Polymer 50 (2009) 434–440

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

New polyacetylene-based chemosensory materials for the "turn-on" sensing of α-amino acids

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ARTICLE INFO

Article history:
Received 7 August 2008
Received in revised form
9 November 2008
Accepted 13 November 2008
Available online 19 November 2008

Keywords:
Polyacetylene
Chemosensor
Fluorescence "turn-on"

ABSTRACT

For the first time, a new disubstituted polyacetylene (**P1**) was utilized to sense α-amino acids based on a "turn-on" model, through an indirect approach. Thus, first, the strong blue fluorescence of **P1** was quenched by trace copper ions efficiently, then the addition of α-amino acids to the **P1**/Cu^{2+} complex could recover the strong fluorescence of **P1** to report the presence of α-amino acids. Interestingly, the **P1**/Cu^{2+} complex demonstrated much higher sensitivity towards histidine, with the detection limit of ~2 ppm (~1.3×10^{-5} mol/L). With the aid of a normal UV lamp, histidine could be differed from other α-amino acids visually by the observation of its strong blue fluorescence, at the concentration as low as 4.0×10^{-5} mol/L. Due to the convenient synthesis of **P1**, and the so far reported many other conjugated fluorescent polymers, the work reported here might open up a new avenue to develop new biosensors.

1. Introduction

Naturally occurring α-amino acids have attracted much attention and special interest due to their biological prominence. Thanks to the enthusiastic efforts of scientists, many analytical methods have been developed to recognize and sense α-amino acids and their derivatives as guests, such as NMR, UV absorption, fluorescent emission and various separation techniques in the molecular recognition of amino acids [1–8]. Among them, the fluorophore chemosensors were becoming increasingly popular due to their easy use in solution as well as the high sensitivity and selectivity, though only limited reports were concerned on the fluorescence-based recognition of α-amino acids [1–8]. On the other hand, conjugated polymer-based fluorescent (CPF) chemosensors were the hot topic in the research field of chemosensors, 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. Many kinds of CPF chemosensors were designed to probe different analytes, including metal ions, anions, explosives, small organic molecules and biomolecules [9–11]. So far, many biomolecules could be detected sensitively and selectively, such as adenosine triphosphate (ATP), sugars, proteins, DNA [12,13]. However, it seemed that there were no reports concerned on the CPF chemosensors for α-amino acids, possibly due to the difficulty in designing fluorescent chemosensors, which could give out fluorescent signal while interacting with α-amino acids directly.

Polyacetylene (PA) was the archetypal conjugated polymer, the seminal discovery of the metallic conductivity of its doped form has triggered a huge surge of interest on conductive polymers and has spawned an exciting area of research on conjugated polymers. Structurally, PA was a linear polyene chain [–(HC═CH)$_n$–]. The existence of two hydrogen atoms in its repeat unit offered ample opportunity to decorate the backbone with pendants: replacement of hydrogen in each repeat unit by one or two substituents yielded monosubstituted and disubstituted PAs, respectively. Till now, thousands of mono- or disubstituted PAs have been prepared, and the research fields were extended from the initial traditional conductive polyacetylenes to the modern liquid crystals, polymeric light emitting diodes, helical polymers, gas separation membranes, organic–inorganic hybrids, nonlinear optical and magnetic materials, etc. [14–16]. Generally, disubstituted PAs were superior to their monosubstituted counterparts in performance: for example, poly(1-phenyl-1-octyne), a disubstituted PA, strongly resisted thermal decomposition (no molecular weight change detectable after annealing in air at 120 °C for 20 h) and efficiently emitted blue light, while poly(phenylacetylene), a monosubstituted PA, readily degraded and emitted weakly [17]. The stability and strong luminescence of disubstituted PAs made them good candidates as polymer chemosensors. However, there were very scarce reports concerned on the properties of disubstituted PAs as chemosensors, since it was still a big challenge for the preparation of disubstituted

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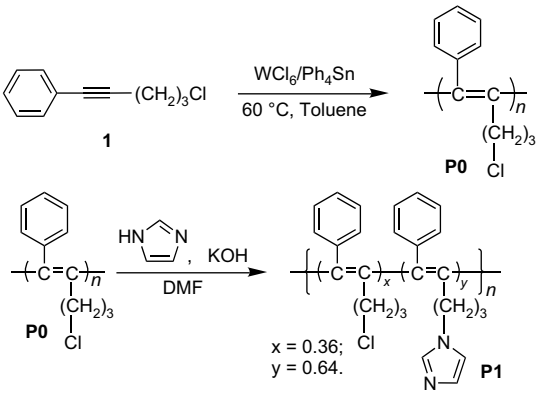
0032-3861/$ – see front matter
doi:10.1016/j.polymer.2008.11.009

PAs containing some acceptor groups to interact with the analytes, such as bipyridyl, terpyridyl, and quinoline segments [17].

Recently, we have successfully prepared some disubstituted polyacetylenes bearing high polar side groups, such as azo moieties, indole groups, amine and pyridine ones, which were inaccessible from the direct polymerization of their corresponding monomers, through the postfunctionalization approach [18]. These results prompted us to design disubstituted PA chemosensors by using the postfunctionalized strategy. Thus, as presented in this paper, we realized this idea, obtained an imidazole-functionalized disubstituted polyacetylene (**P1**) (Scheme 1), which could report



Scheme 1.

the presence of trace copper ions based on the fluorescence "turn-off", and it could also probe the presence of α-amino acids sensitively, by an indirect approach, with the detection limit of histidine as low as ~2 ppm (~2.7×10^{-5} mol/L). Herein, we would like to report the syntheses, characterization, and chemosensing properties of this disubstituted polyacetylene.

