

Fluorescent Chemosensor Based on the Conjugated Polymer Incorporating 2,2'-Bipyridyl Moiety for Transition Metal Ions

Qian Miao,¹ Xiaobo Huang,^{1,2} Yaqian Cheng,¹ Yan Liu,² LiLi Zong,² Yixiang Cheng²

¹College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325027, China

²School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

Received 21 April 2008; accepted 23 September 2008

DOI 10.1002/app.29393

Published online 11 November 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A fluorescent conjugated polymer was synthesized by the polymerization of 1,4-dibromo-2,3-bisbutoxynaphthalene (**M-2**) with 5,5'-divinyl-2,2'-bipyridine (**M-3**) via Heck reaction. The conjugated polymer shows strong blue-green fluorescence because of the extended π -electronic structure between the repeating unit 2,3-bisbutoxynaphthyl group and the conjugated linker 2,2'-bipyridyl (bpy = 2,2'-bipyridine) moiety via vinylene bridge. The responsive properties of the conjugated polymer on transition metal ions were investigated by fluorescent and UV-vis spectra. The results show that Cu^{2+} and Ni^{2+} can form nonradiative metal-to-ligand charge-transfer complexes with the polymer, whereas, Zn^{2+} and Cd^{2+} do not

produce the pronounced differences from the polymer fluorescence and UV-vis spectra. The fluorescent quenching can probably be attributed to the intramolecular photoinduced electron transfer (PET) or photoinduced charge transfer (PCT). The results can also suggest that 2,2'-bipyridyl moiety in the main chain backbone of the conjugated polymer can act as the recognition site of a special fluorescent chemosensor for sensitive detection of transition metal ions. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 3137–3143, 2009

Key words: conjugated polymer; fluorescent chemosensor; 2,2'-bipyridine; Heck reaction

INTRODUCTION

The conjugated polymers based on π -conjugated organic molecules and their regular arrangement have still been of great interest during the past decades.^{1–5} These polymer materials with tunable optical and electronic properties can be obtained by careful combination of designed monomers. They can be used to prepare organic light-emitting diodes, molecular sensors, and other light-emitting devices with colors ranging from blue to red.^{6–8}

Fluorescent chemosensors change their photophysical response to the surrounding medium or through specific molecular recognition events. Because of their simplicity and high sensitivity, fluorescent sensors have been widely utilized as popular tools for chemical, biological, and medical applications.^{9–15}

The most general strategy for the fluorescent sensor design is to combine fluorescent dye molecules with designed receptors for specific analytes, so that the recognition event between receptors and analytes can lead to a fluorescent property change of the dye moiety. Fluorescent conjugated polymers used as chemosensors for metal ions have several advantages over small molecule sensors, such as enhancements associated with electronic interaction between receptors and analytes within the conjugated π -electronic polymer backbone, processability, and ease of structural modification. The research on the conjugated polymer-based fluorescent chemosensors is emerging as an area of current interest in the recent years.^{16–20} Furthermore, the fluorescent conjugated polymers incorporating molecular recognition moieties can show the high sensitivity of chemosensors to external structural perturbations and to electron density changes within the main chain backbone of the conjugated polymer, when they can interact and form complexes with metal ions.^{21–28}

1,10-Phenanthroline (phen) and 2,2'-bipyridyl ligands have been used extensively as two metal-chelating ligands in a variety of approaches dealing with structural coordination chemistry or functional systems based on phen-/bpy-containing metal complexes because of their redox active behavior, luminescent properties, supramolecule-forming reactivity,

Correspondence to: Q. Miao (mq0577@yahoo.com.cn) and Y. Cheng (yxcheng@nju.edu.cn).

Contract grant sponsor: Zhejiang Provincial Natural Science Foundation; contract grant number: Y406068.

Contract grant sponsor: Zhejiang Province (Instrument Analysis Fund); contract grant number: 04064.

Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: 20474028, 20774042.

and ease of functionalization. The conjugated polymers incorporating the metal complexes of phen or bpy are expected to be promising functional materials.^{23,24,29–32} But so far, there have been few reports on the conjugated polymers as fluorescent chemosensors incorporating 2,2'-bipyridyl moiety as the precursor into the main-chain backbone to afford their corresponding polymer complexes with transition metal ions.^{4,15,33–37} In this article, we described fluorescence and UV-vis spectra change features of the conjugated polymer when it binds with transition metal ions. This conjugated polymer emits strong blue-green fluorescence. Moreover, although it was used as a fluorescent chemosensor for transition metal ions, the results show Cu^{2+} and Ni^{2+} can lead to nearly complete fluorescent quenching of the conjugated polymer, whereas, Zn^{2+} and Cd^{2+} do not produce the pronounced differences from the polymer fluorescence and UV-vis spectra. Such distinct ion responsive behaviors reveal the coordination ability differences of transition metal ions with 2,2'-bipyridyl receptors in the main chain backbone of the conjugated polymer.

