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Polymer Communication

A bipyridine-containing water-soluble conjugated polymer: Highly efficient fluorescence chemosensor for convenient transition metal ion detection in aqueous solution

Yi Chen [a], Qu-Li Fan [a,b,*], Pei Wang [a], Bing Zhang [a], Yan-Qin Huang [b], Guang-Wei Zhang [a], Xiao-Mei Lu [a,c], Hardy Sze On Chan [c], Wei Huang [a,b,d,*]

[a] *Institute of Advanced Materials (IAM), Fudan University, 220 Handan Road, Shanghai 200433, People's Republic of China*
[b] *Institute of Advanced Materials (IAM), Nanjing University, 22 Hankou Road, Nanjing 210093, People's Republic of China*
[c] *Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore*
[d] *Faculty of Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117576, Singapore*

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Abstract

A novel sulfonato-functionalized water-soluble conjugated polymer (WSCP), which containing 2′2-bipyridine units as receptors for transition metal ions in the main chain was successfully synthesized by Sonogashira-coupling reaction for the first time. This polymer could easily dissolve in water (5 mg/mL) and some polar organic solvents such as methanol. Its fluorescence in aqueous solution can be completely quenched upon addition of transition metal ions. The K_{sv} of different transition metal ions in aqueous solution were much higher than previous reports in organic solutions and showed highest selectivity to Ni^{2+}. These results opened opportunities for developing novel chemosensors by introducing selective fluorescent chromophore into the water-soluble conjugated backbone.

Keywords: Water-soluble conjugated polymer; Bipyridyl; Fluorescence chemosensor

1. Introduction

In the past few years, many efforts have been focused on the design and construction of conjugated polymers (CPs) based sensory materials as chemo/bio fluorescent sensors to detect specific analytes because of their enhanced sensitivity through signal amplification [1]. In such, metal ionic sensing with CPs tailing receptors was one of the current research interests in chemosensors because of the importance of metal ions in revealing a number of biological processes, disease states, and environmental pollutions [1]. Those former researches, however, were all carried out in organic solvents, which badly limited the application of CPs in practical sensing fields because many metal ions existed in aqueous environment. Therefore, water-soluble conjugated polymers (WSCPs) with charged groups were developed for chemo/bio analyses in aqueous solution [2–5]. Because of lacking of receptors in the molecular structures of previous WSCPs, forming receptor/WSCP complex was inevitable to realize their good selectivity and high sensitivity. Consequently, WSCPs functionalized with kinds of receptors were further developed to realize direct bioanalysis and illustrated good signal amplification [6–8]. Thus, introducing metal ionic receptors into WSCP systems was anticipated to conveniently achieve detecting metal ions in water with good selectivity and high sensitivity. But to our knowledge, WSCPs having specific receptors used as chemosensors for detecting metal ions have not been reported.

We herein reported a fluorene-based anionic water-soluble conjugated polymer containing 2′,2-bipyridine in the main chain and its strong capability to detect transition metal ions in water. As far as we know, this polymer was the first WSCP for detecting metal ions in aqueous solution, which takes advantage of its good water-solubility and its strong luminescence property of the fluorene group as reporter and efficient transition metal ion-coordinating ability of 2,2′-bipyridyl units as receptor [9].

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* Corresponding authors. Address: Institute of Advanced Materials (IAM), Fudan University, 220 Handan Road, Shanghai 200433, People's Republic of China. Tel.: +86 21 5566 4188/4198, fax: +86 21 6565 5123/5566 4192.

E-mail addresses: qlfan@fudan.edu.cn (Q.-L. Fan), wei-huang@fudan.edu.cn (W. Huang), chehw@nus.edu.sg (W. Huang).

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2. Experimental section

2.1. Materials

All chemical reagents used were purchased from Aldrich Chemical Co. THF was purified by distillation from sodium in the presence of benzophenone. Other organic solvents were used without any further purification.