1.1. 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. All of the amino acids were purchased from Japan, and other reagents were of analytical reagent grade and used without further purification. Doubly distilled water was used for all experiments.

^{1}H NMR spectroscopic study was conducted with a Varian Mercury300 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as an internal standard, or ^{1}H and ^{13}C NMR spectra were measured on a Bruker ARX 300 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as an internal standard. The Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer-2 spectrometer in the region of 3000–400 cm^{-1}. UV–vis spectra were obtained using a Shimadzu UV-2550 spectrometer. Elementary analysis was taken on a Vario EL III elementary analysis instrument. 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. Photoluminescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer.

1.2. Synthesis of (5-chloro-pent-1-ynyl)-benzene (*1*)

To a 250 mL flask were added copper(I) iodide (90 mg, 0.47 mmol), dichlorobis(triphenylphosphine)palladium (180 mg, 0.26 mmol) and triphenylphosphine (90 mg, 0.34 mmol) in the glove box. Triethylamine (250 mL), iodobenzene (10.2 g, 50 mmol) and 5-chloro-1-pentyne (5.2 g, 50 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 chloroform as eluent. Colorless oil of **1** was obtained in 89% yield (7.9 g). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.41 (dd, $J = 5.4$ Hz, 2H), 7.28 (m, 3H), 3.70 (t, $J = 8.0$ Hz, 2H), 2.60 (t, $J = 8.1$ Hz, 2H), 2.04 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 131.7, 128.5, 127.7, 123.7, 88.1, 81.4, 43.7, 31.5, 16.9.

1.3. Synthesis of *P0*

Into a baked 80 mL Schlenk tube with a stopcock in the sidearm was added monomer **1** (1.14 g). The tube was evacuated under vacuum and then flushed with dry nitrogen three times through the sidearm. Freshly distilled toluene (16 mL) was injected into the tube to dissolve the monomer. The catalyst solution was prepared in another tube by dissolving tungsten(VI) chloride (127.2 mg, 0.32 mmol) and tetraphenyltin (137.6 mg, 0.32 mmol) in toluene (16 mL). The two tubes were aged at 60 °C for 15 min and the monomer solution was transferred to the catalyst solution using a hypodermic syringe. The reaction mixture was stirred at 60 °C for 24 h. The resultant solution was then cooled to room temperature, diluted with chloroform (35 mL), and added dropwise to methanol (2500 mL) through a cotton filter under stirring. The precipitate was allowed to stand overnight, which was then filtered. The polymer was washed with methanol and dried in a vacuum oven to a constant weight, shallow green powder (0.78 g, 68.4%). $M_w = 15\,700$, $M_w/M_n = 2.27$ (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 3064 (Ar–H stretching), 2954, 2870 (CH_2 stretching). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 0.8–2.6 (–CH_2–), 2.6–3.4 (–CH_2–), 6.5–7.8 (ArH). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 140.8, 128.6, 46.2, 33.4, 31.5, 30.6. UV–vis (Ethanol, 1.06×10^{-4} mol/L): λ_{max} (nm): 302 nm.

1.4. Synthesis of *P1*

P0 (89 mg), imidazole (68 mg, 1.0 mmol), potassium hydroxide (140 mg, 2.5 mmol) were added to dry DMF (10 mL). After stirring at 80 °C for 3 days, the resultant mixture was filtered, then the filtrate was added to a dialyzer bag. The bag was immersed in distilled water (the water was changed every 2 h) for several days to remove small molecules, such as imidazole (which would enter into water as its molecular weight is lower than 800). It was observed that some yellow precipitant yielded in the bag during the dialyzing process. The yellow powder was collected, and dried in a vacuum oven to a constant weight (47 mg, 44.7%). ^{1}H NMR (CH_3OD) δ (ppm): 0.9–2.5 (–CH_2–), 2.5–4.4 (–CH_2–), 6.0–7.9 (ArH). Elemental analysis (EA): Found: C 73.09, H 6.62, N 9.02. UV–vis (Ethanol, 1.06×10^{-4} mol/L): λ_{max} (nm): 302 nm.

2. Preparation of solutions of amino acids, Cu^{2+}, histamine, imidazole, acetic acid and BSA

1 mmol of each amino acid was dissolved in distilled water (10 mL) to afford a 0.10 mol/L aqueous solution. 0.1 mmol of Cu^{2+} was dissolved in distilled water (10 mL) to afford a 1×10^{-2} mol/L aqueous solution. 1 mmol of histamine, imidazole or acetic acid was respectively dissolved in distilled water (10 mL) to afford a 0.10 mol/L aqueous solution. 30 mg BSA was dissolved in distilled water (3 mL) to afford a 10 mg/mL aqueous solution. The stock solutions could be diluted to desired concentrations with water when needed.

2.1. Preparation of polymer solutions

P1 (2.0 mg) was dissolved in ethanol to afford the stock solution with the concentration of 5.81×10^{-4} mol/L. This stock solution was diluted to 1.06×10^{-4} mol/L.

2.2. Fluorescence titration of *P1* with Cu^{2+}

A solution of **P1** (1.06×10^{-4} mol/L) was prepared in ethanol. The solution of Cu^{2+} 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. The Cu^{2+} solution was introduced in portions and fluorescence intensity changes were recorded at room temperature each time (excitation wavelength: 335 nm).

2.3. Fluorescence titration of *P1* + Cu^{2+} with amino acids

A solution of **P1** (1.06×10^{-4} mol/L) was prepared in ethanol. The solutions of amino acids were prepared in distilled water (1×10^{-2} mol/L). A solution of **P1** (3.0 mL) was placed in a quartz cell (10.0 mm width) and the fluorescence spectrum was recorded. The solution of Cu^{2+} (1×10^{-2} mol/L, 4 μL) was added to quench the fluorescence. The amino acid solution was introduced in portions and the fluorescence intensity changes were recorded at room temperature each time (excitation wavelength: 335 nm).

