

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

Chengfen Xing<sup>a</sup>, Zhiqiang Shi<sup>a,\*</sup>, Minghui Yu<sup>b</sup>, Shu Wang<sup>b,\*</sup>

<sup>a</sup> Department of Chemistry, Shandong Normal University, Shandong Province, Jinan 250014, PR China

<sup>b</sup> Beijing National Laboratory for Molecular Sciences, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, No. 2 Zhongguancun North First, Beijing 100080, PR China

## ARTICLE INFO

### Article history:

Received 22 October 2007

Received in revised form 11 April 2008

Accepted 17 April 2008

Available online 20 April 2008

### Keywords:

Conjugated polyelectrolytes

Copper(II) ions

Fluorescence sensors

## ABSTRACT

A series of water-soluble cationic polyfluorene copolymer containing 2,2'-bipyridine moieties (PFP-P<sub>1-3</sub>) in the backbone were designed and synthesized as the fluorescent probes for Cu<sup>2+</sup> ions. In the absence of the Cu<sup>2+</sup> ion, the PFP-P<sub>2</sub> exhibits strong fluorescence emission in aqueous solution. Upon adding the Cu<sup>2+</sup> ion, the PFP-P<sub>2</sub> coordinates to Cu<sup>2+</sup> ions through weak N···Cu interactions, and its fluorescence is efficiently quenched by the Cu<sup>2+</sup> 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-P<sub>2</sub> can be used as the Cu<sup>2+</sup> ion probe with good selectivity.

© 2008 Elsevier Ltd. All rights reserved.

## 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].

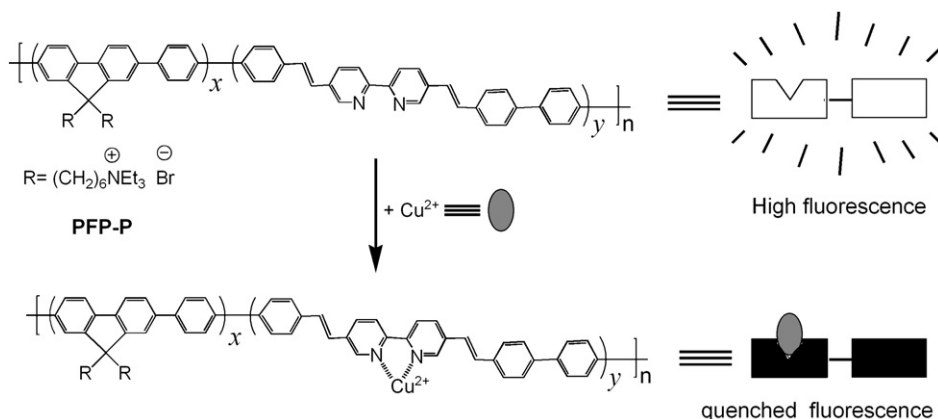
The 2,2'-bipyridine ligand can effectively coordinate transition metal ions and 2,2'-bipyridyl-phenylene-vinylene-based polymers have been used to develop sensitive and selective metal ion sensing [15,16]. However, most of these polymers do not dissolve in water and nonaqueous assay is required. Furthermore 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-P<sub>1-3</sub>) in the backbone. Among them, PFP-P<sub>2</sub> can be used as selective and sensitive fluorescent probe to detect Cu<sup>2+</sup> ions in aqueous medium.

## 2. Results and discussion

The Cu<sup>2+</sup> ion detection system functions as outlined in Scheme 1. In the absence of the Cu<sup>2+</sup> ion, the PFP-P possesses ammonium moieties in the side chain and exhibits strong fluorescence emission in aqueous solution. Upon adding the Cu<sup>2+</sup> ion, the PFP-P

\* Corresponding authors.

E-mail addresses: [zshi@sdu.edu.cn](mailto:zshi@sdu.edu.cn) (Z. Shi), [wangshu@iccas.ac.cn](mailto:wangshu@iccas.ac.cn) (S. Wang).