2.2. General methods

The NMR spectra were collected on a Varian Mercury Plus 400 spectrometer with tetramethylsilane as the internal standard. FT-IR spectra were recorded on a Shimadzu IRPrestige-21 FTIR-8400s spectrophotometer by dispersing samples in KBr. Mass spectra (MS) were obtained using a HP 5973MS mass spectrometer at an ionizing voltage of 70 eV. UV–vis spectra were recorded on a Shimadzu 3150 PC spectrophotometer. The concentrations of copolymer solutions were adjusted to about 0.01 mg/mL or less. Fluorescence measurement was carried out on a Shimadzu RF-5301 PC spectrofluorophotometer with a xenon lamp as a light source. Elemental microanalyses were carried out on a Vario EL III CHNOS Elementar analyzer. The molecular weight (M_n) was estimated by Agilent 1100 gel-permeation chromatography (column: TOSOH TSK-gel, G6000PWXL, G3000PWXL) with standard PEO as a reference using 0.1 M $NaNO_3$ as an eluent at 40 °C.

The quenching behavior was studied by comparing the fluorescence intensities of polymer aqueous solutions in the presence of quenchers with different concentrations. Milli-Q water used in preparing the aqueous solutions of the polymers and quenchers was purged with nitrogen for 4 h before using.

2.3. Synthesis of the monomers

2.3.1. 2,7-Dibromo-9,9-di(3-hydroxylpropyl)-fluorene (**1**)

Into a 250 mL round-bottom flask was added 2,7-dibromofluorene (9.72 g, 30 mmol), catalytic amount TBABR and DMSO (100 mL) under nitrogen. Then 15 mL NaOH (50%) was added. The mixture was stirred at 80–90 °C, and 3-bromopropanol (10.5 g, 69 mmol) was added drop-wise, the solution was heated for reacting for 8 h. The mixture was poured into water and extracted with CH_2Cl_2, the organic extracts were washed with brine and dried over Na_2SO_4. Upon evaporating off the solvent, the product was purified by silical gel column chromatography using ethyl acetate/petrol ether = 4:3 as eluent to give the desired product as yellow powder (11.9 g, yield 90%). ^{1}H NMR (DMSO, 400 MHz, ppm): δ 7.80 (d, 2H, $J=8.0$ Hz), 7.60 (s, 2H), 7.5 (d, 2H, $J=8.0$ Hz), 4.20 (t, 2H, $J=4.0$ Hz), 3.1 (q, 4H, $J=6.4$ Hz), 2.0 (t, 4H, $J=4.0$ Hz), 0.6 (m, 4H, $J=4.8$ Hz).

2.3.2. 2,7-Dibromo-9,9-di(3-methanesulfonatopropyl)-fluorene (**2**)

3.78 g, 2.56 mL (33 mmol, M 114.5, ρ 1.475) of mathanesulfonyl chloride was added dropwise to a THF solution of 4.84 g (11 mmol) of 1 and 6.12 mL (ρ 0.7275, M 101.2 4.45 g, 44 mmol) of triethylamine at room temperature. After stirring for 4 h, the reaction mixture was filtered and the filtrate was evaporated and the crude extract was purified by silica gel column chromatography using hexane/acetone (1:1) as eluent to give the desired product as yellow powder (6.16 g, yield 94%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.5 (m, 6H, $J=8.0$ Hz), 3.9 (t, 4H, $J=6.0$ Hz), 2.9 (s, 6H), 2.1 (t, 4H, $J=5.6$ Hz), 1.0 (m, 4H, $J=6.0$ Hz).

2.3.3. 2,7-Dibromo-9,9-di(3-iodidepropyl)-fluorene (**3**)

To a solution of 13.5 g of NaI (90 mmol) in 250 mL of acetone was added 9.1 g of **2** (15 mmol). The mixture was allowed to react at room temperature (30 °C) for 24 h. The CH_3SO_2Na that had precipitated was separated by filtration. The filtrate was evaporated of the solvent and yellow crude product was obtained which, upon passing through a silica gel column using acetone/hexane = 1:15 as eluent, gave yellow crystals (8.9 g, yield 90%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.5 (m, 6H, $J=8.0$ Hz), 2.9 (t, 4H, $J=6.4$ Hz), 2.1 (t, 4H, $J=4.0$ Hz), 1.0 (m, 4H, $J=4.0$ Hz).