2.4. Fluorescence titration of *P1* + Cu^{2+} with imidazole and water

A solution of **P1** (1.06×10^{-4} mol/L) was prepared in ethanol. The solution of imidazole was prepared in distilled water (1×10^{-2} mol/L). A solution of **P1** (3.0 mL) was placed in a quartz cell (10.0 mm width) and the fluorescence spectrum was recorded. The solution of Cu^{2+} (1×10^{-2} mol/L, 4 μL) was added to quench the fluorescence. The imidazole solution or water was introduced in portions and fluorescence intensity changes were recorded at room temperature each time (excitation wavelength: 335 nm).

2.5. Fluorescence intensity changes of *P1* + Cu^{2+} with histamine, imidazole, acetic acid and BSA

A solution of **P1** (1.06×10^{-4} mol/L) was prepared in ethanol. The solutions of histamine, imidazole, acetic acid (1×10^{-2} mol/L) and BSA (1 mg/mL) 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 solution of Cu^{2+} (1×10^{-2} mol/L, 4 μL) was added to quench the fluorescence. The solution of histamine, imidazole, acetic acid or BSA was introduced (12 μL) respectively and fluorescence intensity changes were recorded at room temperature each time (excitation wavelength: 335 nm).

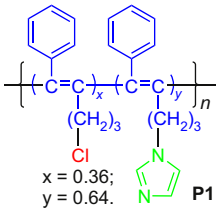
3. Results and discussion

3.1. Synthesis and characterization

P1 was obtained by a postfunctional strategy. As shown in Scheme 1, monomer **1** was easily prepared from the coupling reaction of iodobenzene and 5-chloro-1-pentyne with high yield, by using Pd as catalyst under mild reaction conditions [19]. Then through the direct polymerization, this monomer was successfully converted to its corresponding polymer, **P0**, whose chlorine atoms could be readily substituted by imidazole groups in the presence of a base to give the final product, **P1**. This synthetic route was designed according to our previous case of the disubstituted polyacetylene bearing indolyl moieties in the side chain (Scheme S1) [18c], since both indole and imidazole moieties would be "toxic" to the transition-metal catalysts used in the polymerization process of alkyne monomers. The successful synthesis of **P1** further confirmed that the postfunctionalization strategy was a good alternative approach to yield disubstituted polyacetylenes inaccessible from their corresponding monomers through the direct polymerization reactions. This route avoided the problem that the functional groups poisoned the transition-metal catalysts for acetylene polymerization and opened up a new avenue for attaching polar functional groups to the PA backbone. It should be pointed out that **P0** with chlorine atoms in the side chains could be considered as reactive PA intermediate; it was anticipated that many other functional disubstituted PAs could be prepared by this versatile polymer reaction strategy. And actually, we have successfully partially converted the chlorine atoms to azido groups, and many high polar groups were introduced to the PA backbone through the popular "click" reactions [18a]. Further research on the preparation of functional disubstituted polyacetylenes through the postfunctionalization strategy was still under way in our laboratory.

The purification procedure was very simple; we only needed to isolate monomer **1** by a silica gel column and **P0** could be purified easily by precipitations from their THF solutions into methanol. After most of the chlorine atoms in **P0** were converted to imidazole moieties, the solubility of the resultant polymer **P1** changed dramatically: **P1** could dissolve in alcohol, in contrast to most of the reported disubstituted polyacetylenes. Thus, after the polymer reaction between **P0** and imidazole in DMF, the reaction mixture was filtered to remove some inorganic salt and the excess base, the filtrate was added to a dialyzer bag, which was immersed in distilled water for several days to remove small molecules, such as imidazole. The yellow precipitate in the bag during the dialyzing process was collected, and dried in a vacuum oven to give **P1**.

Monomer **1** and polymers **P0** and **P1** were well characterized, and gave satisfactory data corresponding to their expected molecular structures (see Experimental section and Supporting information). As it was not an easy way to estimate the exact concentration of imidazole moieties in **P1** from its ^{1}H NMR spectrum (Figs. S2 and S3), the results of the elemental analysis were used to calculate the ratio of chlorine atoms and the imidazole groups, which was determined to be about 36:64 as follows:



x and y were calculated according to the results of elementary analysis. EA: Found: C 73.09, H 6.620, N 9.015.

$$\left.\begin{array}{l}(2 \times 14.01)y/(210.27y + 178.66x) \times 100\% = 9.015\% \\ x + y = 1\end{array}\right\} \begin{array}{l} x = 0.36 \\ y = 0.64 \end{array}$$

3.2. Optical properties

UV–vis absorption spectra of polymers are demonstrated in Fig. 1. The absorption peaks of **P0** and **P1** at about 302 nm could be assigned to the π–π^* transition of the PA conjugated backbone, indicating that the linkage of the imidazole moieties to the PA backbone did not influence the absorption behavior in a larger degree. However, upon excitation, the maximum emission