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

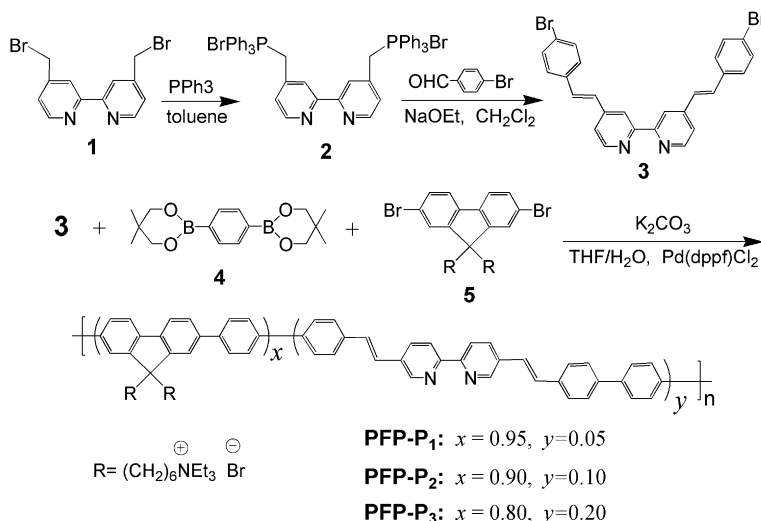
coordinates to  $\text{Cu}^{2+}$  ions through weak  $\text{N}\cdots\text{Cu}$  interactions, and its fluorescence is efficiently quenched by the  $\text{Cu}^{2+}$  ion [16]. By triggering the change of emission intensity of PFP-P, it is possible to assay  $\text{Cu}^{2+}$  ions in aqueous solution.

A series of water-soluble cationic polyfluorene copolymers (PFP- $\text{P}_{1-3}$ , 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  $\text{Cu}^{2+}$  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- $\text{P}_{1-3}$  were synthesized by Suzuki coupling of monomers **3** and **5** with 1,4-phenyldiboronate ester (**4**) in the presence of 2.0 M aqueous  $\text{K}_2\text{CO}_3$  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- $\text{P}_1$ , PFP- $\text{P}_2$  and PFP- $\text{P}_3$ . The actual 2,2'-bipyridine ratios for PFP- $\text{P}_1$ , PFP- $\text{P}_2$ , and PFP- $\text{P}_3$  were determined to be 0.08, 13.2, and 17.7%, respectively, which were obtained from their  $^1\text{H}$  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- $\text{P}_1$ , PFP- $\text{P}_2$  and PFP- $\text{P}_3$  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- $\text{P}_2$  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  $\text{Cu}^{2+}$  ion ( $[\text{Cu}^{2+}] = 0\text{--}10 \mu\text{M}$ ) with an excitation wavelength of 380 nm. The addition of the  $\text{Cu}^{2+}$  ion resulted in a gradual quenching of the PFP- $\text{P}_2$  emission, and a maximum quenching efficiency of 72% was obtained. The quenching efficiencies of PFP- $\text{P}_1$  and PFP- $\text{P}_3$  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  $\text{Cu}^{2+}$  ions to be measured was 20 nM. It is demonstrated that the use of water-soluble cationic conjugated polymers provides an approach to detect  $\text{Cu}^{2+}$  ions with high sensitivity.

The fluorescence quenching response of PFP- $\text{P}_2$  upon adding  $\text{Cu}^{2+}$  ions was compared to that of monomer **3**. The Stern–Volmer quenching constant ( $K_{\text{sv}}$ ) is determined by monitoring measurable changes in the fluorescence of PFP- $\text{P}_2$  via the Stern–Volmer equation (Eq. (1)) [32]:



**Scheme 2.** Synthesis of the monomers and PFP- $\text{P}_{1-3}$ .

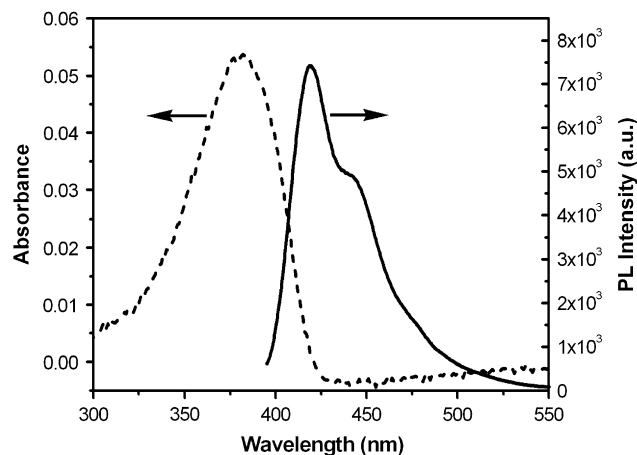


Fig. 1. The absorption and emission spectra of PFP-P<sub>2</sub> in aqueous solution. The excitation wavelength for emission spectra is 380 nm.

$$I_0/I = 1 + K_{sv}[Q] \quad (1)$$

At low concentrations of metal ion (0–4.0  $\mu\text{M}$ ) profiles, linear Stern–Volmer plot for PFP-P<sub>2</sub> was obtained with the  $K_{sv}$  values of  $1.44 \times 10^7 \text{ M}^{-1}$  (see Fig. 3c), which is 100 times greater than that of monomer **3**, indicating that the conjugated polymer chain significantly amplified the quenching.

