

Cationic conjugated polyelectrolyte-based fluorometric detection of copper(II) ions in aqueous solution

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ABSTRACT

A series of water-soluble cationic polyfluorene copolymer containing 2,2'-bipyridine moieties (PFP-P₁₋₃) in the backbone were designed and synthesized as the fluorescent probes for Cu²⁺ ions. In the absence of the Cu²⁺ ion, the PFP-P₂ exhibits strong fluorescence emission in aqueous solution. Upon adding the Cu²⁺ ion, the PFP-P₂ coordinates to Cu²⁺ ions through weak N···Cu interactions, and its fluorescence is efficiently quenched by the Cu²⁺ ion with a Stern–Volmer constant (K_{SV}) of $1.44 \times 10^7 \text{ M}^{-1}$. The new method has high sensitivity with a detection limit of 20 nM. The minor interference from other heavy metal ions clearly shows that the PFP-P₂ can be used as the Cu²⁺ ion probe with good selectivity.

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1. Introduction

Water-soluble conjugated polymers (CPs) have recently attracted much attention as the optical platforms in highly sensitive chemical and biological sensors [1–12]. In comparison to small molecule counterparts, these CPs coordinate the action of a large number of absorbing units, and exhibit exceptional fluorescence quenching or energy transfer efficiencies in the presence of oppositely charged acceptors and therefore result in the amplification of optical signals for transduction of chemical or biological recognizing events [13,14]. Since heavy metal ions are significant pollutants and essential trace elements in biological systems, many fluorescent sensors of heavy metal ions based on CPs have been developed [1,15–23]. However, the nonaqueous assay requirements for most of these systems prevent their practical application. Although the progress has been made to design sensors for these ions in aqueous solution based on water-soluble CPs [24–28], good selectivity against other interference ions is difficult to achieve using these water-soluble CPs because the binding of metal ions to these materials is driven by nonspecific electrostatic interactions [1]. As a way to circumvent the limitations, Bunz and Kim have applied carboxylated poly(*p*-phenylene ethynylene)/papain complex for selective mercury(II) ion sensing [29]. Recently we have also developed a highly selective mercury(II) ion assay in aqueous solution using water-soluble polythiophene/DNA complex [30]. However,

these biological macromolecules are relatively unstable and expensive. Development of convenient and selective analytical approaches for heavy metal ions in aqueous solution with minor or no interference from other metal ions is still needed [31].

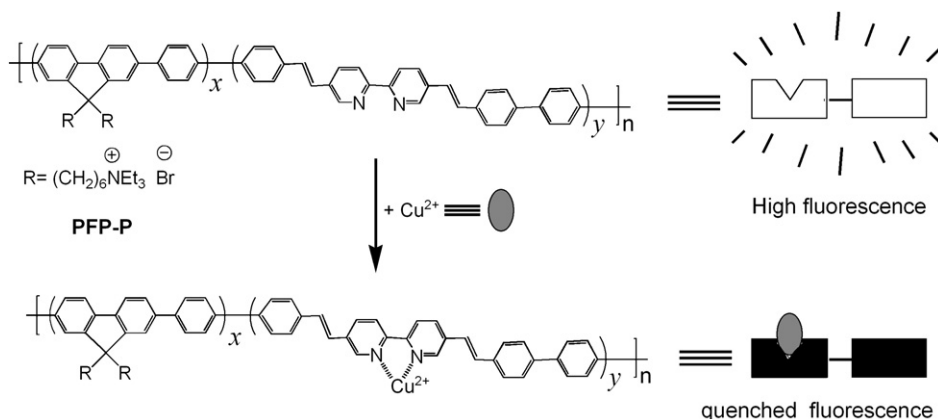
The 2,2'-bipyridine ligand can effectively coordinate transition metal ions and 2,2'-bipyridyl-phenylene-vinylene-based polymers have been used to develop sensitive and selective metal ion sensing [15,16]. However, most of these polymers do not dissolve in water and nonaqueous assay is required. Furthermore their quantum yields are usually lower. Polyfluorene and their derivatives are well-known conjugated polymers that have rigid planar units, high photoluminescence quantum efficiencies and unique chemical and physical properties. Water-soluble polyfluorenes are widely used as optical platforms for highly sensitive chemical and biological sensors [1,2,6,7]. To combine the advantages of 2,2'-bipyridyl-phenylene-vinylene and water-soluble polyfluorenes in sensor application, in this paper we design and synthesize a new series of water-soluble cationic polyfluorene copolymers containing 2,2'-bipyridyl-phenylene-vinylene moieties (PFP-P₁₋₃) in the backbone. Among them, PFP-P₂ can be used as selective and sensitive fluorescent probe to detect Cu²⁺ ions in aqueous medium.

2. Results and discussion

The Cu²⁺ ion detection system functions as outlined in Scheme 1. In the absence of the Cu²⁺ ion, the PFP-P possesses ammonium moieties in the side chain and exhibits strong fluorescence emission in aqueous solution. Upon adding the Cu²⁺ ion, the PFP-P

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Scheme 1. Schematic representation of the Cu^{2+} ion assay based on the fluorescence quenching of the conjugated polymer.