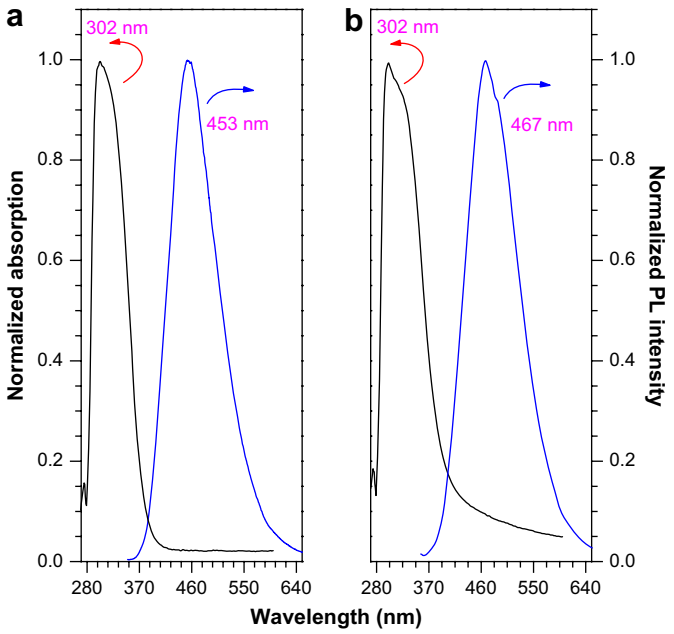


Fig. 1. The UV–vis absorption and fluorescence spectra of **P1** (a) and **P0** (b) in ethanol. The polymer concentration is 1.06×10^{-4} mol/L. Excitation wavelength (nm): 335.

wavelength of **P1** was blue-shifted 14 nm, in comparison with **P0**. This disclosed that there might be still some interactions between the PA backbone and the introduced imidazole groups, leading to the big difference in the emission process, although the excitation wavelength was the same. And this interaction might offer **P1** the chemosensing ability towards analytes, due to the metal ion-coordinating ability of imidazoles.

In the reported literature [20], other conjugated polymers containing imidazole moieties demonstrated good selective sensing property for copper ions with high sensitivity, thus, we checked if **P1** could report the presence of trace copper ions based on the fluorescence "turn-off". As shown in Fig. 2, **P1** demonstrated

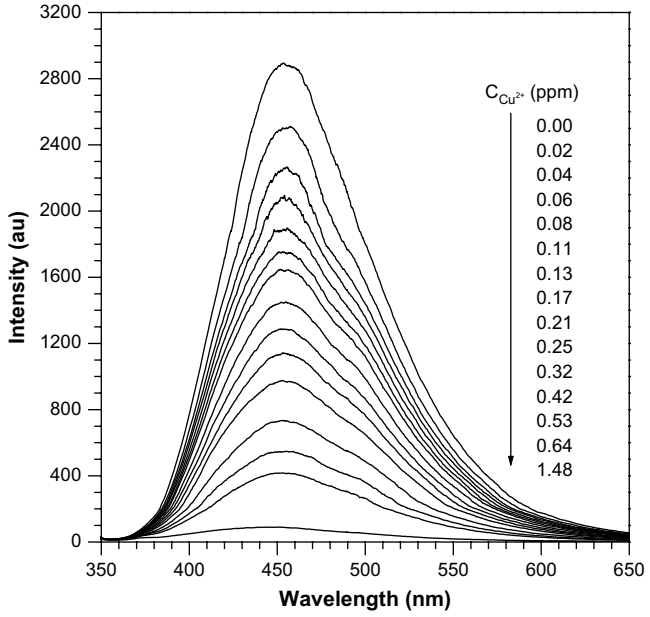
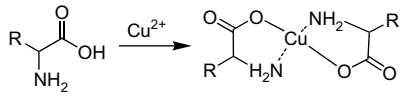


Fig. 2. Emission quenching of the solution of **P1** by Cu^{2+}. Polymer concentration: 1.06×10^{-4} mol/L. Excitation wavelength (nm): 335.

sensitive response to the added trace copper ions (Fig. 2), due to the affinity of imidazole moieties towards copper ions: the quenching of the fluorescence of **P1** was observed at very low level of Cu^{2+} (0.02 ppm), and the fluorescent intensity decreased rapidly upon the increase of the added concentration of Cu^{2+}. While the concentration of Cu^{2+} was 1.48 ppm, 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 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** with Cu^{2+}, K_{sv} was determined to be 3.7×10^5 M^{-1}.

It was known that α-amino acids could form stable complexes with some metal ions, i.e. copper ions (Scheme 2) [21]. Thus, if some α-amino acids were added into the solution of the **P1**/Cu^{2+} complex, the added α-amino acid might snatch the copper ions from the **P1**/Cu^{2+} complex to form a 2:1 amino acid/Cu^{2+} complex as shown in Scheme 2. If this was the case, the quenched strong fluorescence of **P1** might recover, while the copper ions, actually the quencher, were snatched by the added α-amino acid.



Scheme 2.

To test the above idea, Glycine (Gly) was added to the solution of the **P1**/Cu^{2+} complex, immediately, the quenched fluorescence of **P1** turned on (Fig. 3) at the concentration as low as 7.0×10^{-6} mol/L. While the concentration of Gly increased, the intensity increased rapidly, and the fluorescent intensity could recover to about 87% of the original one of **P1**, when the concentration of Gly was about 6.5×10^{-4} mol/L. Thus, the obtained results confirmed that the **P1**/Cu^{2+} complex could report the presence of α-amino acids. Or in another word, **P1** could sense trace copper ions based on the fluorescence "turn-off", then the quenched fluorescence of **P1** could be recovered upon the addition of the α-amino acid, making **P1** a new chemosensor for α-amino acids based on the fluorescence "turn-on". Thus, this was an indirect approach for **P1** to probe α-amino acids, and we could summarize the cycle of "turn-off–on" more visually as demonstrated in Scheme 3.