Fig. 3 shows the emission spectra and the fluorescence quenching efficiency ( $1 - I/I_0$ ) of PFP-P<sub>2</sub> in the presence of various metal ions ( $[\text{PFP-P}_2] = 1.0 \times 10^{-6} \text{ M}$ ,  $[\text{metal ion}] = 3 \times 10^{-5} \text{ M}$  for each). The fluorescence of PFP-P<sub>2</sub> is effectively quenched upon the addition of  $\text{Cu}^{2+}$  ions. The fluorescence of PFP-P<sub>2</sub> is nearly not influenced by the addition of  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  ions. For the other heavy metal ions,  $\text{Hg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Mn}^{2+}$  and  $\text{Pb}^{2+}$ , a small fluorescence quenching of PFP-P<sub>2</sub> is observed, however, the fluorescence quenching efficiencies (20–25%) are also much lower than that of the  $\text{Cu}^{2+}$  ion. Fig. 3c shows the Stern–Volmer plots of PFP-P<sub>2</sub> in the presence of  $\text{Hg}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  ions. The linear Stern–Volmer plots were obtained with the  $K_{sv}$  values of  $1.44 \times 10^7$ ,  $1.45 \times 10^6$ ,  $1.95 \times 10^6$ ,  $1.80 \times 10^6$  and  $2.39 \times 10^6 \text{ M}^{-1}$  for  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Ag}^+$ , respectively. The  $K_{sv}$  value for  $\text{Cu}^{2+}$  ions is approximately 10 times higher than that for  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$  ions, 8

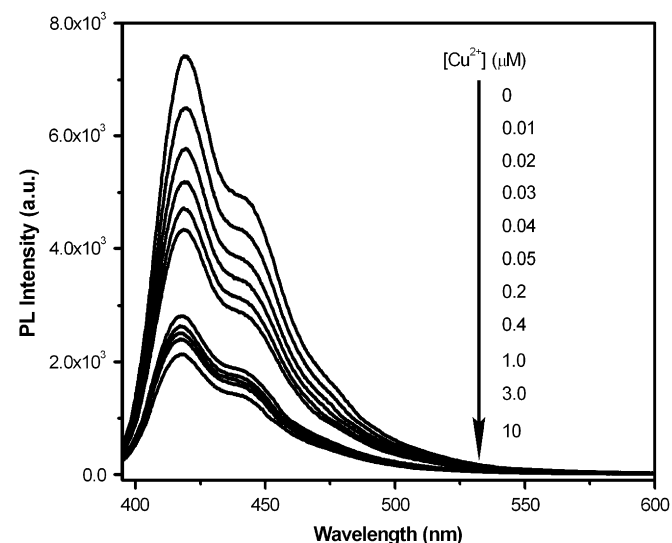


Fig. 2. The fluorescence emission spectra of PFP-P<sub>2</sub> in water with successive addition of  $\text{Cu}^{2+}$  ions.  $[\text{PFP-P}_2] = 1.0 \times 10^{-6} \text{ M}$  in RU,  $[\text{Cu}^{2+}] = 0\text{--}1.0 \times 10^{-5} \text{ M}$ . The excitation wavelength is 380 nm.

times higher than that for  $\text{Hg}^{2+}$  ions and 6 times higher than that for  $\text{Ag}^+$  ions (Fig. 3d). It can be easily recognized that the PFP-P<sub>2</sub> has specific recognition ability for the  $\text{Cu}^{2+}$  ion.

To study the effect of copolymer composition on the selectivity to metal ions, the fluorescence quenching efficiency ( $1 - I/I_0$ ) of PFP-P<sub>1</sub> and PFP-P<sub>3</sub> was also studied in the presence of various metal ions ( $[\text{PFP-P}_1 \text{ or PFP-P}_3] = 1.0 \times 10^{-6} \text{ M}$ ,  $[\text{metal ion}] = 3 \times 10^{-5} \text{ M}$  for each) (Fig. 4). For PFP-P<sub>1</sub> with lowest 2,2'-bipyridine content, the selectivity to other heavy metal ions except for  $\text{Hg}^{2+}$  ions is a little smaller than that of PFP-P<sub>2</sub> due to the decreased fluorescence quenching efficiency upon the addition of  $\text{Cu}^{2+}$  ions. For PFP-P<sub>3</sub> with highest 2,2'-bipyridine content, the fluorescence quenching efficiencies are increased upon adding most of other heavy metal ions in comparison to those for PFP-P<sub>2</sub>, which also lower the selectivity of  $\text{Cu}^{2+}$  ion detection.