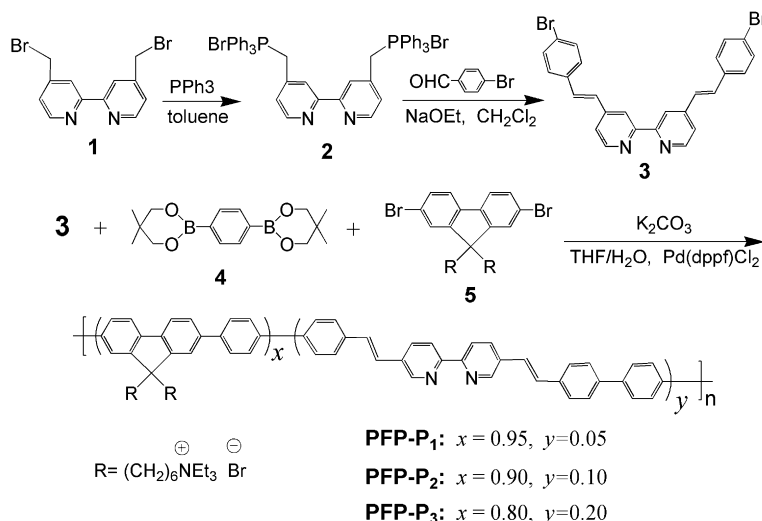
coordinates to Cu^{2+} ions through weak $\text{N}\cdots\text{Cu}$ interactions, and its fluorescence is efficiently quenched by the Cu^{2+} ion [16]. By triggering the change of emission intensity of PFP-P, it is possible to assay Cu^{2+} ions in aqueous solution.

A series of water-soluble cationic polyfluorene copolymers (PFP- P_{1-3} , see Scheme 2 for their chemical structures and synthesis) containing the 2,2'-bipyridine moieties in backbone were designed and synthesized as the fluorescent probe for Cu^{2+} ions. Reaction of 5,5'-dimethyl-2,2'-bipyridine (**1**) with excess triphenylphosphine in toluene under reflux provides compound **2** in 88% yield. Compound **3** was prepared by Wittig condensation reaction of compound **2** with 4-bromobenzaldehyde in anhydrous methylene chloride in the presence of an excess of sodium ethoxide in 24% yield. The PFP- P_{1-3} were synthesized by Suzuki coupling of monomers **3** and **5** with 1,4-phenyldiboronate ester (**4**) in the presence of 2.0 M aqueous K_2CO_3 and catalytic $\text{Pd}(\text{dppf})\text{Cl}_2$ in tetrahydrofuran. The molar feed ratios of monomers **3** to **5** were 5:95, 10:90 and 20:80, respectively, and the corresponding copolymers were referred to as PFP- P_1 , PFP- P_2 and PFP- P_3 . The actual 2,2'-bipyridine ratios for PFP- P_1 , PFP- P_2 , and PFP- P_3 were determined to be 0.08, 13.2, and 17.7%, respectively, which were obtained from their ^1H NMR spectra using the ratio of the integrations of **3** to **5** characteristic proton signals. The crude polymers were purified by dialysis using a dialysis membrane with a cutoff at $M = 7000 \text{ g mol}^{-1}$ for 2 days to afford yellow powders. The UV-vis absorption spectra of these

polymers in water exhibit maximum peak at 381 nm, and the emission spectra show maximum peak at 418 nm (Fig. 1). The fluorescence quantum yield of PFP- P_1 , PFP- P_2 and PFP- P_3 is 33, 26 and 15% in water with 9,10-diphenylanthracene as the standard and that of monomer **3** is 1%. The higher 2,2'-bipyridine content in the copolymer can decrease the fluorescence quantum yield.

Fig. 2 shows the emission spectra of PFP- P_2 in water with a constant concentration ($[\text{PFP-}\text{P}_2] = 1.0 \times 10^{-6} \text{ M}$ in RU) upon successive addition of the Cu^{2+} ion ($[\text{Cu}^{2+}] = 0\text{--}10 \mu\text{M}$) with an excitation wavelength of 380 nm. The addition of the Cu^{2+} ion resulted in a gradual quenching of the PFP- P_2 emission, and a maximum quenching efficiency of 72% was obtained. The quenching efficiencies of PFP- P_1 and PFP- P_3 were also obtained as 60 and 70%, respectively. These results show that the higher 2,2'-bipyridine content in the copolymer is favorable to increase the quenching efficiency, whereas to decrease the fluorescence quantum yield. The lowest concentration of Cu^{2+} ions to be measured was 20 nM. It is demonstrated that the use of water-soluble cationic conjugated polymers provides an approach to detect Cu^{2+} ions with high sensitivity.

The fluorescence quenching response of PFP- P_2 upon adding Cu^{2+} ions was compared to that of monomer **3**. The Stern–Volmer quenching constant (K_{sv}) is determined by monitoring measurable changes in the fluorescence of PFP- P_2 via the Stern–Volmer equation (Eq. (1)) [32]:



Scheme 2. Synthesis of the monomers and PFP- P_{1-3} .

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