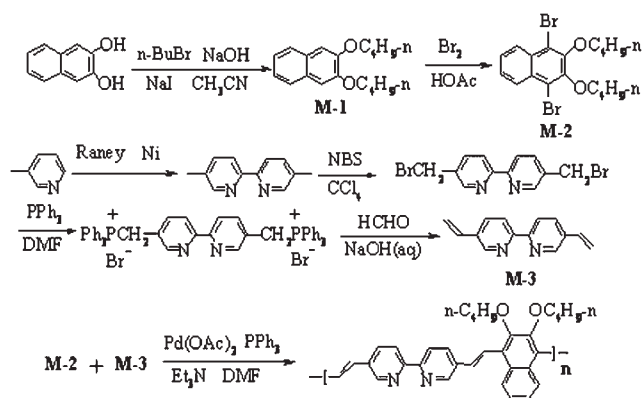
EXPERIMENTAL

General

^1H , ^{13}C NMR spectra measurements (all in CDCl_3) were recorded on a 300-Bruker spectrometer with TMS as reference. FTIR spectra were taken on a Nexus 870 FTIR spectrometer. UV-vis spectra were obtained from a Shimadzu UV-2501PC UV-Vis Recording spectrophotometer. DSC-TGA was performed on a Perkin-Elmer pyris-1 instrument under a N_2 atmosphere. Fluorescent spectra were obtained from a Thermo Spectronic Aminco Bowman Series 2 Luminescence spectrometer. MS was determined on a Micromass GCT. C, H, and N of elemental analyses were performed on an Elementar Vario MICRO analyzer. Molecular weight was determined by gel permeation chromatography (GPC) with Waters-244 HPLC pump and THF was used as an eluent and polystyrenes as external standards. All solvents and reagents were commercially available A.R. grade. All reactions were performed under a N_2 atmosphere using Schlenk techniques.

Metal ion titration

Each metal ion titration experiment was started with 3.0 mL of the polymer in THF solution with the known concentration ($1.0 \times 10^{-5} \text{ mol L}^{-1}$). Aqueous metal ion nitrate salts ($2.0 \times 10^{-3} \text{ mol L}^{-1}$) were used for the titration. Metal-containing polymer complexes were produced by adding aliquot of a solution of the selected metal salt to a THF solution of



Scheme 1 Synthesis procedures for **M-1**, **M-2**, **M-3**, and the polymer.

the polymer (3.0 mL). The mixture was stirred constantly during the titration. Steady-state fluorescence and absorption spectra were monitored for 5 min after addition of aqueous metal ion to the polymer solution. Distilled water was monitored as the same way to be the blank.

Preparation of the monomers (**M-2** and **M-3**) and the conjugated polymer

The synthesis procedures of the monomers **M-2**, **M-3** and the conjugated polymer are shown on Scheme 1. The repeating unit 2,3-bisbutoxynaphthalene (**M-1**) and the monomer 1,4-dibromo-2,3-bisbutoxynaphthalene (**M-2**) were synthesized according to the reported literatures,^{38,39} the overall yield of **M-2** was 90%. ^1H NMR: δ 8.25 (dd, $J = 6.5, 3.3 \text{ Hz}$, 2H), 7.56 (dd, $J = 6.6, 3.2 \text{ Hz}$, 2H), 4.15 (t, $J = 6.6 \text{ Hz}$, 4H), 1.85–1.94 (m, 4H), 1.56–1.67 (m, 4H), 1.04 (t, $J = 7.3 \text{ Hz}$, 6H); FTIR cm^{-1} : 3057, 2958, 2934, 2872, 1577, 1541, 1454, 1360, 1336, 1325, 1117, 1021, 961, 754.

5,5'-divinyl-2,2'-bipyridine (**M-3**) could be synthesized from 3-methylpyridine by a four-step reaction according to the literatures, and the overall yield of **M-3** could reach 11%.^{15,32,40} **M-3** needs to be kept in the dark at -4°C before using. MP: $56\text{--}58^\circ\text{C}$; ^1H -NMR: δ 8.68–8.69 (d, 2H, $J = 1.9 \text{ Hz}$), 8.37–8.39 (d, 2H, $J = 8.3 \text{ Hz}$), 7.87–7.91 (dd, 2H, $J = 8.3, 2.2 \text{ Hz}$), 6.74–6.83 (dd, 2H, $J = 17.7, 11.0 \text{ Hz}$), 5.89–5.95 (d, 2H, $J = 17.6 \text{ Hz}$), 5.42–5.46 (d, 2H, $J = 11.0 \text{ Hz}$). ^{13}C -NMR (CDCl_3): δ 155.34, 148.17, 133.94, 133.67, 133.42, 121.85, 116.82. Anal. Calcd. for $\text{C}_{14}\text{H}_{12}\text{N}_2$: C, 80.74; H, 5.82; N, 13.45. Found: C, 80.76; H, 5.75; N, 13.37. FTIR cm^{-1} : 3002, 1629, 1589, 1542, 1468, 1367, 1250, 1023, 911, 846, 750. MS (EI, m/z): 208 (M^+ , 100).

