SHORT COMMUNICATION

Poly(1-amino-5-chloroanthraquinone): Highly Selective and Ultrasensitive Fluorescent Chemosensor For Ferric Ion

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Abstract Poly(1-amino-5-chloroanthraquinone) (PACA) was firstly synthesized by a chemically oxidative interfacial polymerization. The PACA has been developed as a fluorescent sensor for the determination of Fe(III) in semi-aqueous solution at pH 7.0. The sensor exhibited remarkably high sensitivity toward Fe³⁺ since the fluorescence of the polymer could be significantly quenched even though trace Fe³⁺ was added. The sensor showed a linear fluorescence emission response over a wide concentration range from 1.0×10^{-10} to 1.0×10^{-4} M, with an ultra-low detection limit of 2.0×10^{-11} M. The quenching of the fluorescence was found to be static one due to the formation of non-fluorescent complex in the ground state.

Keywords Poly(1-amino-5-chloroanthraquinone) · Fluorescence · Sensor · Ferric ion

Introduction

In recent years, environmental pollution has been a major concern in industrial societies. The development of various sensors and probes able to detect metal cations in atmosphere,

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soil and water sources is a significant scientific goal. Iron (Fe^{3^+}) plays an important role in metabolic processes, biological materials and environmental samples. The deficiency of Fe^{3^+} in human body leads to anemia, while the excess of Fe^{3^+} causes severe vomiting, diarrhea, abdominal pain, and liver/kidney damage [1, 2]. Besides, both deficiency and overloading of Fe^{3^+} impair cellular functions and induce various disorders in most organisms, leading to neurodegenerative diseases such as Alzheimer's and Parkinson's disease [2]. According to the drinking water standards and health advisories proposed by U.S. Environmental Protection Agency (EPA), the safety amount of iron is limited to 0.3 mg/L (5.36×10^{-6} M) [3, 4]. Hence, the monitoring of trace Fe^{3^+} is an intriguing subject in industrial, environmental and biological analysis.

Up to now, a considerable number of chemosensory systems based on organic low-molecular-weight molecules and conjugated polymers have been applied to Fe^{3+} detection. Among all the systems reported, the chemosensors based on the conjugated polymers with metal cation recognition groups or binding ligands have been demonstrated several advantages over low-molecular-weight sensors in terms of electronic communication and amplification along the skeleton structure [5–9]. They take advantage of the high sensitivity to external structural perturbations and to electron density changes within the polymer skeleton when they interact with metal ions [10–13]. However, only a paucity of research in this field has been focused on conjugated polymers with fluorescent units in the main chain, or as pendant groups, in order to avoid migrating or leaching of small molecules while in use [14]. These fluorescent chemosensors toward Fe³⁺ based on phenothiazylene-containing poly(arylene vinylene), polyfluorenes with phosphonate groups in the side chains, ploypyrene, and epoxy-based polymer have very narrow response range of only one or two orders of magnitude, with an unsatisfactory detection limit of 10^{-5} – 10^{-4} M [15–18]. Such a low sensitivity is obtained because the molecular chains of these conjugated polymers are not entire π -conjugated, and the localized structural perturbation can not cause noticeable changes in the electron density of the entire molecular chain. The aminoanthraquinone polymers containing a moiety of 1,4-benzoquinone groups and the polyaniline-like main chains, is a new class of π -conjugated polymers. They have received an increasing attention because of their superior multifunctionalities including electroconductivity, electroactivity, electrocatalysis, optical activity, heavy metal ion adsorbability, and environmental and thermal stability [19-22]. Particularly, aminoanthraquinone polymers possess fluorescent fused aromatic rings, entire π -conjugated structures, and a large amount of ---NH--, ---N=, ---NH₂, and =-O groups containing lone pair electrons on the polymer chains, thus showing great potential applications in the field of detection of heavy metal ions.

Herein, we report a unique chemically oxidative method using an interface between two immiscible solvents for the synthesis of a novel π -conjugated polymer poly(1-amino-5chloroanthraquinone) (PACA). PACA was unequivocally characterized by ultraviolet–visible (UV–vis) spectroscopy and matrix–assisted laser desorption/ionization time–of– flight mass (MALDI/TOF MS) spectrometry. The ability of PACA to function as a fluorescent probe for Fe³⁺ in aqueous solution was investigated in detail.