For the  $\text{Cu}^{2+}$  ion detection, one of the essential requirements is minor or no interference from mixed other heavy metal ions. The fluorescence signal response of the PFP-P<sub>2</sub> to  $\text{Cu}^{2+}$  ion was examined in the presence of other metal ions (Fig. 5). To the solution of PFP-P<sub>2</sub> in aqueous solution mixed metal ions ( $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ag}^+$ ) were added, the integrated fluorescence intensity of PFP-P<sub>2</sub> was quenched by approximately 30%. After  $\text{Cu}^{2+}$  ion was added to the mixture solution, the fluorescence intensity of PFP-P<sub>2</sub> significantly decreased and about 70% fluorescence of PFP-P<sub>2</sub> was quenched. The minor interference from other metal ions clearly shows that the PFP-P<sub>2</sub> can be used as  $\text{Cu}^{2+}$  ion probe with good selectivity.

To gain insight into the optical response mechanism of the PFP-P<sub>2</sub> to  $\text{Cu}^{2+}$  ions, we studied the absorption spectra of PFP-P<sub>2</sub> in the presence of  $\text{Cu}^{2+}$  ions. As shown in Fig. 6a, the absorbance intensity of PFP-P<sub>2</sub> and its absorption maximum at about 381 nm in the presence of  $\text{Cu}^{2+}$  ions were hardly shifted in comparison to those of PFP-P<sub>2</sub> itself. It was noted that the absorption spectrum of PFP-P<sub>2</sub> may not be altered significantly upon adding  $\text{Cu}^{2+}$  ions due to the low content of 2,2'-bipyridine moieties in the polymer backbone. Thus the electrochemical behavior of monomer **3** and PFP-P<sub>2</sub> was investigated by cyclic voltammetry (CV). As shown in Fig. 6b and c, the oxidation potentials of monomer **3** were increased in the presence of  $\text{Cu}^{2+}$  ions, however, those of PFP-P<sub>2</sub> (1.44 and 1.25 V) were decreased to 1.03 V upon adding  $\text{Cu}^{2+}$  ions (the peaks at 0.38 and 0.78 V are due to  $\text{Cu}^{2+}$  ions). It implies that the fluorescence quenching of PFP-P<sub>2</sub> originates from the changes in the electron density along the polymer backbone [1,22].