Preparation of the conjugated polymer

A mixture of **M-2** (225 mg, 0.52 mmol) and **M-3** (109 mg, 0.52 mmol) was dissolved in the mixed solvents of 6 mL of DMF and 0.8 mL of Et_3N . The solution

was first degassed with N_2 for 15 min before 5 mol % $Pd(OAc)_2$ (5.9 mg, 0.026 mmol) and 25 mol % PPh_3 (34.3 mg, 0.13 mmol) were added to the above solution. The temperature of the mixture was kept at $120^\circ C$ for 12 h under a N_2 atmosphere. After the reaction mixture was refluxed at $140^\circ C$ for 2 h, styrene (10.4 mg, 0.10 mmol) was added for endcapping the polymer for an additional 2 h. The mixture was cooled to room temperature, and was then filtered through a short silica gel column, and the filtrate was dropped into methanol (50 mL) to precipitate out the crude polymer. The resulting polymer was filtered and washed with methanol several times. Further purification could be conducted by dissolving the polymer in CH_2Cl_2 to precipitate in methanol again. The polymer was dried in vacuum to give 207 mg in 83.6% yield. GPC analysis result: $M_w = 3280 \text{ g mol}^{-1}$, $M_n = 1780 \text{ g mol}^{-1}$, PDI = 1.84. 1H -NMR (300 MHz, $CDCl_3$): 8.89 (br, 2H), 8.53 (br, 2H), 8.27 (br, 2H), 8.12 (br, 2H), 7.73 (br, 2H), 7.54 (br, 2H), 7.37–7.28 (m, 2H), 4.19–4.06 (m, 4H), 1.81 (br, 4H), 1.61 (br, 4H), 1.08–0.95 (m, 6H). Anal. Calcd. for $C_{32}H_{32}N_2O_2$: C, 80.67; H, 6.72; N, 5.88. Found: C, 78.75; H, 6.57; N, 5.79. FT-IR (KBr)/ cm^{-1} : 3037, 3005, 2956, 2870, 1628, 1589, 1466, 1421, 1371, 1269, 1213, 1021, 965, 755.

RESULTS AND DISCUSSION

Synthesis and features of the conjugated polymer

Heck coupling reaction is one of the most important C–C coupling reactions in organic synthesis.^{15,41–46} When compared to the Wittig method, the Pd-catalyzed Heck polycondensation is relatively mild and gives an easy access to various monomers in the preparation of functionalized PPVs.^{47–51} In this article, a typical Heck reaction condition was applied to the polymerization. The C–C cross coupling process was easily carried out in DMF in the presence of a catalytic amount (5 mol %) of $Pd(OAc)_2$ with Et_3N and triphenylphosphine (PPh_3) under a N_2 atmosphere. The polymerization was obtained in a good yield (83.6%). The molecular weight was determined by gel permeation chromatography (GPC): $M_w = 3280 \text{ g mol}^{-1}$, $M_n = 1780 \text{ g mol}^{-1}$, PDI = 1.84. It was introduced an electron-deficient ligand 5,5'-divinylbipyridine as a monomer into the conjugated polymer backbone by Heck reaction. The 2,2'-bipyridyl moiety can orient a well-defined spatial arrangement in the linear conjugated polymer so that the electron transporting properties of the conjugated polymer may be improved, and the electron density may shift away along the extended π -electronic chain backbone via vinylene linkage. Furthermore, the vinylene bridge can reduce steric hindrance between naphthyl and bipyridyl groups, and also have a beneficial influence on the polymer stability. The alkyl group substituents on

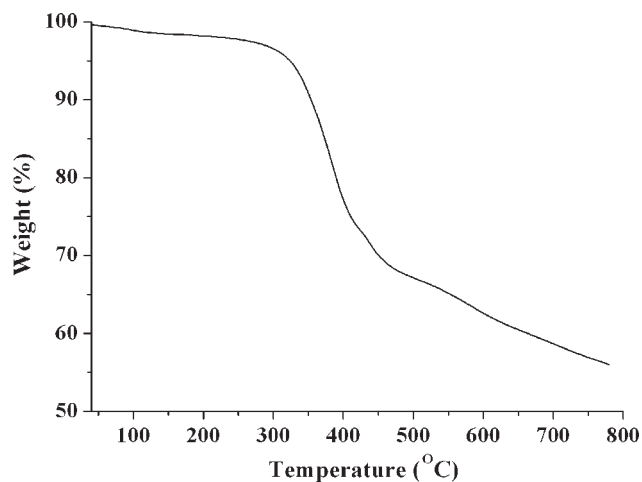


Figure 1 TGA curve for the polymer.

naphthyl rings as side chain of the polymer cannot only improve its solubility in common organic solvents, but also modify the electronic properties of the conjugated polymer structure. The polymer can emit strong blue-green fluorescence. Although the conjugated polymer was used as a fluorescent chemosensor for transition metal ions, this bipyridyl ligand can act as the binding site by chelating coordination with transition metal ions to afford the corresponding metal-containing polymer complexes. On the basis of the fluorescence and UV-vis spectra changes of the metal-containing polymer complexes, we found the responsive behaviors of the conjugated polymer on metal ions can be attributed to the obvious differences of coordination abilities of transition metal ions with 2,2'-bipyridyl receptor.

