace water (Figure S3,Supporting Information). The intensity of **P1** really decreased upon the addition of trace water, however, only at a limited degree, which would not affect the quenching results of the titration experiment.

Some other metal ions were tested to possibly quench the fluorescence of **P1** at the fixed concentration of 3.2 × 10^{-5} mol/L, as shown in Figure S4, Supporting Information, there was nearly no difference between the fluorescence intensity of **P1** in the presence and absence of alkali and alkaline earth metal ions, due to the poor coordination ability of the imidazole receptor with these ions; Mn^{2+}, Fe^{2+}, Cd^{2+}, Cr^{3+}, Pb^{2+}, and Al^{3+} could quench the fluorescence, but not completely; while Ag^+, Zn^{2+}, Fe^{3+}, Ni^{2+}, and Co^{2+} could quench the fluorescence of **P1** more efficiently. Thus, **P1** could act as an efficient chemosensor for the detection of Cu^{2+}, Co^{2+}, and Ni^{2+}. However, all the metal ions could not quench the fluorescence as efficiently as Cu^{2+}. Figure 4 exhibited the difference quenching efficiencies of different metal ions, it was easily seen

Chart 1. Schematic Representation of Cu^{2+} and CN^- Sensors Based on the Fluorescence "Turn-off" and "Turn-on" of P1



that **P1** showed good selectivity for the detection of Cu^{2+}. The influence of other metal ions to the sensing of Cu^{2+} was also conducted (the inset in Figure 4). Without the presence of Cu^{2+}, the fluorescence of **P1** could not be quenched completely, indicating that other metal ions resulted very little disturbance to the selective sensing of **P1** toward Cu^{2+}. The above obtained results were different from those of other conjugated polymers containing imidazole or oligopyridine moieties,[12] indicating that the selectively sensing of metal ions by using imidazole groups as receptor could be adjusted by the choice of different conjugated backbones. This was reasonable, since the various degrees of affinity of imidazole moieties toward metal ions should lead to different influence to the interaction between the imidazole groups and the conjugated polymer backbones, due to their different electronic properties. Also, it was believed that if other receptors were used instead of imidazole ones, different sensing behavior should be observed accordingly. Actually, for example, as reported by Tang et al., the fluorescence of acidic protons carrying polyacetylene could not be quenched completely by the added copper ions,[2g] different from the quenching behavior of PA as discussed above. This partially proved our above points.

From the obtained experimental results, we could conclude that **P1** could report the presence of trace Cu^{2+} ions based on the fluorescence "turn-off", since the imidazole 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. Then, if the interaction between the Cu^{2+} ions and the imidazole moieties was interrupted, or the Cu^{2+} ions did not coordinate with imidazole moieties any longer, the strong luminescence of **P1** might not be quenched. Considering this stuff on another side, if some species, which could interrupt the interaction between the Cu^{2+} ions and the imidazole moieties or snatch the Cu^{2+} ions from the imidazole moieties to form more stable new complexes, were added in the **P1**/Cu^{2+} complex, the quenched luminescence of **P1** might recover. Our previous preliminary experiments realized this idea: upon the addition of CN^-, the quenched luminescence of polyacetylene (**PA**) by Cu^{2+} turned on,[9] since more stable complex between CN^- and Cu^{2+} could be formed with very high stability constant (equation 1 and 2).[13] However, the sensitivity was not satisfied for the potential practical application (70 μM, much higher than the lethal cyanide concentration in the blood of fire victims, 20 μM). Here, **P1** exhibited much higher sensitivity toward Cu^{2+} (3.2×10^{-6} mol/L, that is about 0.2 ppm) than **PA** (1.48 ppm), thus, we expected that the **P1**/Cu^{2+} complex would be more sensitive toward CN^-.

Equation 1: the reaction between Cu^{2+} and CN^-

$$2Cu^{2+}+4CN^{-}=2CuCN+(CN)_2 \quad \text{(CuCN is white precipitant)} \qquad (1)$$

Equation 2: the reaction between CuCN and CN^-

$$CuCN+(x-1)CN^{-}=[Cu(CN)_x]^{1-x} \quad (x = 2, 3, \text{ or } 4, \text{ and generally } 2 \text{ and } 4) \qquad (2)$$

The stability constants (K): $[Cu(CN)_2]^-$, $K = 1.00 \times 10^{24}$; $[Cu(CN)_4]^{3-}$, $K = 2.00 \times 10^{30}$.