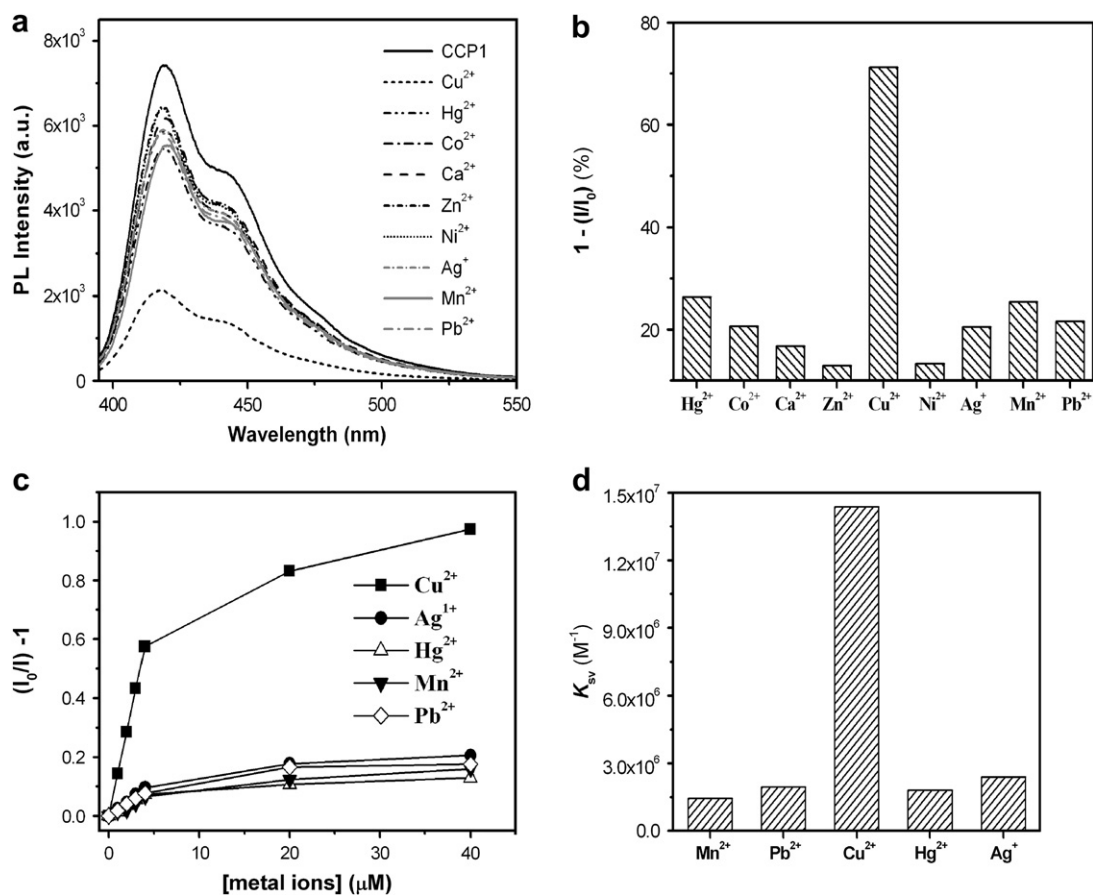
### 3. Conclusions

In summary, we report a fluorescent detection for  $\text{Cu}^{2+}$  ions in aqueous solution with good sensitivity and minor interference from other metal ions using a cationic polyfluorene copolymer containing 2,2'-bipyridine moieties in the backbone. The fluorescence quenching of the conjugated polymer is mainly attributed to the changes in the electron density along the polymer backbone. The assay benefits from the sensitivity of optical signals from conjugated polymers and the simplicity of fluorescence measurement techniques. To improve the selectivity of  $\text{Cu}^{2+}$  ion detection, it will be our further work in the near future to synthesize cationic conjugated polymers containing functional groups that bind  $\text{Cu}^{2+}$  ions more specifically and tightly.

### 4. Experimental part

#### 4.1. Materials and measurements

Starting materials were purchased from Aldrich Chemical Company or Alfa-Aesar and used without further purification. 5,5'-Dimethyl-2,2'-bipyridine (**1**) [33] and 2,7-dibromo-9,9-bis(6-



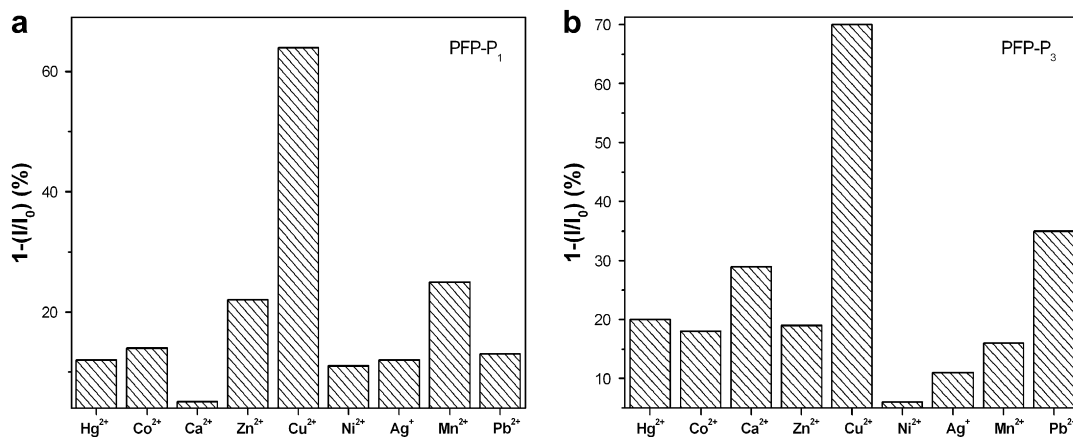
**Fig. 3.** Fluorescence spectra (a) and fluorescence quenching efficiencies (b) of PFP-P<sub>2</sub> ([PFP-P<sub>2</sub>] = 1.0 × 10<sup>-6</sup> M in RU) in the presence of various metal ions (each 3.0 × 10<sup>-5</sup> M) in aqueous solution; Stern-Volmer plots (c) and K<sub>sv</sub> value (d) of PFP-P<sub>2</sub> in the presence of various metal ions. [PFP-P<sub>2</sub>] = 1.0 × 10<sup>-6</sup> M in RU, [metal ion] = 0–4.0 × 10<sup>-5</sup> M. The excitation wavelength is 380 nm.