2.3.4. Sodium 2,7-dibromo-9,9-dipropanesulfonato-fluorene (monomer **1**) [10]

To a solution of 6.6 g of **3** (10 mmol) in 80 mL anhydrous acetone was added an aqueous solution of 2.772 g of Na_2SO_3 (22 mmol) in 30 mL H_2O. The reaction mixture was heated to 75 °C for 72 h. Then a plenty of water was added to the system and the residue was filtrated. Evaporation of the solvent offered a white powder. The washed twice by anhydrous acetone and methanol, removing the solvent, crude product was obtained. Recrystallized by 320 mL mixture of methanol/1,4-dioxane (7:1) gave the desired product as white powders (2.1 g, yield 34.3%). ^{1}H NMR (D_2O, 400 MHz, ppm): δ 7.6 (m, 4H, $J=8.0$ Hz), 7.4 (d, 2H, $J=8.0$ Hz), 2.4 (t, 4H, $J=8.0$ Hz), 2.0 (t, 4H, $J=8.0$ Hz), 0.8 (m, 4H, $J=4.0$ Hz). ^{13}C NMR (CD_3OD, 400 Hz, ppm) δ 151.5, 139.5, 130.7, 126.8, 121.8, 121.5, 55.2, 51.1, 37.9, 19.1. Anal. Calcd for $C_{19}H_{18}Br_2Na_2O_6S_2$:2.4$H_2O$: C, 34.81; H, 3.51; S, 9.78. Found: C, 34.84; H, 3.47; S, 9.12.

2.3.5. 5,5′-Diethynyl-2,2′-bipyridine (monomer **2**)

The compound was synthesized according to Ref. [11].

2.4. Synthesis of the polymer

2.4.1. Poly[9,9-di(3-sulfonatopropyl)fluoren-2,7-yleneethylene-co-alt-5,5′-(2,2′-bipyridyl-ethylene)] (**P1**)

(0.3 mmol) of monomer **1** and (0.3 mmol) of monomer **2** were added in a Schlenk flask with a gentle flow of argon. Then a mixture of (9.0 μmol) $Pd(PPh_3)_4$ and (9 μmol) of CuI were added in a glove-box with a gentle flow of argon. A mixture of 4 mL of H_2O, 2 mL of diisopropylamine and 6 mL of DMF was likewise deoxygenated and was subsequently added to the former by means of a cannula. The final mixture was again deoxygenated by vacuum-argon cycling and was then warmed to 70 °C and stirred under a positive pressure of argon for 27 h. And then the solution was filtered after adding a large amount of methanol. The filtrate was precipitated in acetone and redissolved in methanol/water (70:30) for three times. Finally, the resulting solution was dialyzed against water (Millipore NanopureTM) using a 7 kD MWCO cellulose membrane. After removing the solvent and drying under vacuum, 80 mg (yield: 41%) of **P1** was obtained as brown yellow powder. ^{1}H NMR (CD_3OD, 400 MHz, ppm) δ 8.81 (br, 2H), 8.42 (br, 2H), 8.22 (br, 2H), 7.59 (br, 2H), 7.46 (br, 4H), 2.48 (br, 2H), 2.06 (br, 2H), 0.88 (br, 2H). ^{13}C NMR (CD_3OD, 400 Hz, ppm) δ 154.8, 152.6, 151.5, 140.1, 139.5, 130.7, 126.8, 121.8, 121.5, 120.9, 119.6, 81.8, 80.8, 55.2, 51.1, 37.9, 19.1. FT-IR (cm^{-1}): 3068, 3026, 2937, 2861, 2207, 1628, 1508, 1465, 1377, 1205, 1175, 1037, 890, 815, 753, 708. Anal. Calcd for $(C_{33}H_{24}N_2Na_2O_6S_2 \cdot 4H_2O)_n$: C, 54.54; H, 4.44; N, 3.85; S, 8.82. Found: C, 52.35; H, 4.68; N, 3.14; S, 8.04.

3. Results and discussion

3.1. Synthesis and characterization

P1, poly[9,9-di(3-sulfonatopropyl)fluoren-2,7-yleneethylene-*co*-*alt*-5,5′-(2,2′-bipyridylethylene)] was obtained by Sonogashira-coupling polymerization using $Pd(PPh_3)_4$ as catalyst. **P1** was purified by dialyzing against water using a 7 kD MWCO cellulose membrane and had the molecule weight $M_n = 8.25 \times 10^3$ by using gel-permeation chromatography. This polymer could easily dissolve in water (5 mg/mL) and some polar organic solvents such as methanol. The spectroscopic properties of **P1** were measured in aqueous solution. **P1** exhibited the absorbance maximum at 367 nm. In comparison with the organic system in our group reported before [11], **P1** showed an obvious spectral blue shift in absorption, which could be attributed to the mutual repulsion among the negative charges leading to a more twisted main chain conformation, and hence a decreased effective conjugation length [12–15].