Materials and Methods

1-amino-5-chloroanthraquinone (ACA), chromium trioxide (CrO_3) , nitrobenzene $(C_6H_5NO_2)$, perchloric acid $(HClO_4)$, N,N-dimethylformamide (DMF), and other chemicals and organic solvents were procured from Chemical Reagent Corp. in China. All reagents and solvents were of AR grade. Absorbance spectra were recorded on a TU-1901 UV-vis spectrophotometer made by Beijing Purkinje General Instrument Co., Ltd., at a wavelength range of 190-900 nm at a scanning rate of 400 nm/min. The fluorescence excitation and emission spectra were recorded using a LS50B luminescence spectrometer made by PerkinElmer Inc. MALDI/TOF MS of PACA in THF with sinapinic acid as the matrix was recorded on an auto flex speed TOF/TOF mass spectrometer made by Bruker Daltonik GmbH. The atomic emission spectra of Fe³⁺ in actual water samples were recorded on a PS1000 inductively coupled plasma atomic emission spectrometer made by Leeman Labs. in America.

Synthesis of PACA Particles

The chemically oxidative interfacial polymerization for synthesis of the PACA particles in $C_6H_5NO_2$ phase was carried out with CrO_3 as an oxidant in water phase under air. The



Scheme 1 Synthesis of PACA polymer

typical procedure is as follows: ACA (1.2884 g, 5 mmol) and 70 % HClO₄ (750 μ L, 8.75 mmol) were added to 30 mL of C₆H₅NO₂ in a 100 mL conical flask in a water bath at 30 °C and then stirred vigorously for 20 min. An oxidant solution was prepared separately by dissolving the oxidant CrO₃ (1.0029 g, 10 mmol) in 5 mL of distilled water at 30 °C. The ACA monomer solution was then treated with the oxidant solution in one portion. The reaction mixture was magnetically and continuously stirred for 72 h at 30 °C. Subsequently, the



Fig. 1 a The normalized UV–vis absorption spectra of PACA polymer and ACA monomer in DMF; **b** fluorescent excitation (Ex, *left*) and emission (Em, *right*) spectra of PACA (6.03 μ g/mL) in DMF

PACA particles as precipitates were isolated from the reaction mixture by centrifugation and washed with an excess of distilled water and alcohol in order to remove the residual oxidant, water-soluble reduced byproduct, remaining monomer, and oligomers. All of the final polymer particles were left to dry at 80 °C in ambient air for 2 days. The PACA polymer was obtained as very fine solid black powders that are quite different from relatively coarse reddish powders of the ACA monomer. The black color is a characteristic indication of the polymer having a largely π -conjugated chain structure that has been further verified by UV–vis and MALDI/TOF MS analyses. The polymerization yield was calculated on the basis of theoretical molar mass of 255.65 for PACA repeated units.

Fluorescence Detection of Fe³⁺ Ions

PACA solution (9.0 mL of 6.70 μ g/mL) in DMF was added to a 10 mL colorimetric tube, containing 1.0 mL of HEPES– buffered Fe³⁺ solution (pH7.0), then diluted to the mark with DMF. The solution was mixed thoroughly and left to react at room temperature (22 °C) for 5 min. The fluorescence quenching spectra were then recorded (excitation 334 nm; maximum emission 417 nm); the slit widths for the excitation and emission were both set at 5.0 nm. The interfering effects of other metal ions were investigated individually in the presence of the fluorescent PACA. All fluorescence experiments were performed at room temperature (22 °C).

Results and Discussion

The target polymer PACA particles with a yield of 56.5 % was synthesized in one step as described in the following

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Scheme 1 by the facile chemically oxidative interfacial polymerization of 1-amino-5-chloroanthraquinone (ACA). The synthesis was carried out by mixing the ACA/C₆H₅NO₂ as monomer solution and CrO₃/water as an oxidant solution under air. Solubility experiments showed that the polymer is readily soluble in common organic solvents such as *N*,*N*-dimethylformamide (DMF), tetrahydrofuran (THF), dimethyl sulfone (DMSO) and *N*-methyl-2-pyrrolidone (NMP).

The normalized UV-vis spectra of PACA and ACA are shown in Fig. 1a. The UV-vis spectrum of monomer showed a strong absorption band at 267 nm and a weak band at 481 nm, while that of the polymer showed a new strong and broad band at 612 nm. The band at 267 nm is consistent with π - π^* transition of the benzene rings [23, 24], the bands at 403 and 481 nm are assigned to a $\pi - \pi^*$ transition of the anthraquinone moieties while the band at 612 nm is associated with an intramolecular charge transfer of the entire conjugated molecules [25, 26]. This implies that the polymer has long conjugated sequences and a wide conjugated chain length distribution. The fluorescence of PACA was examined using DMF as the solvent in solution at room temperature (22 °C) through the excitation-emission wavelength scans. As shown in Fig. 1b, the fluorescence spectra of PACA represented several excitation peaks at 301, 334 and 385 nm with an excitation maximum of 334 nm, and a strong broad emission band at ca. 414 nm (Fig. 1b), which also indicates the long conjugated sequences. If keeping the other fluorescence spectra test conditions unchanged except to replace the solvent pure DMF with semi-aqueous DMF/H₂O (9:1, v/v), the excitation maximum, relative fluorescence intensities, and profiles of excitation spectrum and emission spectrum underwent almost no change though the emission maximum had a red shift from 414 nm to 417 nm. This means that the presence of small amounts of water in the detection system may have no significant effect on the fluorescence emission. So the