Really, the qualitative analysis demonstrated that the addition of CN^- to the **P1**/Cu^{2+} complex turned on the fluorescence of **P1** (Chart 1), verifying the above idea again. Thus, our thought should be a common method to probe anions by utilizing the CPF metal ion chemosensors, but not special example only in the case of disubstituted polyacetylene. The recovering behavior of the fluorescence of the complex of **P1** and Cu^{2+} was studied in detail (Figure S5, Supporting Information). The completely quenched fluorescence of **P1** by Cu^{2+} turned on after the addition of CN^-, at very low concentration (4.0×10^{-6} mol/L). Further increasing the concentration of CN^- led to stronger fluorescence, especially the intensity was enhanced more than two times while the concentration was increased from 8.0×10^{-6} to 1.0×10^{-5} mol/L. When the added concentration of CN^- was 1.2×10^{-5} mol/L (0.31 ppm), the fluorescent intensity could recover to more than 80% of the original intensity of **P1** without Cu^{2+}, and this intensity was strong enough to be used as "turn-on" to probe trace CN^- (the difference between the "off" and "on" state was also shown in the inset in Figure 5). Thus, by applying a "turn-off-turn-on" circle, **P1** was both selective chemosensor for Cu^{2+} and sensitive one for CN^-. To exclude the possibility of the fluorescent signal response of **P1** toward CN^- directly without the presence of Cu^{2+}, another control experiment was conducted: successive aliquots of aqueous solutions of CN^- were added to the diluted solution of **P1**, and the changes of the fluorescence spectra were recorded. As shown in Figure S6, Supporting Information, no changes could be observed before and after the addition of the CN^- solutions, even the concentration of CN^- was the same as 1.2×10^{-5} mol/L used in the above experiment. Thus, the obtained results confirmed the speculated mechanism (Chart 1) for the sensing of CN^- again.

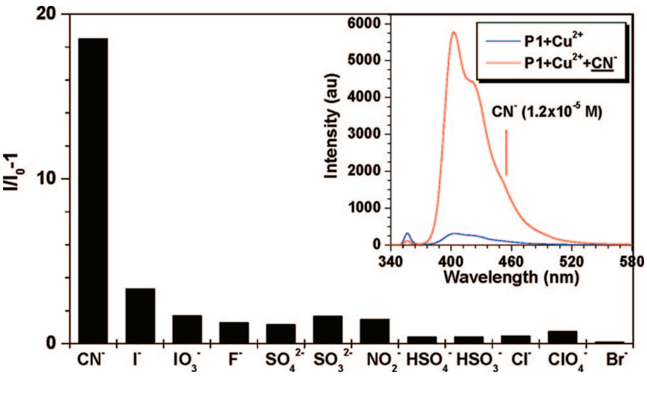


Figure 5. Fluorescence emission response profiles of **P1** + Cu^{2+}. Insert: Fluorescence emission spectra of **P1** in THF after added Cu^{2+} (3.2×10^{-6} mol/L), and turned on by CN^-. The polymer concentration was 5.0×10^{-6} mol/L. Excitation wavelength (nm): 355.

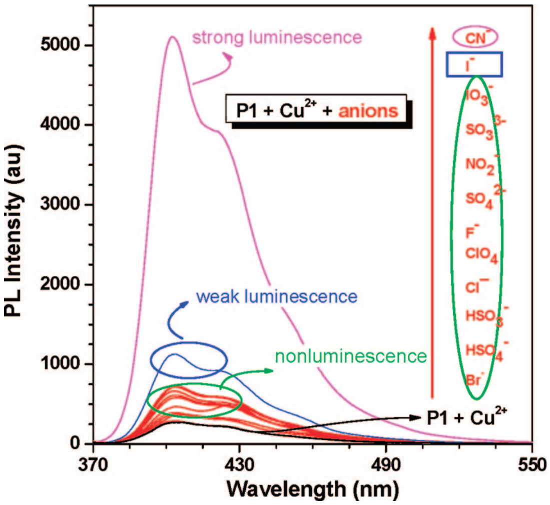


Figure 6. Fluorescence emission spectra of **P1** in THF after the addition of Cu^{2+} (3.2×10^{-6} mol/L), and turned on by CN^- and other anions. The polymer concentration was fixed at 5.0×10^{-6} mol/L, and concentration of all anions was 1.2×10^{-5} mol/L. Excitation wavelength (nm): 355.