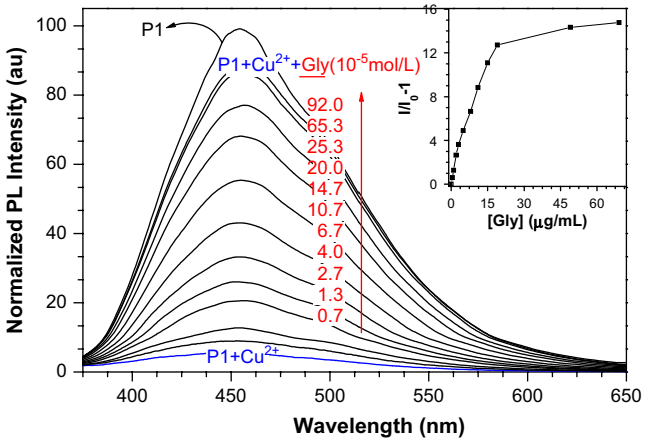
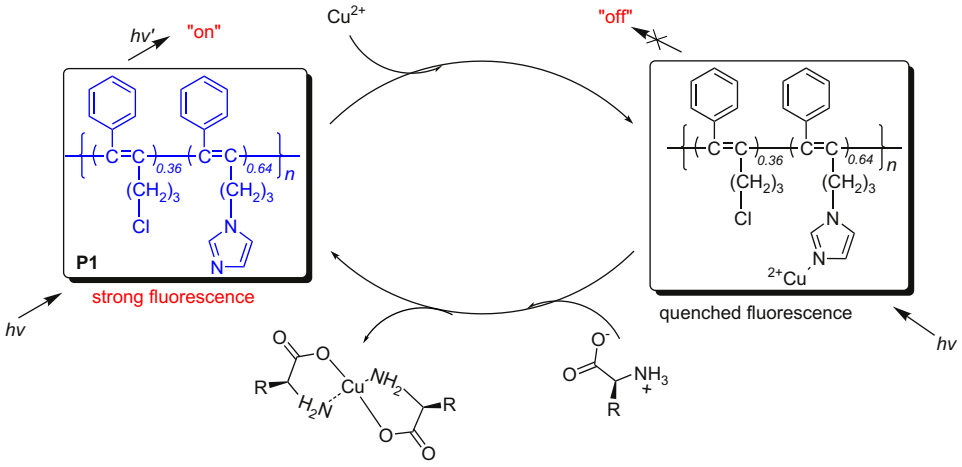


Fig. 3. Fluorescence emission spectra of **P1** before and after the addition of Cu^{2+}, and fluorescence titration of **P1** + Cu^{2+} with increasing amounts of Gly. The polymer concentration is fixed at 1.06×10^{-4} mol/L. Excitation wavelength (nm): 335. Inset: emission difference $(I/I_0 - 1)$ *versus* the concentration of Gly. I_0: the emission intensity of **P1** + Cu^{2+}; I: the emission intensity of **P1** + Cu^{2+} + Gly.



Scheme 3.

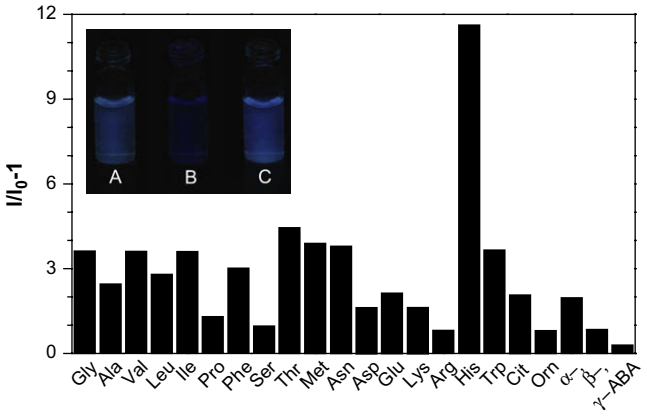


Fig. 4. Fluorescence emission response profiles of **P1** + Cu^{2+} towards amino acids. The polymer concentration is fixed at 1.06×10^{-4} mol/L, while those of amino acids are 4.0×10^{-5} mol/L. Inset: the photographs of solutions of **P1** (A), the complex of **P1** and copper ions before (B) and after (C) the addition of His, taken under UV illumination.

To check whether the method was a common one for all the α-amino acids or just special case for Gly, we repeated the experiment by utilizing other α-amino acids (their structures are shown in Chart S1) instead of Gly. As shown in Figs. S4–S40, all the other α-amino acids could be detected, indicating that this indirect approach was a normal method to probe α-amino acids. However, different α-amino acids demonstrated different sensitivity, in accordance with their different structure. Among them, the detection of histidine (His) demonstrated even higher sensitivity with the detection limit lower than 1.3×10^{-5} mol/L (2.1 ppm) (Fig. S33), and the fluorescent intensity of **P1** could recover to about 88% at the concentration as low as 1.1×10^{-4} mol/L. Because of the high sensitivity of **P1** towards His, we wondered if it was possible to know the presence of His at very low concentration just with the aid of a normal UV lamp, but not a fluorescence spectrophotometer. As shown in the photographs of the solutions of **P1**, the **P1**/Cu^{2+} complex before/after the addition of His, under UV illumination (Inset in Fig. 4), really, the difference was apparent and could be observed visually, even the concentration of His was only 4.0×10^{-5} mol/L.