3.2. Ion responsive properties

The ion responsive properties of **P1** were studied by using absorption and fluorescence emission spectroscopy in aqueous solution at a polymer concentration of 1.0×10^{-5} M. Many kinds of metal ion, such as alkali, alkali earth, and transition metal ions were used in our experiment. We found clearly red-shift in absorption spectra with addition of transition metal ions, such as Ag^+, Cu^{2+}, Zn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Mn^{2+}, Fe^{3+}, Al^{3+}, Cr^{3+}, and Au^{3+}. Fig. 1 showed the UV–vis absorption and PL emission spectra of **P1** at different concentration of the typical metal ion Ni^{2+}. The absorption maximum ($\Delta\lambda_{max}$) shifts from the metal ion-free polymer to metal-chelated polymer ranged from 15 to 50 nm according to the type of metal ion we analyzed. The spectral response of 2,2′-dipyridyl-containing conjugated polymers to metal ions was believed to be based on the chelation between the 2,2-bipyridyl units and the metal ions. Chelating with the metal ions forced the bipyridyl group, which had a 20° dihedral angle between two pyridine planes to become more planar and thus resulted in an increased effective conjunction length on the entire polymer [16]. We thus considered that the difference of absorption maximum ($\Delta\lambda_{max}$) shifts arisen from the different coordination capability of metal ions to the 2,2-bipyridyl units, i.e. the stronger chelation the larger spectral red shift obtained. The $\Delta\lambda_{max}$ in absorption spectra of different metal ions is shown in Fig. 2. It is noteworthy that compared with the data of system in organic solvent reported before, the absorption maximum shifts of most transition metal ions increased about 5–7 nm, and for those transition metal ions, which had no absorption response in organic solvent before, 20–30 nm red-shifts also appeared in aqueous solution [11]. Such increased red-shifts in aqueous solution may be explained by the decreased twist angle of the backbone resulting from the decreased mutual electrostatic repulsion of the anionic sulfonato pendant and the increased interchain aggregation after adding cationic metal ions and forming cationic metal complexes [5,15]. We found that Au^{3+} had the largest $\Delta\lambda_{max}$ in all the selected metal ions. It implied that Au^{3+} with high valents may more efficiently weaken the electrostatic repulsion of the polymer chain and enhance interchain aggregation than other bivalent and monovalent metal ions and then made more elongated conjugation length.

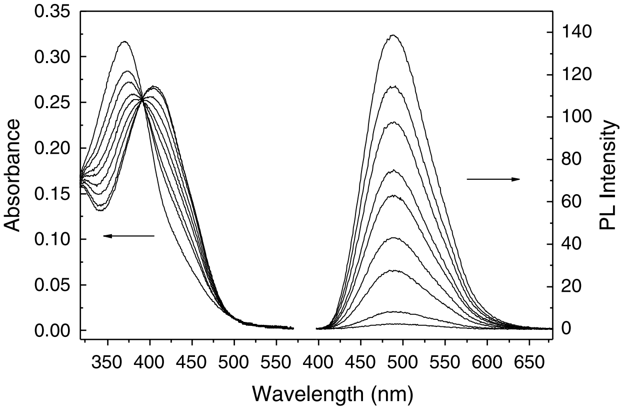

Fig. 1. The UV–vis absorption and PL emission spectra of **P1** in aqueous solution with different concentration of Ni^{2+}.

We also studied the fluorescence quenching behavior of the polymer in the existence of different concentration of some kinds of metal ions. Completely fluorescence quenching was found to all the transition metal ions. Under the excitation wavelength of 350 nm, the fluorescence of **P1** was quenched completely at a very low concentration of the transition metal ions (ranged from 10^{-7} to 10^{-5} M), implying that a signal amplification through the molecular wire approach was involved [1,17]. The fluorescence quenching of the polymer when adding transition metal ions was most likely caused by energy or electron-transfer reactions between the polymer backbone and binding metal complexes, which was a nonradiative center and trapped the excitation energy passing through them [9]. The Stern–Volmer constant (K_{sv}) for fluorescence quenching of **P1** with each transition metal ions as the quencher were shown in Fig. 3. We found Ni^{2+} was the most sensitive ion ($K_{sv} = 8.5 \times 10^8$ M^{-1}) for oligopyridine receptors and this was the same as reported previously [18].