To evaluate the cyanide-selective nature of **P1**, the influence of other anions toward the complex of **P1** and Cu^{2+} was investigated (Figure 5-6). Nearly nonluminescence could be observed upon the addition of most of anions at the concentration of 1.2×10^{-5} mol/L, such as F^-, Cl^-, Br^-, ClO_4^-, NO_2^-, and SO_4^-, while the addition of I^- resulted in very weak luminescence. Thus, as shown in Figure 5, except for a little influence from I^-, other anions gave nearly no disturbance to the selective sensing of CN^-, indicating that the selectivity for CN^- was relatively high. Therefore, the experimental results obtained so far confirmed two points mentioned in the introduction part:

1. 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 another word, 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 Cu^{2+} chemosensors.
2. In comparison with our previous polyacetylene,[7] the polyfluorene (**P1**) presented in this paper demonstrated much improved sensitivity toward CN^- (12 μM versus 70 μM). Since the lethal cyanide concentration in the blood of fire victims was ca. 20 μM, **P1** might be utilized as sensitive chemosensor to probe trace CN^- in the practical applications.

Also, if we thought about the deep reason of the different detection limit of **PA** (70 μM, 1.82 ppm) and **P1** (12 μM, 0.31 ppm) toward CN^- by the indirect strategy carefully, the big difference should be derived from the different detection limit of **PA** (1.48 ppm) and **P1** (0.20 ppm) toward Cu^{2+}. It was reasonable. In the detection process for CN^-, Cu^{2+} ions was first added to the diluted solution of the luminescent polymer to quench its fluorescence completely due to the large degree of affinity of imidazole moieties toward the Cu^{2+} ions, then some CN^- anions were introduced to snatch the Cu^{2+} ions from imidazole moieties to interrupt its interaction with the Cu^{2+} ions and hamper the energy transferring from the conjugated polymer backbone to the Cu^{2+} ions, leading to the quenched fluorescence of the polymer turning on. According to Equations 1 and 2, although we did not know exact ratio between the Cu^{2+} ions and CN^- anions, more CN^- anions were needed if larger amount of the Cu^{2+} ions was required for the completely quenching of the fluorescence of the polymer. For example, 1.48 ppm of the Cu^{2+} ions was used to quench the fluorescence of **PA**, then the detection limit of CN^- anions was detected to be 1.82 ppm (70 μM); however, correspondingly, the detection limit of CN^- anions was found to be as low as 0.31 ppm (12 μM), while only 0.20 ppm of the Cu^{2+} ions were needed to quench the fluorescence of **P1** completely.

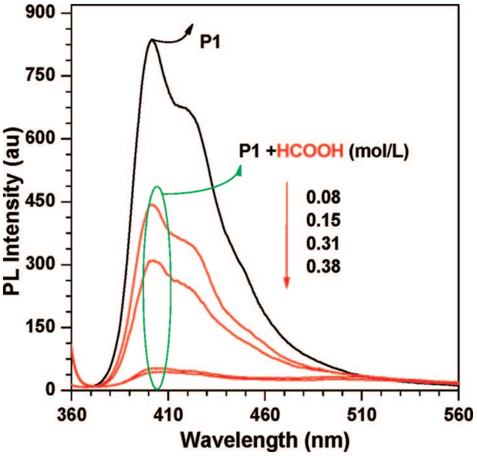


Figure 7. Emission quenching of the solution of **P1** in $CHCl_3$ by HCOOH. The polymer concentration: 5.0×10^{-6} mol/L. Excitation wavelength (nm): 355.

Thus, if we would like to further improve the sensitivity of the CPF chemosensors toward CN^- anions, we should develop new CPF Cu^{2+} ion sensors with even higher sensitivity. Also, we might claim that high sensitive CPF *metal* ion sensors (not only for Cu^{2+} ions) should be developed to obtain better anion chemosensors (not only for CN^- anions). In the past decades, thanks to the great efforts of scientists, many CPF chemosensors were designed, most of which were CPF metal ion sensors, while reports of fluorescent polymer sensors for anions were comparatively scarce. And so far, scientists knew much better how to design good CPF metal ion sensors, than for CPF anion sensors.[8] Therefore, by apply the indirect strategy reported in this paper, it perhaps might be easier to develop new anion chemosensors with good performance. From this point, our example might provide new idea for the further development of novel CPF anion chemosensors.

It was well-known that there is an imidazole group in the molecule of histidine, which plays an important role in human body.[14] The imidazole moieties in histidine could be both of hydrogen donor and acceptor in the acid–base reaction.[15] Encouraged by this point, we thought that perhaps **P1** could be hydrogen acceptor, and might give out some detectable signals upon the addition of acids. As shown in Figure 7, the fluorescence of **P1** in chloroform could be quenched by the addition of formic acid, and no luminescence could be observed while the concentration of formic acid was increased to be 0.31 mol/L. This phenomenon indicated that the imidazole 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. If the solution of **P1** in THF was used instead of the above one, the fluorescence of **P1** could only be quenched a little but not completely, even at the concentration of formic acid as high as 0.68 mol/L (Figure S7, Supporting Information). This might be attributed to the hydrogen-bonding interactions between THF and formic acid molecules, as reported previously.[16] However, if not formic acid, but hydrochloric acid was added to the THF solution of **P1**, the quenching efficiency became higher. At the concentration of 3.0×10^{-5} mol/L, the fluorescent intensity of **P1** was quenched to about 25% of the original one (Figure S8, Supporting Information). Further increasing the concentration