*N,N,N*-triethylammoniumhexyl)fluorene (**5**) [34] were prepared according to the literature procedure. The <sup>1</sup>H NMR spectra were recorded on AV400 spectrometer. UV-vis absorption spectra were taken on a JASCO V-550 spectrometer. Fluorescence measurements were obtained in a 3 mL quartz cuvette at room temperature using a Hitachi F-4500 fluorometer equipped with a Xenon lamp excitation source. The measurements were all in water solution. The cyclic voltammetry experiments were performed at room temperature in dried acetonitrile/DMSO (9:1) solutions containing 0.04 M TBAPF<sub>6</sub> as supporting electrolyte. A three-electrode

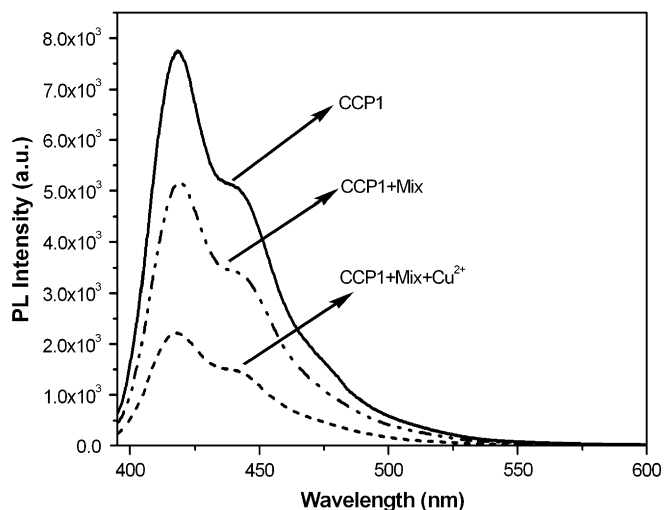
configuration consisting of a glassy carbon working electrode, a Pt counter electrode and an Ag wire quasi-reference electrode was used. The scan rate is 50 mV/s. The water was purified using a Millipore filtration system.

#### 4.2. Synthesis of compound 2

A solution of compound **1** (100 mg, 0.29 mmol) and triphenylphosphine (380 mg, 1.45 mmol) in 20 mL toluene was refluxed for 2 h. The precipitate was filtered off while the suspension was still



**Fig. 4.** Fluorescence quenching efficiencies of PFP-P<sub>1</sub> and PFP-P<sub>3</sub> in the presence of various metal ions in aqueous solution. [PFP-P<sub>1</sub> or PFP-P<sub>3</sub>] = 1.0 × 10<sup>-6</sup> M in RU, [metal ion] = 3.0 × 10<sup>-5</sup> M. The excitation wavelength is 380 nm.



**Fig. 5.** Fluorescence emission spectra of solutions containing PFP-P<sub>2</sub>, a mixture of metal ions (mix: Pb<sup>2+</sup>, Hg<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, and Ag<sup>+</sup>, each  $3.0 \times 10^{-5}$  M) and Cu<sup>2+</sup> ions in water. [PFP-P<sub>2</sub>] =  $1.0 \times 10^{-6}$  M in RU, [Cu<sup>2+</sup>] =  $3.0 \times 10^{-5}$  M. The excitation wavelength is 380 nm.