The conjugated polymer is a red solid and stable in the air. The polymer shows good solubility in THF, CH_2Cl_2 , $CHCl_3$, and DMF. The flexible *n*-butyl substituents on naphthyl moieties can render the polymer soluble in common organic solvents. It could not be possible to be observed the glass transition temperature (T_g) of the conjugated polymer by DSC determination. Thermogravimetric analysis (TGA) of the polymer was carried out under a N_2 atmosphere at a heating rate of $10^\circ C/min$. In accordance with the Figure 1, two main degradation processes could be observed to the polymer. The first step was observed from 310 to $420^\circ C$, and there is about 23% loss weight. The second step appeared a slow decomposition process from 420 to $600^\circ C$, and there is about 12% loss weight. The polymer tends to complete decomposition at $800^\circ C$. There is a total loss of about 43% when heated to $800^\circ C$.

Optical properties

Optical properties of the repeating units **M-1**, **M-3**, and the conjugated polymer in CH_2Cl_2 and THF

TABLE I
Optical Properties of the Repeating Units and the Polymer

	UV-vis (λ_{\max})/nm	PL (λ_{\max})/nm		Stokes Shift ^a /nm	$\Phi_{\text{PL}}^{\text{b}}$
		λ_{ex}	λ_{em}		
M-1 (in CH ₂ Cl ₂)	236	352	394	–	–
M-3 (in CH ₂ Cl ₂)	272(w), 321	346	364	–	–
Polymer (in CH ₂ Cl ₂)	235, 394	358	494, 521(sh)	100	0.27
Polymer (in THF)	244, 399	368	491	92	–

^a Stokes shift = PL λ_{\max} (nm) – UV-vis λ_{\max} (nm).

^b These values were estimated by using the quinine sulfate solution (ca. 1.0×10^{-5} mol L⁻¹) in 0.5 mol L⁻¹ H₂SO₄ ($\Phi_{\text{f}} = 55\%$) as a standard.

solution are summarized in Table I. Figures 2 and 3 illustrate UV-vis and fluorescence spectra of M-1, M-3, and the conjugated polymer in CH₂Cl₂ and THF. According to Figure 2, the maxima absorption wavelengths λ_{\max} of M-1 and M-3 appear at 236 and 321 nm. The polymer' UV absorption spectrum displays great red shift compared with the repeating units M-1 and M-3. UV spectrum of the polymer shows the maxima absorption λ_{\max} at 394 nm in CH₂Cl₂ solution and a broad absorption at the region from 340 to 430 nm, which can be attributed to the effective π - π^* conjugated segment of the conjugated linker M-1 and 2,2'-bipyridyl group via vinylene bridge along the main chain backbone of the linear conjugated polymer.^{15,45,50} According to Figure 3, it can be found that M-1 and M-3 do not show visible fluorescence. The conjugated polymer can emit blue-green light under ultraviolet light (340 nm) or sunlight even in low concentration ($\sim 1.0 \times 10^{-4}$ mol L⁻¹). The fluorescent spectrum of the conjugated polymer in CH₂Cl₂ appears two bands at 494 and 521 nm and only one emission peak at 491 nm in THF. PL efficiency (Φ_{PL}) of the polymer in CH₂Cl₂ is 0.27. The conjugated polymer can show strong fluorescence, which can be attributed to the

extended π -electronic structure within the conjugated polymer backbone.^{4,32,45,52}

Responsive signal changes of the conjugated polymer on metal ions

The UV-vis responses and fluorescent quenching behaviors of the conjugated polymer on transition metal ions were examined in THF solution. The concentration of the polymer corresponding to 2,2'-bipyridyl receptor moiety was fixed at 1.0×10^{-5} mol L⁻¹. Ni²⁺, Cu²⁺, Cd²⁺, Zn²⁺ ions were used at a concentration of 2.0×10^{-3} mol L⁻¹. The influences of various transition metal ions on the fluorescent quenching ratios of the polymer are shown in Table II. On the basis of the fluorescent signal changes of the polymer and the metal-containing polymer complexes, the fluorescent emission wavelengths of the metal-polymer complexes do not show an obvious difference from the metal-free polymer [Fig. 4(a)]. On the contrary, the fluorescent intensities of metal-containing polymer complexes show gradual reduction as the increase of metal ion concentrations. The quenching efficiency is related to the Stern-Volmer constant, K_{SV} , and is determined by monitoring

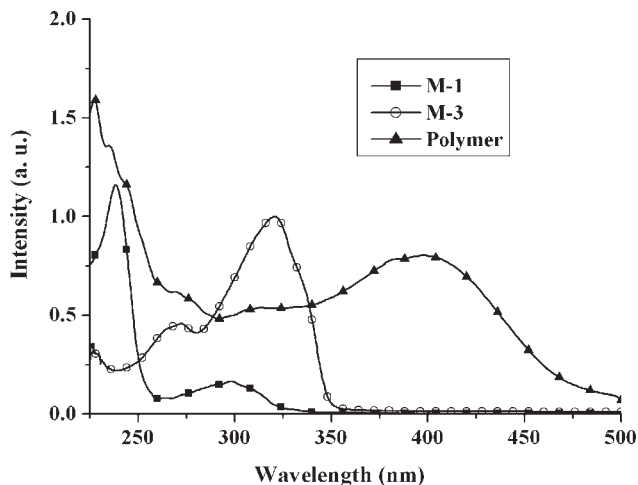


Figure 2 UV-Vis spectra of M-1, M-3, and the polymer (in CH₂Cl₂).