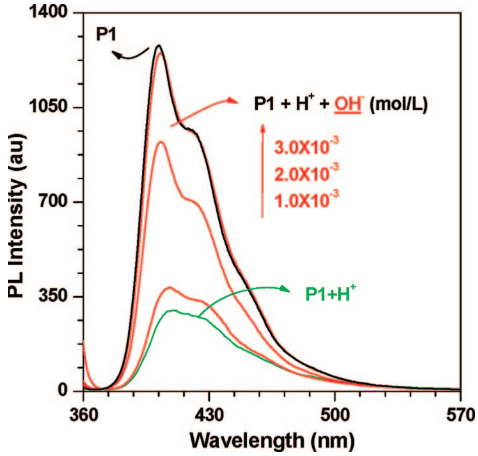


Figure 8. Fluorescence emission spectra of **P1** in THF before and after the addition of H^+, and recovered by the addition of OH^-. The polymer concentration was fixed at 5.0×10^{-6} mol/L. Excitation wavelength (nm): 355.

of hydrochloric acid from 3.0×10^{-5} to 1.0×10^{-4} mol/L, the intensity nearly remained unchanged. This indicated that there might be hydrogen-bonding interactions between THF and hydrochloric acid, which might hamper the coordination of hydrogen ions with imidazole moieties.

Inspired by the fact that the quenched fluorescence of **P1** by Cu^{2+} ions could recover after the Cu^{2+} ions was coordinated with the added CN^- anions, we wondered what would happen if some base was added to the complex of **P1** and hydrochloric acid. Thus, the fluorescence intensity was investigated by adding successive aliquots of aqueous stock solutions of base to the diluted solution of the complex of **P1** and hydrochloric acid. As shown in Figure 8, the fluorescence intensity increased rapidly upon the addition of hydroxyl anions, and recovered to nearly same strong as the original one while the concentration of hydroxyl anions was 3.0×10^{-3} mol/L. These experimental results demonstrated that the diluted solution of **P1** gave response to the changes of the concentrations of hydrogen ions in solutions. Chart S2,Supporting Information, described the possible mechanism for this phenomenon: the imidazole moieties could coordinate with the added hydrogen ions, then the energy could be transferred from the conjugated polymer backbone to the hydrogen ions similar as to the copper ions, leading to the quenching of the fluorescence of the polymer; after the addition of some base, the hydroxyl anions could grab the hydrogen ions from the imidazole moieties to form water, resulting in the recovering of the fluorescence rapidly. However, it was a pity that this process took place in the organic solution, if in aqueous solution, **P1** should be a good pH sensor. The related work was under way in our laboratory.

Conclusions

In summary, we have successfully prepared a new imidazole-functionalized polyfluorene by utilizing the postfunctional strategy, and studied its ability to sense metal ions and anions by the fluorescence spectra. The obtained preliminary results demonstrated that:

1. **P1** could report the presence of trace CN^- anions as low as 0.31 ppm selectively by an indirect strategy, making it good candidate for potential application of human safeguard.

2. The utilization of the metal ion chemosensor to probe anions by an indirect strategy, perhaps, is a novel idea to develop new chemosensors. Thus, the reported good chemosensors for metal ions could be used to sense trace anions. Otherwise, the anion chemosensors could also be applied to detect metal ions.

3. While the sensitivity of CPF Cu^{2+} ion chemosensors was improved, correspondingly, its sensitivity for CN^- anions became higher. So, to obtain satisfied CPF CN^- anions probes, we could try to design new CPF Cu^{2+} ion chemosensors with high sensitivity. Or perhaps, we could claim that to obtain satisfied CPF anions probes, we should try to design new CPF metal ion chemosensors with high sensitivity.

Therefore, our study might provide useful information for the design of new CPF anion chemosensors with high sensitivity and selectivity. Further study was still in progress in our laboratory.

Acknowledgment. We are grateful to the National Science Foundation of China (No. 20674059), the National Fundamental Key Research Program and Hubei Province for financial support.

Supporting Information Available: Figures showing TGA and IR spectra, PL spectra of solutions of **P1** at the presence of different ions with different concentrations or different amount of water, and PL spectra of **P1** in the presence of different acids and charts giving the structure of **PA** and a cartoon picture for the possible mechanism of the change of the fluorescence of **P1** after different treatment. This information is available free of charge via the Internet at http://pubs.acs.org.

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MA8013096