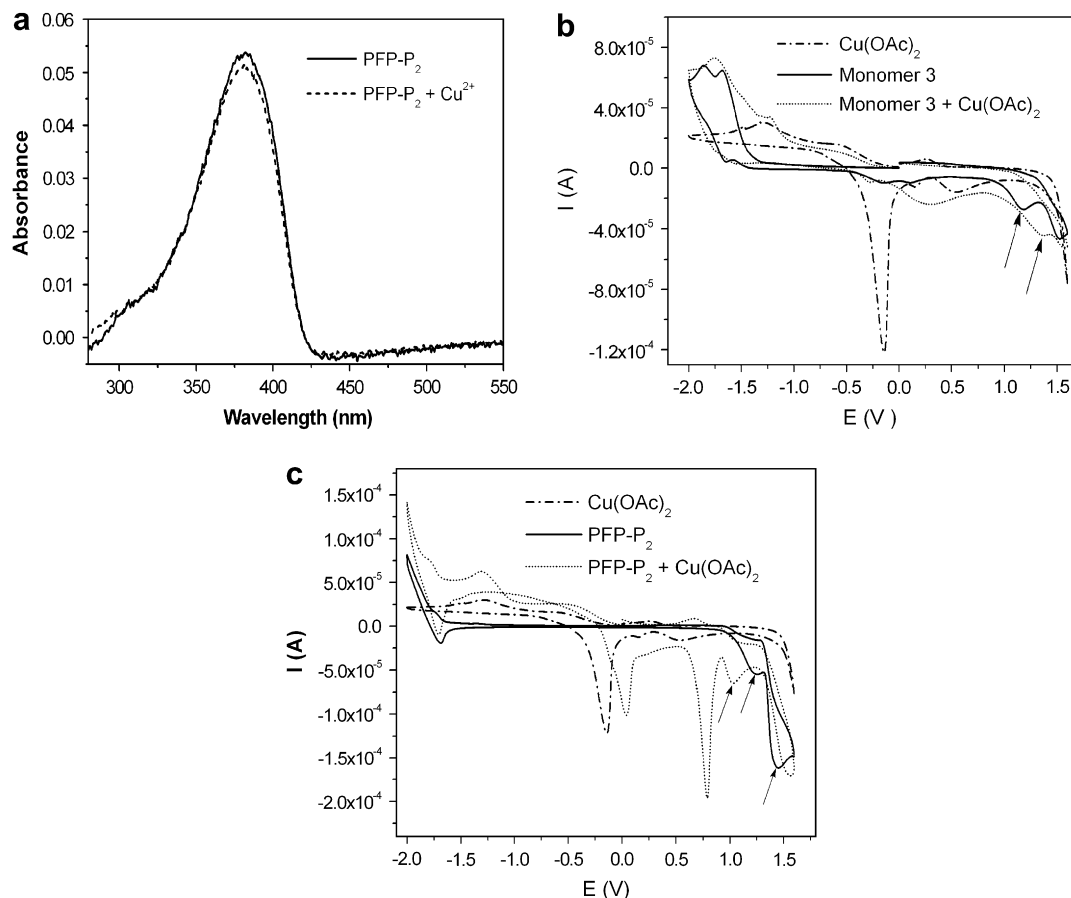
hot. The collected solid was washed with toluene subsequently and dried under vacuum to afford a white solid (220 mg, 88%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.35–8.33 (d, 2H), 7.89 (s, 2H), 7.81–7.70 (m, 18H), 7.62–7.57 (m, 12H), 7.47 (d, 2H), 5.61–5.58 (d, 4H). MS (MALDI-TOF):  $m/z$  = 705.8 (M<sup>+</sup>).

### 4.3. Synthesis of compound 3

To a solution of compound **2** (350 mg, 0.4 mmol) and 4-bromobenzaldehyde (150 mg, 0.8 mmol) in anhydrous methylene chloride (25 mL) was added sodium ethoxide (3.0 mL, 1.0 M solution in ethanol). The solution was allowed to stir at room temperature overnight, and then was poured into water. The organic phase was separated and washed with water. After the organic solvent was evaporated to near dryness, hexane was added and the precipitate was discarded. The residue was purified by silica gel column chromatography with MeOH/CHCl<sub>3</sub> (1/400) as eluent to give a light yellow solid (50 mg, 24%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.25–8.19 (d, 4H), 7.38–7.36 (d, 4H), 7.12–7.09 (d, 6H), 6.75–6.62 (m, 4H). MS (MALDI-TOF):  $m/z$  = 519.1 (M<sup>+</sup>).

### 4.4. A typical synthesis of PFP-P<sub>2</sub>

A mixture of compound **5** (296 mg, 0.35 mmol), compound **3** (20 mg, 0.04 mmol) and 5,5-dimethyl-2-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)-1,3,2-dioxaborinane (116.6 mg, 0.39 mmol) in 6 mL of THF and 3 mL of aqueous potassium carbonate (2.0 M) was degassed and Pd(dppf)Cl<sub>2</sub> (10 mg) was subsequently added in nitrogen stream. The resulted mixture was vigorously stirred at 85 °C for 2 days. After cooling to room temperature, the resulting solution was poured into acetone to get the precipitate, and then purified by dialysis using a dialysis membrane with a cutoff at  $M = 7000$  g mol<sup>-1</sup> for 2 days to yield 60 mg of PFP-P<sub>2</sub> (yield 22%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 7.95 (br), 7.37 (br), 3.12–2.88 (br), 2.71 (br), 2.07 (br), 1.36–1.05 (br), 0.65 (br).



**Fig. 6.** (a) The absorption spectra of PFP-P<sub>2</sub> in aqueous solution in the presence of Cu<sup>2+</sup> ions. [PFP-P<sub>2</sub>] =  $1.0 \times 10^{-6}$  M in RU, [Cu<sup>2+</sup>] =  $3.0 \times 10^{-5}$  M. (b) and (c) The cyclic voltammograms of monomer **3** and PFP-P<sub>2</sub> before and after adding Cu<sup>2+</sup> ions in acetonitrile/DMSO (9:1) solutions containing 0.04 M TBAPF<sub>6</sub>. Scan rate: 50 mV/s.

#### 4.5. Fluorescence quenching of PFP-P<sub>2</sub> by metal ions

The quenching experiment was performed by successive additions of metal ions ([metal ion] = 0–40 μM) to the solution of PFP-P<sub>2</sub> ([PFP-P<sub>2</sub>] = 1.0 μM) in aqueous solution at room temperature, and the fluorescence spectra were measured at once.