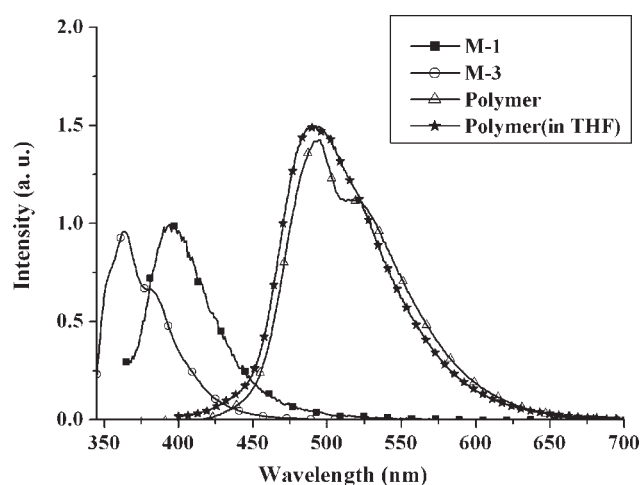


Figure 3 Fluorescent spectra of M-1, M-3, and the polymer (in CH₂Cl₂ and THF).

TABLE II
The Quenching Ratio (η , %) and Average $\lg K_{SV}$ of the Polymer on Metal Ions

	$n_{\text{Polymer}} : n_{\text{ion}}$							$\lg K_{SV}$
	1 : 0.1	1 : 0.2	1 : 0.4	1 : 0.5	1 : 0.8	1 : 1	1 : 2	
Cd^{2+}	2.31	2.57	2.58	2.59	3.10	3.30	6.47	3.67
Zn^{2+}	0.06	7.14	9.93	12.0	13.1	17.0	18.4	4.40
Ni^{2+}	14.9	24.5	47.3	58.8	79.4	86.4	89.0	5.42
Cu^{2+}	19.8	37.2	66.8	77.5	97.4	97.8	97.9	6.14

measurable changes in the fluorescent spectra via the Stern-Volmer equation: $I_0/I = 1 + K_{SV}[Q]$. Herein, I_0 is the fluorescent emission intensity in the absence of the quencher, and I is the fluorescent emission intensity in the presence of the quencher. $[Q]$ is the quencher concentration, that is, transition metal ion concentration. In this article, the quenching ratios (η) of the polymer to different transition metal ions can be calculated according to equation: $\eta = 1 - I/I_0$. As a result, the fluorescent quenching ratios (η) of the conjugated polymer are 3.30%, 17.0%, 86.4%, and 97.8% for Cd^{2+} , Zn^{2+} , Ni^{2+} , and Cu^{2+} upon the 1 : 1 molar ratio addition of a metal

salt solution, and average $\lg K_{SV}$ of the polymer on Cd^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} are 3.67, 4.40, 5.42, and 6.14, respectively. According to Table II, the tested metal ions can be categorized into two groups. Cu^{2+} and Ni^{2+} lead to nearly complete fluorescent quenching of the conjugated polymer, whereas, Zn^{2+} or Cd^{2+} do not produce a obvious fluorescent difference from the metal-free polymer. Herein, metal ions with an open shell electronic structure, which generally show the strong metal–ligand orbital interaction to form low-lying ligand-to-metal (LM) charge transfer state, may exhibit highly quenching responses as in the case of Ni^{2+} with $3d^8$ electronic structure and Cu^{2+} with $3d^9$ electronic structure. Metal ions with a full-occupancy outer-shell orbital or half-occupancy outer-shell orbital, which generally show the weak metal–ligand orbital interaction, may exhibit low quenching responses as in the case of Zn^{2+} ($3d^{10}$) and Cd^{2+} ($4d^{10}$). The obvious quenching effects can also be attributed to the intramolecular photoinduced electron transfer (PET) or photoinduced charge transfer (PCT).^{15,20,24,27,53} Such distinct ion responsive behaviors can also reveal the obvious coordination ability differences of transition metal ions with 2,2'-bipyridyl receptor in the polymer main chain backbone. As a result, the design of the novel polymers used as fluorescent chemosensors for selectively sensing of metal ions can be realized through appropriate alteration of receptors with various degrees of affinity toward metal ions.