Fig. 3 a Fluorescence spectra of PACA (6.03 µg/mL, ~2.36×10⁻⁵ M with respect to repeat unit) in the absence (blank) and presence of different metal salts $(1.0 \times 10^{-5} \text{ M})$ recorded in a DMF/H₂O (9:1, v/v) solvent system at pH 7.0, excitation wavelength is 334 nm; **b** selectivity plot for PACA where $(F_0 - F)/F_0$ is plotted against each metal ion (F_0 is the fluorescence intensity in absence of metal ion, and F is the intensity when metal ion is present)

PACA fluorescent probe can be used for direct detection of metal ions in water. In the subsequent fluorescence experiments 334 nm was then chosen as optimum excitation wavelength. We could not measure the molecular weight



Fig. 4 Fluorescence spectral changes of PACA (6.03 µg/mL) with different concentrations of Fe³⁺ ion (up to 1.0×10^{-4} M) in DMF/H₂O (9:1, v/v) at pH 7.0 (λ_{exc} =334 nm); inset shows variations of maximum emission wavelength as a function of Fe³⁺ concentration

of PACA by normal gel permeation chromatography (GPC) method due to the high rigidity of polymer chains and strong absorption of the polymer on the column fillers possibly induced by the high polarity groups including =0, -Cl, -NH— and $-NH_2$ on the polymer chains. Instead, the molecular weights of PACA were estimated by MALDI/TOF MS spectrometry. The MALDI/TOF MS spectrum indicates that the PACA has a wide polymer chain length distribution (Fig. 2). The PACA consists mainly of oligomers with 9–14 repeat units, and the longest chain length is up to 24 repeat units. This is consistent with the analyses of UV–vis spectra carried out for PACA. The detected masses for the corresponding oligomers coincide well with the theoretical values, indicating the polymer may have regular chain structures.

The selectivity of PACA as a fluorescent probe for Fe³⁺ was investigated in a DMF/H₂O (9:1, v/v) solvent system at pH7.0 by incubating PACA (6.03 µg/mL; ~2.36×10⁻⁵ M with respect to repeat unit) with a wide range of alkali, alkaline earth, transition, and heavy metal ions (environmentally and biologically important metal ions included) (1.0×10^{-5} M) as their nitrate salts (Fig. 3), and F_0 and F denote the fluorescence intensities of the PACA solution in absence and presence of metal ion, respectively. The

Table 1 Ionic radius (r) and charge density (ρ) of metal ions

Na ⁺	Mg ²⁺	Al ³⁺	K^+	Ca ²⁺	Cr^{3+}	Mn ²⁺	Fe ³⁺	Fe ²⁺	Co ²⁺
0.97	0.66	0.535	1.33	0.99	0.69	0.80	0.55	0.74	0.72
0.26	1.66	4.68	0.10	0.49	2.18	0.93	4.30	1.18	1.28
Ni ²⁺	Cu ²⁺	Zn^{2+}	Ag^+	Cd^{2+}	Ba ²⁺	Ce ³⁺	Hg ²⁺	Pb^{2+}	Bi ³⁺
0.69	0.72	0.74	1.26	0.97	1.34	1.034	1.10	1.32	0.96
1.45	1.28	1.18	0.12	0.52	0.20	0.65	0.36	0.21	0.81
	Na ⁺ 0.97 0.26 Ni ²⁺ 0.69 1.45	Na ⁺ Mg ²⁺ 0.97 0.66 0.26 1.66 Ni ²⁺ Cu ²⁺ 0.69 0.72 1.45 1.28	$\begin{array}{c cccc} Na^{+} & Mg^{2+} & Al^{3+} \\ \hline 0.97 & 0.66 & 0.535 \\ 0.26 & 1.66 & 4.68 \\ Ni^{2+} & Cu^{2+} & Zn^{2+} \\ 0.69 & 0.72 & 0.74 \\ 1.45 & 1.28 & 1.18 \\ \hline \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$					