The difference between His and other α-amino acids could be presented more clearly as shown in Fig. 4 and Fig. S41. This indicated that the **P1**/Cu^{2+} complex could probe His selectively to some degree. In the photographs of the solutions of **P1**, the **P1**/Cu^{2+} complex before/after the addition of α-amino acids, under UV illumination (Fig. 5), the difference was also apparent, and the

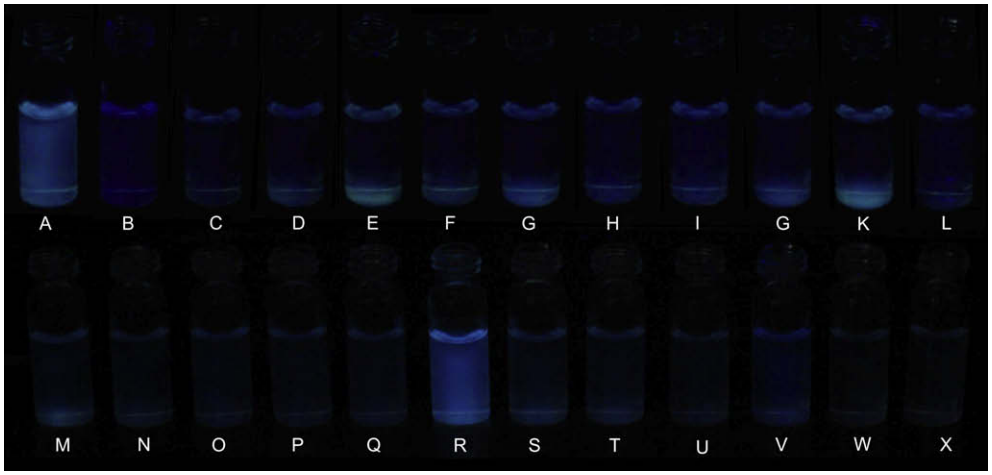


Fig. 5. Photographs of solutions of **P1** (A), **P1** + Cu^{2+} (B), and **P1** + Cu^{2+} + amino acids (C–X): Gly (C), Ala (D), Val (E), Leu (F), Ile (G), Pro (H), Phe (I), Ser (J), Thr (K), Met (L), Asn (M), Asp (N), Glu (O), Lys (P), Arg (Q), His (R), Trp (S), Cit (T), Orn (U), α-ABA (V), β-ABA (W), γ-ABA (X), taken under UV illumination. The concentrations of **P1** and Cu^{2+} were 1.06×10^{-4} and 1.33×10^{-5} mol/L, respectively. The concentration of all the amino acids was fixed at 4.0×10^{-5} mol/L.

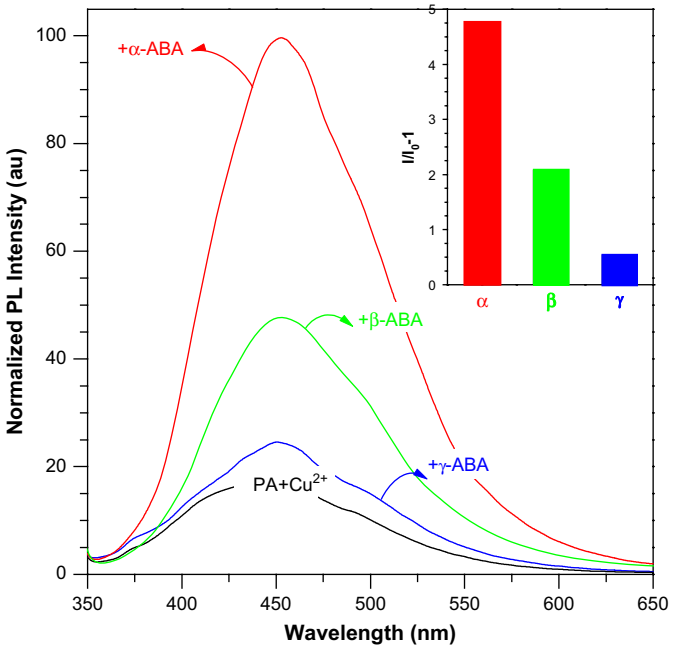


Fig. 6. Fluorescence emission spectra of P1 + Cu^{2+}, before and after the addition of α-, β- and γ-aminobutyric acids (ABAs) (1.47×10^{-4} mol/L), respectively. Inset: fluorescence emission response profiles of **P1** + Cu^{2+} upon the addition of ABAs. The polymer concentration is 1.06×10^{-4} mol/L. Excitation wavelength (nm): 335.

bottle of His (R) could be differed visually. Thus, with the aid of an UV lamp, His could not only be detected but also differed selectively. In the literature, there were reports concerned on the selective sensing of His over other α-amino acids, since His could form more stable 2:1 amino acid/Cu^{2+} complex [7a].

Some of the related analytes were used to evaluate the α-amino acid-selective nature of **P1**, such as imidazole, acetic acid, *n*-butylamine, histamine and BSA. Also, to know the affect of water in the added α-amino acid solutions, the influence of pure water on the fluorescent signal was studied. As shown in Figs. S42 and S43, it was easily seen that these analytes nearly gave no disturbance to the selective sensing of amino acids. Thus, the selectivity of **P1** for amino acids over other related analytes was relatively high.

Considering there were generally three isomers of amino acids, α-, β- and γ-amino acids, we would like to study if **P1** could give different response to them. Accordingly, α-, β- and γ-aminobutyric acids (ABAs) (Chart S2) were used to evaluate the selectivity of **P1** towards α-amino acids. As shown in Fig. 6, while the addition of α-ABA turned on the strong fluorescence of **P1**, the **P1**/Cu^{2+} complex only emitted weak fluorescence upon the addition of β- and γ-ABAs, respectively. The difference could be also observed visually (Fig. S50): under the UV illumination, α-ABA-containing Bottle C emitted visible luminescence, while nearly no light could be seen in Bottles D and E, to which β- and γ-ABAs were added respectively. The main reason might be that the complexes of α-amino acids and copper ions were more stable with the formed five-membered rings, than those from β- and γ-amino acids. These results demonstrated that **P1** could be considered as a good selective chemosensor for α-amino acids.