UV–vis absorption spectra changes of the conjugated polymer on the four metal ions are shown in Figure 5. As is evident from Figure 5(a,b), UV–vis spectra of the polymer appear little change upon the various molar ratio additions of Cd^{2+} or Zn^{2+} from 1 : 0.5 to 1 : 5. On the contrary, titration curves of UV–vis of the polymer exhibit obvious changes as the increasing concentration of Ni^{2+} or Cu^{2+} . UV–vis spectra of Ni^{2+} -containing polymer complex appears both the decreasing of the absorption intensity and about 20 nm red-shift relative to the free-metal polymer [Fig. 5(c)]. Moreover, the UV–vis absorption intensity and wavelength of the conjugated polymer on Cu^{2+} addition show a pronounced difference from the other three metal ions [Fig. 5(d)]. The intensity of UV–vis absorption maxima of the Cu^{2+} -containing polymer show the gradual reduction, and

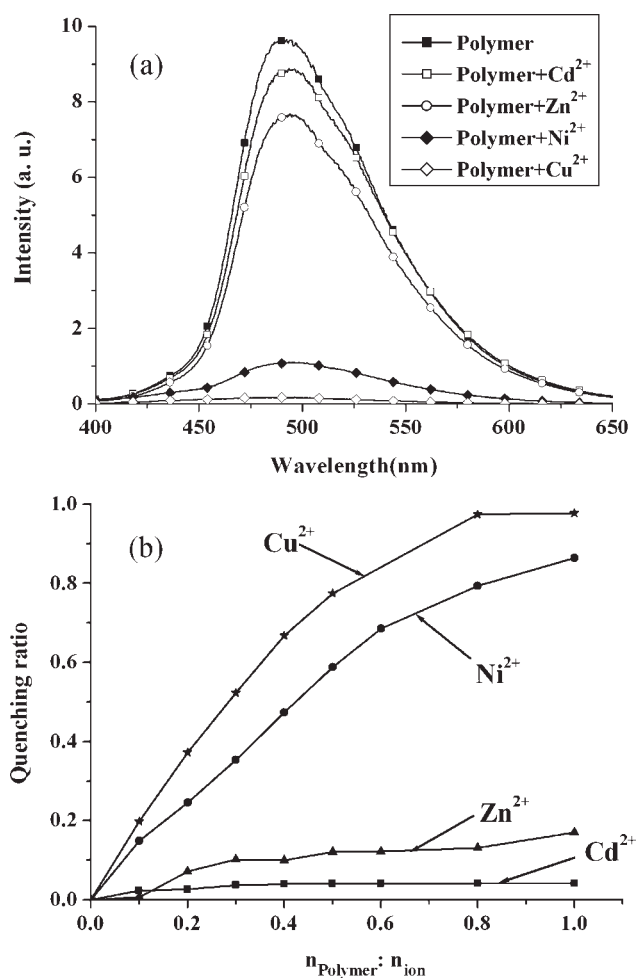


Figure 4 Fluorescent spectra (a) and the quenching ratio (b) of the polymer on metal ions ($\lambda_{\text{ex}} = 368 \text{ nm}$).

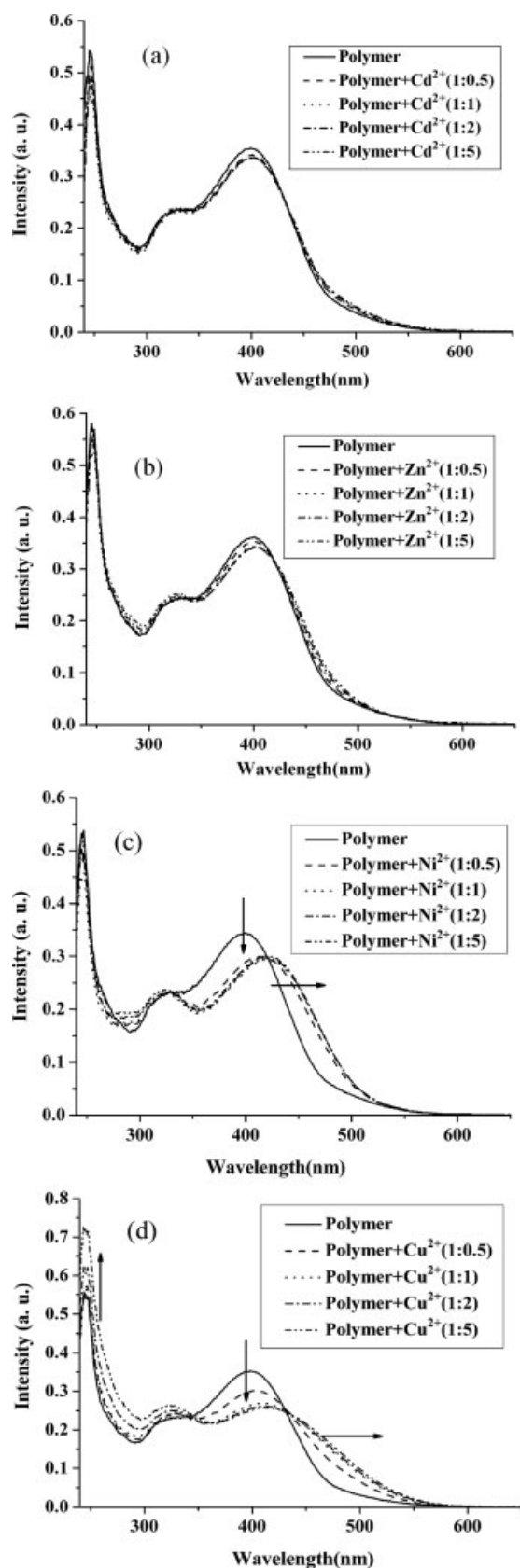


Figure 5 UV-Vis spectra of the polymer on Cd^{2+} (a), Zn^{2+} (b), Ni^{2+} (c), and Cu^{2+} (d).