Fig. 5 A plot of $\log(F_0/F-1)$ as a function of the logarithm of metal ion concentration $(1.0 \times 10^{-10} - 1.0 \times 10^{-4} \text{ M})$ for Fe³⁺, and for Fe³⁺ in the presence of equimolar Al³⁺; Mⁿ⁺ denotes metal ion of Fe³⁺ or Fe³⁺+Al³⁺; inset shows difference fluorescence intensity (ΔF) as a function of the concentration of Fe³⁺ in DMF/H₂O (9:1, v/v) at pH 7.0

addition of Na^+ , Mg^{2+} , K^+ , Ca^{2+} , Fe^{2+} , Ni^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , Ba^{2+} , Hg^{2+} and Pb^{2+} gave negligible changes in the fluorescence profile of PACA, suggesting that acceptors (cations) bound weakly to the receptors (PACA). The addition of Mn²⁺ and Cu²⁺ caused minor enhancements of the fluorescence intensities while the addition of Cr³⁺, Co²⁺, Ce^{3+} and Bi^{3+} led to small fluorescence quenches (Fig. 3a). In contrast, the addition of Fe³⁺ resulted in a substantial quenching (85.9 %) of the original fluorescence intensity although the addition of Al^{3+} also led to a 34.8 % quenching. When a plot of the relative intensity $(F_0 - F)/F_0$ at 417 nm was performed for each metal ion, excellent selectivity was observed for Fe³⁺ over all the tested cations (Fig. 3b). This high selectivity can be interpreted based on the difference in charge densities of metal ions [27], and the charge density (ρ) of a metal ion is defined as the amount of electric charge per unit volume. It is one of the most important characterizations of the relative electrophilicity ability of metal ions. The charge densities of metal ions are calculated according to Eq. (1), and the calculated results are listed in Table 1.

$$\rho = \frac{q}{\frac{4}{3}\pi r^3} \tag{1}$$

Where, q is the formal charge (+1, +2, +3) and r (Å) denotes the Shannon ionic radius [28, 29]. The calculated charge densities of the cations increase as the following

order: $K^+ < Ag^+ < Ba^{2+} < Pb^{2+} < Na^+ < Hg^{2+} < Ca^{2+} < Cd^{2+} < Cd^{2+}$ $Ni^{2+} < Mg^{2+} < Cr^{3+} < Fe^{3+} < Al^{3+}.$ The results indicate that the charge density of Fe^{3+} ion is the biggest among the cations except Al³⁺. As an expression of electrophilicity ability of cations, the charge density of a metal ion is reasonable to be used to interpret the capability of forming a coordination complex with electron-rich ligands. The higher charge density of a cation possesses, the stronger electronic affinity it provides [30]. On the other hand, another important electronic affinity parameter, namely the standard electrode potential, should be taken into account [31]. Fe^{3+} (0.77 V) has a much higher standard electrode potential than Al^{3+} (-1.66 V) even though they possess very close charge densities. That is to say, the Fe³⁺ possesses the strongest electrophilicity ability among the cations mentioned above. The strong coordinate interaction between Fe^{3+} ion and the large π electron conjugated system of PACA in DMF/H₂O (9:1, v/v) dramatically quenches the fluorescence of PACA due to the strong electrophilicity ability of Fe³⁺.

To determine the sensitivity range over which PACA can measure Fe³⁺, a series of solutions were prepared in which the concentration of PACA was kept constant but the concentration of Fe³⁺ was gradually increased. Figure 4 shows that the addition of Fe^{3+} to the solution of PACA induced significant fluorescence quenching. Furthermore, the emission maximum exhibited an obvious blue-shift up to 68 nm at the Fe³⁺ concentration above 5.0×10^{-7} M (inset of Fig. 4) , implying of a strong interaction between Fe³⁺ ions and PACA molecules. The response curve of the PACA-based sensor is illustrated in Fig. 5, and the corresponding linear regression equation and other analytical parameters are listed in Table 2. The linear response range covers from 1.0×10^{-10} to 1.0×10^{-4} M Fe^{3+} in a pH 7.0 DMF/H_2O (9:1, v/v) solution and the limit of detection (LOD) based on the fluorescence titration or at a signal-to-noise ratio of 3 (S/N=3) is as low as 2.0×10^{-11} M (the determination of LOD is described in detail in Supplementary Information). The relative standard deviation (RSD) of 10 determinations of 2.0×10^{-8} M of Fe³⁺ is 3.2 %. For comparison, representative analytical attributes of various fluorescent ferric ion detection methods is summarized in Table S1 (Supplementary Information). Obviously, to the best of our knowledge, the sensor based on PACA gives highest sensitivity toward Fe³⁺. Additionally, a pronounced hypochromic shift of UV-vis