4. Conclusion

In summary, we have successfully prepared a new imidazole-functionalized disubstituted polyacetylene (**P1**) by utilizing the postfunctional strategy. The strong fluorescence of **P1** could be efficiently quenched by trace copper ions. By utilization of the coordinating properties of α-amino acids towards the copper ions, the quenched fluorescence of **P1** could turn on upon the addition of α-amino acids, making **P1** a new and good chemosensor for α-amino acids. It is believed that the indirect approach of the "turn-off–on" cycle reported here would benefit the further development of new CPF chemosensors, and many good chemosensors could be developed according to this idea.

Acknowledgments

We are grateful to the National Science Foundation of China (nos. 20674059, 20402011), the National Fundamental Key Research Program, Hubei Province for financial support.

Appendix. Supporting information

It consists of figures of IR spectra, fluorescence emission spectra, the structure of general α-amino acid and α-, β- and γ-aminobutyric acids, photographs. Supplementary data associated with this article can be found in the online version at doi:10.1016/j.polymer.2008.11.009.

References

[1] (a) Tundo P, Fendler JH. J Am Chem Soc 1980;102:1760;
(b) Gafni A. J Am Chem Soc 1980;102:7367;
(c) Corradini R, Sartor G, Marchelli R, Dossena A, Spisni A. J Chem Soc Perkin Trans 2 1992:1979;
(d) Pagliari S, Corradini R, Galaverna G, Sforza S, Dossena A, Marchelli R. Tetrahedron Lett 2000;41:3691.
[2] (a) Lehn JM. Angew Chem Int Ed Engl 1988;27:89;
(b) Cram D. Angew Chem Int Ed Engl 1988;27:1009;
(c) Yan Y, Myrick ML. Anal Chem 1999;71:1958;
(d) Kumar CV, Buranaprapuk A, Sze HC. Chem Commun 2001:297.
[3] (a) Leipert D, Nopper D, Bauser M, Gauglitz G, Jung G. Angew Chem Int Ed 1998;37:3308;
(b) Mizutani T, Wada K, Kitagawa S. J Am Chem Soc 1999;121:11425;
(c) Yang H, Bohne C. J Photochem Photobiol A Chem 1995;86:209;
(d) Godoy-Alcantar C, Nelen MI, Eliseev AV, Yatsimirsky AK. J Chem Soc Perkin Trans 2 1999:353.
[4] (a) Aït-Haddou H, Wiskur SL, Lynch VM, Anslyn EV. J Am Chem Soc 2001;123:11296;
(b) Sasaki S, Hashizume A, Citterio D, Fujii E, Suzuki K. Angew Chem Int Ed 2002;41:3005.
[5] (a) Lin J, Li Z, Zhang H, Pu L. Tetrahedron Lett 2004;45:103;
(b) Ryu D, Park E, Kim DS, Yan S, Lee JY, Chang BY, et al. J Am Chem Soc 2008;130:2394;
(c) Feuster EK, Glass TE. J Am Chem Soc 2003;125:16174;
(d) Czarnik AW. Chem Biol 1995;2:423.
[6] (a) Zhang M, Yu M, Li F, Zhu M, Li M, Gao Y, et al. J Am Chem Soc 2007;129:10322;
(b) Imai H, Munakata M, Uemori Y, Sakura N. Inorg Chem 2004;43:1211;
(c) Fabbrizzi L, Licchelli M, Parotti A, Poggi A, Rabaioli G, Sacchi D, et al. J Chem Soc Perkin Trans 2 2001;11:2108;
(d) Kruppa M, Mandl C, Miltschitzky S, König B. J Am Chem Soc 2005;127:3362.
[7] (a) Folmer-Andersen JF, Lynch VM, Anslyn EV. Chem—Eur J 2005;11:5319;
(b) Severin K, Bergs R, Beck W. Angew Chem Int Ed 1998;37:1634;
(c) Gerley A, Sovago I, Nagypal I, Kiraly R. Inorg Chim Acta 1972:435;
(d) Schmuck C, Bickert V. Org Lett 2003;5:4579.
[8] (a) Hortala MA, Fabbrizzi L, Marcitte N, Stomeo F, Taglietti A. J Am Chem Soc 2003;125:20;
(b) Buryak A, Severin K. Angew Chem Int Ed 2004;43:4771;
(c) Chin J, Lee SS, Lee KJ, Park S, Kim DH. Nature 1999;401:254;
(d) Pagliari S, Corrandini R, Galaverna G, Sforza S, Dossena A, Montalti M, et al. Chem—Eur J 2004;10:2749.
[9] (a) Thomas III SW, Joly GD, Swager TM. Chem Rev 2007;107:1339;
(b) de Silva AP, Gunaratne HQN, Gunnlaugsson T, Huxley AJM, McCoy CP, Rademacher JT, et al. Chem Rev 1997;97:1515;
(c) Beer PD, Gale PA. Angew Chem 2001;113:502;
(d) Martínez-Máñez R, Sancenón F. Chem Rev 2003;103:4419;
(e) Yoon J, Kim SK, Singh NJ, Kim KS. Chem Soc Rev 2006;35:355;
(f) Beer PD, Gale PA. Angew Chem Int Ed Engl 2001;40:486;
(g) Snowden TS, Anslyn EV. Curr Opin Chem Biol 1999;3:740.
[10] (a) Schmidtchen FP, Berger M. Chem Rev 1997;97:1609;
(b) Rudkevich DM, Brzozka Z, Palys M, Visser HC, Verboom W, Reinhoudt DN. Angew Chem Int Ed Engl 1994;33:467;
(c) Gale PA. Coord Chem Rev 2001;213:79;