the absorption wavelength arisen from the conjugated structure of the polymer main-chain backbone appears the gradual red-shift from 399 to 405, 408, 415, and 416 nm upon the various molar ratio additions from 1 : 0.5 to 1 : 1, 1 : 2, and 1 : 5. Moreover, the absorption peak of Cu^{2+} -containing polymer at 244 nm which is regarded as the absorption band of the naphthyl group shows a gradual enhancement as the increasing concentration of Cu^{2+} addition. On the basis of Wang and Wasielewski's report,⁴ the ionochromic responses of 16 different di and trivalent main group and transition metal ions and six trivalent lanthanide ions on the ion-recognition-induced polymers incorporating 2,2'-bipyridyl moiety in the conjugated polymer main chain were measured in CHCl_3 solution. Both absorption and fluorescent emission bands of the metal-containing polymer complexes appeared considerable changes, depending on the different metal ions presented and the polymers used. The results indicated that the group of Ag^+ , Al^{3+} , Cd^{2+} , Hg^{2+} , Zn^{2+} , and the lanthanide ions induced red shifts in the absorption spectra, whereas, Pb^{2+} , Fe^{3+} , Fe^{2+} , Cu^+ , and Sb^{3+} induced blue shifts. As postulated by the authors, the red shifts of the absorption bands could be ascribed to electron density changes caused by the complexation of cationic mono-, di-, or trivalent metal ions or to conformational changes in the polymer's backbone as a result of the chelation. Blue shifts caused by the coordination of specific metal ions could be attributed to a deconjugation effect on the polymer's backbone.

CONCLUSIONS

Pd-catalyzed Heck reaction was found to offer a simple access to the conjugated polymer. The conjugated polymer is air stable and shows good solubility in some organic solvents. The polymer emits strong blue-green fluorescence. The bipyridyl moiety can orient a well-defined spatial arrangement in main chain backbone of the conjugated polymer. While the conjugated polymer was used as a fluorescent chemosensor for transition metal ions, the results show that Cu^{2+} and Ni^{2+} can form nonradiative metal-to-ligand charge-transfer complexes with the polymer, whereas, Zn^{2+} or Cd^{2+} do not produce a pronounced difference from the polymer fluorescence and UV-vis spectra. The quenching effects can be attributed to the coordination ability differences from transition metal ions with 2,2'-bipyridyl receptor. The results demonstrate that the 2,2'-bipyridyl moiety in the main chain backbone of the conjugated polymer can act as the recognition site of a special fluorescent chemosensor for sensitive detection of transition metal ions.