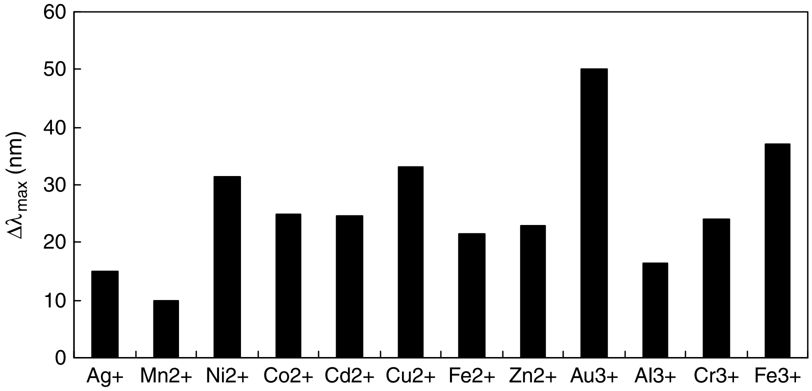

Fig. 2. The absorption maximum ($\Delta\lambda_{max}$) of **P1** for different metal ions.

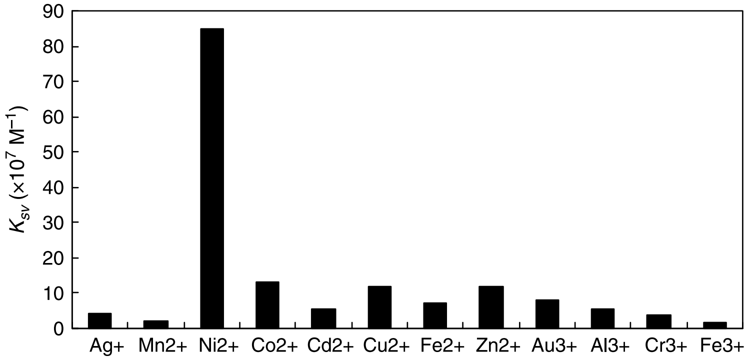

Fig. 3. The K_{sv} of **P1** for different transition metal ions.

This result suggested that the change of conjugation length may play less important roles in fluorescence quenching ability (Au^{3+} was not the most sensitive ion in quenching though it had the biggest red-shift in absorption spectra), and the electron/energy transfer efficiency of the bipyridine–ion complex may be the most important reason in quenching [18]. On the other hand, not only for Ni^{2+} but for all the other transition metal ions the values increased about $1\sim2$ magnitude compared with the data in organic solvent [11,18]. The observed higher K_{sv} of the water-soluble polymer was believed to originate from the following factors. Firstly, the good solubility of the polymer in water could increase the touching probability of the polymer to ions in aqueous solution (metal ions can move more freely in aqueous solution). Secondly, the static affinity of anionic sulfonato group to metal ions may make it easier for the polymer to chelate cationic ions. Thirdly, as we discussed in previous section , adding cationic metal ions may further increase the effective conjugation length of the polymer in aqueous solution (formed from the decreased twist angle of the polymer backbone and the increased interchain aggregation) and then improve the efficiency of electron/energy transfer along the conjugated backbone. We considered these were the characteristic advantage of **P1** in this communication. On the other hand, **P1** had no response by adding of alkali (K^+, Na^+) and alkali earth (Mg^{2+}, Ca^{2+}) metal ions ($<10^{-4}$ M) for either UV–vis absorption or PL fluorescence spectra because of the poor coordination ability of the bipyridyl units with such metal ions [19,20]. The results obviously showed the good selectivity of the water-soluble conjugated polymer for transition metal ions.

4. Conclusion

In summary, we have successfully designed and synthesized an anionic bipyridyl-containing water-soluble conjugated polymer for the first time. Its fluorescence in aqueous solution could be completely quenched upon addition of transition metal ions. So we can conveniently detecting metal ions in water. The K_{sv} of different transition metal ions in aqueous solution were much higher than previous reports in organic solutions and showed highest selectivity to Ni^{2+} [11,18]. Considering the high sensitivity and good selectivity of this WSCP-based chemosensor in aqueous solution, our results opened opportunities for developing novel chemosensors by introducing selective fluorescent chromophore into the water-soluble conjugated backbone.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2006.05.045.

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