Table 2 Analytical parameters for the determination of Fe(III)

Sample	Linear range (M)	Linear regression equation ([Fe ³⁺], M)	Detection limit (M)	Correlation coefficient (R ²)	RSD (%)
Fe(III)	$1.0 imes 10^{-10} - 1.0 imes 10^{-4}$	$\log(\frac{F_0}{F} - 1) = 2.5957 + 0.36626 \log[\text{Fe}^{3+}]$	2.0×10^{-11}	0.998	3.2

Sample	Fe ³⁺ conce		Relative error (%)			
	this method	d	ICP-AES			
	Test times				Average	
	1	2	3			
Tap water ^a	2.93	2.92	2.88	2.91	3.036	-4.2
Lake water ^a	1.19	1.17	1.25	1.20	1.159	3.5

Table 3 The concentration of $Fe^{3+}(\mu M)$ in actual water samples determined by fluorescence quenching method of this work and by ICP-AES method

^a Tap water sample was collected from our laboratory (Residual rust water in water pipe was discharged before collecting tap water) and used in fluorescence quenching experiments without any treatment. Lake water sample was collected from Dianchi lake in southwest Kunming and filtered three times to completely remove any suspended particles

absorption was observed if adding 10^{-4} M Fe³⁺ to the PACA solution (the resulting UV–vis spectra are not shown) clearly indicating the strong binding nature of PACA toward Fe³⁺ in its ground state [17]. Considering the UV–vis spectral change, the fluorescence quenching effect is most likely resulted from the formation of non-fluorescent PACA–Fe³⁺ complex, which is static quenching [32, 33].

To get further insight into the stoichiometry and the possible structure of the PACA-Fe³⁺ complex, a plot of difference fluorescence intensity ($\Delta F = F_0 - F$) as a function of the concentration of Fe³⁺ was performed. From the inset of Fig. 5 one can see that ΔF value is close to its maximum at the Fe³⁺ concentration of 5.0×10^{-6} M, which can be considered as the complexing leap point because the ΔF value increased very slowly with further addition of Fe³⁺ after the Fe³⁺ concentration reached 5.0×10^{-6} M. The molar concentration of PACA repeat units, calculated from the mass concentration of 6.03 µg/mL for PACA and the theoretical molar mass of 255.65 for PACA repeated units, is about 2.36×10^{-5} M. Thus, the molar ratio of Fe³⁺ to PACA repeat units was found to be approximately 1:5 at the complexing leap point. That is to say, one ferric ion can cause remarkable fluorescence quenching of approximately 5 repeating units of PACA, probably due to the "molecular wire effect" for conjugated polymer [10, 34].

As illustrated in Fig. 3, the only ion of those tested that could interfere with the determination of Fe^{3+} using PACA was Al^{3+} . To prove that PACA is capable of operating in a competitive environment, we performed a titration in which Al^{3+} and Fe^{3+} were present in equimolar concentration. Figure 5 shows the results of this and the plot illustrates a good fit between the Fe^{3+} only samples and those containing both Fe^{3+} and Al^{3+} . This means the binding affinity of PACA toward Fe^{3+} is much greater than that between PACA and Al^{3+} .

The present method was applied to determine real samples like tap water and lake water. In order to determine the total amount of iron ion in the sample, $1 \sim 2$ drops of 0.02 M

KMnO₄ were added to the sample solutions to oxidize Fe^{2+} to Fe^{3+} . The sample solutions were analyzed for Fe(III) without a preconcentration process. The results shown in Table 3 are in good agreement with those obtained by inductively coupled plasma atomic emission spectrometry (ICP–AES) with a little relative error. Therefore, the present method could be applied for the accurate analysis of Fe(III).

Conclusions

In summary, we have successfully synthesized a novel conjugated poly(1-amino-5-chloroanthraquinone) (PACA) by chemically oxidative interfacial polymerization. The polymer fluorescent sensor demonstrated high selectivity and ultra-high sensitivity for Fe³⁺ among common metal ions. The remarkably high sensitivity toward Fe³⁺ is due to the enhanced electronic communication properties of the conjugated polymer. The sensor based on PACA showed a linear fluorescence emission response over a wide Fe³⁺ concentration range from 1.0×10^{-10} to 1.0×10^{-4} M, with an ultra-low detection limit of 2.0×10^{-11} M. PACA is a promising material to fabricate high-performance fluorescent sensor for detection of Fe³⁺.

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