References

1. Burroughs, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* 1990, 347, 539.
2. Bredas, J. L.; Deljonne, D.; Coropcean, V.; Cornil, J. *Chem Rev* 2004, 104, 4971.
3. Yu, W. L.; Meng, H.; Pei, J.; Huang, W.; Li, Y. F.; Heeger, A. L. *Macromolecules* 1998, 31, 4838.
4. Wang, B.; Wasielewski, M. R. *J Am Chem Soc* 1997, 119, 12.
5. Peng, Z. H.; Gharavi, A. R.; Yu, L. P. *J Am Chem Soc* 1997, 119, 4622.
6. Peng, Z. H.; Bao, Z. N.; Galvin, M. E. *Adv Mater* 1998, 10, 680.
7. Hwang, S. W.; Chen, Y. *Macromolecules* 2002, 35, 5438.
8. Zhan, X. W.; Liu, Y. Q.; Wu, X.; Wang, S.; Zhu, D. B. *Macromolecules* 2002, 35, 2529.
9. Descalzo, A. B.; Rurack, K.; Weisshoff, H.; Ramon, M. M.; Marcos, M. D.; Amoros, P.; Hoffmann, K.; Soto, J. *J Am Chem Soc* 2005, 127, 184.
10. Badugu, R.; Lakowicz, J. R.; Geddes, C. D. *J Am Chem Soc* 2005, 127, 3635.
11. Tang, Y. L.; Feng, F. D.; He, F.; Wang, S.; Zhu, D. B. *J Am Chem Soc* 2006, 128, 14972.
12. Lu, G.; Grossman, J. E.; Lambert, J. B. *J Org Chem* 2006, 71, 1769.
13. Ramon, M. M.; Felix, S. *Chem Rev* 2003, 103, 4419.
14. Tang, Y. L.; He, F.; Yu, M. H.; Wang, S.; Li, Y. L.; Zhu, D. B. *Chem Mater* 2006, 18, 3605.
15. Liu, Y.; Zhang, S. W.; Miao, Q.; Zheng, L. F.; Zong, L. L.; Cheng, Y. X. *Macromolecules* 2007, 40, 4839.
16. Wang, S. L.; Chang, Y. T. *J Am Chem Soc* 2006, 128, 10380.
17. Li, Z. B.; Lin, J.; Pu, L. *Angew Chem Int Ed* 2005, 44, 1690.
18. Pu, L. *Chem Rev* 2004, 104, 1687.
19. Kokil, A.; Yao, P.; Weder, C. *Macromolecules* 2005, 38, 3800.
20. McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem Rev* 2000, 100, 2537.
21. Zhou, G.; Cheng, Y. X.; Wang, L. X.; Jing, X. B.; Wang, F. S. *Macromolecules* 2005, 38, 2148.
22. Pei, J.; Liu, X. L.; Yu, W.; Lin, L.; L. ai, Y. H.; Niu, Y. H.; Cao, Y. *Macromolecules* 2002, 35, 7274.
23. Yasuda, T.; Yamaguchi, I.; Yamamoto, T. *Adv Mater* 2003, 15, 293.
24. Kimura, M.; Horai, T.; Hanabusa, K.; Shirai, H. *Adv Mater* 1998, 10, 459.
25. Eichen, Y.; Nakhmanovich, G.; Gorelik, V.; Epshtein, O.; Poplawski, J. M.; Ehrenfreund, E. *J Am Chem Soc* 1998, 120, 10463.
26. Zhang, M.; Lu, P.; Ma, Y. G.; Shen, J. C. *J Phys Chem B* 2003, 107, 6535.
27. Murphy, C. B.; Zhang, Y.; Troxler, T.; Ferry, V.; Martin, J. J.; Jones, W. E. *J Phys Chem B* 2004, 108, 1537.
28. Zhang, Y.; Murphy, C. B.; Jones, W. E. *Macromolecules* 2002, 35, 630.
29. Joshi, H. S.; Jamshidi, R.; Tor, Y. *Angew Chem Int Ed* 1999, 38, 2722.
30. Chen, L. X.; Jalger, W. J. H.; Gosztola, D. J.; Niemczyk, M. P.; Wasielewski, M. R. *J Phys Chem B* 1990, 2000, 104.
31. Kaes, C.; Katz, A.; Hosseini, M. W. *Chem Rev* 2000, 100, 3553.
32. Cheng, Y. X.; Zou, X. W.; Zhu, D.; Zhu, T. S.; Liu, Y.; Zhang, S. W.; Huang, H. J.; *Polym Sci Part A: Polym. Chem* 2007, 45, 650.
33. Liu, Y.; Miao, Q.; Zhang, S. W.; Huang, X. B.; Zheng, L. F.; Cheng, Y. X. *Macromol Chem & Phys* 2008, 209, 685.
34. El-Ghayoury, A.; Ziessel, R. *Tetrahedron Lett* 1997, 38, 2471.
35. Wen, G. A.; Zhu, X. R.; Wang, L. H.; Feng, J. C.; Zhu, R.; Huang, W. *J Polym Sci Part A: Polym Chem* 2007, 45, 388.
36. Belser, P.; Bernhard, S.; Jandrasics, E.; Von Zelewsky, A.; De Cola, L.; Balzani, V. *Coord Chem Rev* 1997, 159, 11.
37. Ward, M. D.; White, C. M.; Barigelletti, F.; Armaroli, N.; Calogero, G.; Flamigni, L. *Coord Chem Rev* 1998, 171, 481.
38. Song, J. F.; Zou, X. W.; Cheng, Y. X.; Huang, Z. L. *Acta Polym Sin* 2006, 8, 1007.
39. Lau, K.; Foster, J.; Williams, V. *Chem Commun* 2003, 17, 2172.
40. Ebmeyer, F.; Vogtle, F. *Chem Ber* 1989, 122, 1725.
41. Heck, R. F.; Nolleyjr, J. P. *J Org Chem* 1972, 37, 2320.
42. Heck, R. F. *Acc Chem Res* 1979, 12, 146.
43. Cheng, Y. X.; Liu, T. D.; Chen, L. W. *Chin J Chem* 2003, 21, 1101.
44. Tao, W.; Silverberg, L. J.; Rheingold, A. L.; Heck, R. F. *Organometallics* 1989, 8, 2550.
45. Cheng, Y. X.; Chen, L. W.; Song, J. F.; Zou, X. W.; Liu, T. D. *Polym J* 2005, 17, 355.
46. Song, J. F.; Cheng, Y. X.; Chen, L. W.; Zou, X. W.; Wang, Z. L. *Euro Polym J* 2006, 42, 663.
47. Meijere, A. D.; Meyer, F. E. *Angew Chem Int Ed Engl* 1994, 33, 2379.
48. Zhang, H. C.; Pu, L. *Tetrahedron* 2003, 59, 1703.
49. Scherf, U.; Mullen, K.; *Synthesis* 1992, 1/2, 23.
50. Cheng, Y. X.; Liu, T. D.; Chen, L. W. *Chin J Polym Sci* 2004, 22, 327.
51. You, W.; Wang, L. M.; Wang, Q.; Yu, L. *Macromolecules* 2002, 35, 4636.
52. Cheng, Y. X.; Song, J. F.; Zou, X. W.; Zhang, S. W.; Liu, Y.; Huang, H. *Polymer* 2006, 47, 6598.
53. Zotti, G.; Zecchin, S.; Schiavon, G.; Berlin, A.; Penso, M. *Chem Mater* 1999, 11, 3342.