#### Acknowledgments

The authors are grateful for the financial supports from the National Natural Science Foundation of China (20473050, 20601027) and the “100 Talents” program of Chinese Academy of Sciences.

#### References

- [1] Thomas III SW, Joly GD, Swager TM. *Chem Rev* 2007;107:1339.
- [2] Liu B, Bazan GC. *Chem Mater* 2004;16:4467.
- [3] Ho HA, Béra-Abérem M, Leclerc M. *Chem—Eur J* 2005;11:1718.
- [4] Bunz UHF. *Chem Rev* 2000;100:1605.
- [5] Achyuthan KE, Bergstedt TS, Chen L, Jones RM, Kumaraswamy S, Kushon SA, et al. *J Mater Chem* 2005;15:2648.
- [6] Gaylord BS, Heeger AJ, Bazan GC. *Proc Natl Acad Sci USA* 2002;99:10954.
- [7] He F, Tang Y, Wang S, Li Y, Zhu D. *J Am Chem Soc* 2005;127:12343.
- [8] Ho HA, Doré K, Boissinot M, Bergeron MG, Tanguay RM, Boudreau D, et al. *J Am Chem Soc* 2005;127:12673.
- [9] Xu H, Wu H, Huang F, Song S, Li W, Cao Y, et al. *Nucleic Acids Res* 2005;33:e83.
- [10] Nilsson KPR, Inganäs O. *Nat Mater* 2003;2:419.
- [11] Nelson TL, O'Sullivan C, Greene NT, Maynor MS, Lavigne JJ. *J Am Chem Soc* 2006;128:5640.
- [12] Tan C, Atas E, Müller JG, Pinto MR, Kleiman VD, Schanze KS. *J Am Chem Soc* 2004;126:13685.
- [13] McQuade DT, Pullen AE, Swager TM. *Chem Rev* 2000;100:2537.
- [14] Swager TM. *Acc Chem Res* 1998;31:201.
- [15] Wang B, Wasielewski MR. *J Am Chem Soc* 1997;119:12.
- [16] Smith RC, Tennyson AG, Lim MH, Lippard SJ. *Org Lett* 2005;7:3573.
- [17] Tang Y, He F, Yu M, Feng F, An L, Sun H, et al. *Macromol Rapid Commun* 2006;27:389.
- [18] Kim IB, Erdogan B, Wilson JN, Bunz UHF. *Chem—Eur J* 2004;10:6247.
- [19] Zhou X-H, Yan J-C, Pei J. *Macromolecules* 2004;37:7078.
- [20] Kokil A, Yao P, Weder C. *Macromolecules* 2005;38:3800.
- [21] Zhang Y, Murphy CB, Jones Jr WE. *Macromolecules* 2002;35:630.
- [22] Liu B, Yu W-L, Pei J, Liu S-Y, Lai Y-H, Huang W. *Macromolecules* 2001;34:7932.
- [23] Huang H, Wang K, Tan W, An D, Yang X, Huang S, et al. *Angew Chem Int Ed* 2004;43:5635.
- [24] Ramachandran G, Smith TA, Gómez D, Ghiggino KP. *Synth Met* 2005;152:17.
- [25] Kim IB, Dunkhorst A, Gilbert J, Bunz UHF. *Macromolecules* 2005;38:4560.
- [26] Pinto MR, Schanze KS. *Synthesis* 2002:1293.
- [27] Tan C, Pinto MR, Kose ME, Ghiviriga I, Schanze KS. *Adv Mater* 2004;16:1208.
- [28] Fan Q-L, Zhang G-W, Lu X-M, Chen Y, Huang Y-Q, Zhou Y, et al. *Polymer* 2005;46:11165.
- [29] Kim IB, Bunz UHF. *J Am Chem Soc* 2006;128:2818.
- [30] Liu X, Tang Y, Wang L, Zhang J, Song S, Fan C, et al. *Adv Mater* 2007;19:1471.
- [31] Yu M, He F, Tang Y, Wang S, Li Y, Zhu D. *Macromol Rapid Commun* 2007;28:1333.
- [32] Lakowicz JR. *Principles of fluorescence spectroscopy*. New York: Kluwer Academic/Plenum Publishers; 1999.
- [33] Gould S, Strouse GF, Meyer TJ, Sullivan BP. *Inorg Chem* 1991;30:2942.
- [34] Xing C, Yu M, Wang S, Shi Z, Li Y, Zhu D. *Macromol Rapid Commun* 2007;28:241.