(d) Sessler JL, Davis JM. Acc Chem Res 2001;34:989;
(e) Lee DH, Kim SY, Hong JI. Angew Chem Int Ed 2004;43:4777.
[11] (a) McQuade DT, Pullen AE, Swager TM. Chem Rev 2000;100:2537;
(b) Kimura M, Horai T, Hanabusa K, Shirai H. Adv Mater 1998;10:459;
(c) Zotti G, Zecchin S, Schiavon G, Berlin A, Perso M. Chem Mater 1999;11:3342;
(d) Liu B, Yu WL, Pei J, Liu SY, Lai YH, Huang W. Macromolecules 2001;34:7932;
(e) Tong H, Wang LX, Jing XB, Wang FS. Macromolecules 2002;35:7169;
(f) Yasuda T, Yamaguchi I, Yamamoto T. Adv Mater 2003;15:293.
[12] (a) Chen L, McBranch DW, Wang HL, Helgeson R, Wudl F, Whitten DG. Proc Natl Acad Sci U S A 1999;96:12287;
(b) Li C, Numata M, Takeuchi M, Shinkai S. Angew Chem Int Ed 2005;44:6371;
(c) Ho HA, Leclerc M. J Am Chem Soc 2004;126:1384;
(d) Shi S, Wudl F. Macromolecules 1990;23:2119;
(e) Wang D, Wang J, Moses D, Bazan GC, Heeger AJ. Langmuir 2001;17:1262;
(f) Gaylord BS, Wang S, Heeger AJ, Bazan GC. J Am Chem Soc 2001;123:6417;
(g) DiCesare N, Pinto MR, Schanze KS, Lakowicz JR. Langmuir 2002;18:7785.
[13] (a) He F, Tang Y, Yu M, Wang S, Li Y, Zhu D. Adv Funct Mater 2006;16:91;
(b) Dwight SJ, Gaylord BS, Hong JW, Bazan GC. J Am Chem Soc 2004;126:16850;
(c) Miranda OR, You CC, Phillips R, Kim IB, Ghosh PS, Bunz UHF, et al. J Am Chem Soc 2007;129:9856;
(d) Rininsland F, Xia W, Wittenburg S, Shi X, Stankewicz C, Achyuthan K, et al. Proc Natl Acad Sci U S A 2004;101:15295;
(e) Andersen JFF, Lynch VM, Anslyn EV. J Am Chem Soc 2005;127:7986.
[14] (a) Masuda T. J Polym Sci Part A Polym Chem 2007;45:165;
(b) Hawker CJ, Wooley KL. Science 2005;309:1200;
(c) Percec V, Rudick JG, Peterca M, Wagner M, Obata M, Mitchell CM, et al. J Am Chem Soc 2005;127:15257;
(d) Okoshi K, Sakurai S, Ohsawa S, Kumaki J, Yashima E. Angew Chem Int Ed 2006;45:8173;
(e) Aoki T, Kaneko T. Polym J 2005;37:717.
[15] (a) Choi SK, Cal YS, Jin SH, Kim HK. Chem Rev 2000;100:1645;
(b) Xu H, Xie B, Yuan W, Sun J, Yang F, Dong Y, et al. Chem Commun 2007:1322;
(c) D'Amato R, Sone T, Tabata M, Sadahiro Y, Russo MV, Furlani A. Macromolecules 1998;31:8660;
(d) Akagi K, Piao G, Kaneko S, Sakamaki K, Shirakawa H, Kyotani M. Science 1998;282:1683;
(e) Ginsburg EJ, Gorman CB, Grubbs RH. In: Stang PJ, Diederich F, editors. Modern acetylene chemistry. Weinheim: VCH; 1995 [chapter 10].
[16] (a) Saunders RS, Cohen RE, Schrock RR. Acta Polym Sci 1987;81:121;
(b) Koltzenburg S, Stelzer F, Nuyken O. Macromol Chem Phys 1999;200:821;
(c) Sedlacek J, Vohlidal J. Collect Czech Chem Commun 2003;68:1745;
(d) Schenning APH, Fransen M, Meijer EW. Macromol Rapid Commun 2002;23:266.
[17] (a) Lam JWY, Tang BZ. Acc Chem Res 2005;38:745;
(b) Lam JWY, Tang BZ. J Polym Sci Part A Polym Chem 2003;41:2607;
(c) Cheuk KKL, Li BS, Tang BZ. Curr Trends Polym Sci 2002;7:41.
[18] (a) Zeng Q, Li Z, Li Z, Ye C, Qin J, Tang BZ. Macromolecules 2007;40:5634;
(b) Li Z, Dong Y, Qin A, Lam JWY, Dong Y, Yuan W, et al. Macromolecules 2006;39:467;
(c) Li Z, Li Q, Qin A, Dong Y, Lam JWY, Dong Y, et al. J Polym Sci Part A Polym Chem 2006;44:5672;
(d) Zeng Q, Cai P, Li Z, Qin J, Tang BZ. Chem Commun 2008:1094;
(e) Li Z, Dong Y, Häußler M, Lam JWY, Wu L, Wong KS, et al. J Phys Chem B 2006;110:2302;
(f) Hua J, Li Z, Lam JWY, Xu H, Sun J, Dong Y, et al. Macromolecules 2005;38:8127.
[19] Li Z, Qin A, Lam JWY, Dong Y, Dong Y, Ye C, et al. Macromolecules 2006;39:1436.
[20] (a) Zhou X, Yan J, Pei J. Macromolecules 2004;37:7078;
(b) Xing C, Yu M, Wang S, Shi Z, Li Y, Zhu D. Macromol Rapid Commun 2007;28:241.
[21] (a) Xing Q, Xu R, Zhou Z, Pei W. Organic chemistry. 2nd ed. Beijing, China: Higher Education Press; 1994;
(b) Everin K, Bergs R, Beck W. Angew Chem Int Ed Engl 1998;37:1635.