Polymer 52 (2011) 6029-6036

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



(R,R)-salen/salan-based polymer fluorescence sensors for Zn^{2+} detection

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ARTICLE INFO

Article history: Received 20 April 2011 Received in revised form 2 November 2011 Accepted 9 November 2011 Available online 16 November 2011

Keywords: Chiral fluorescence polymer (R,R)-salen/salan Zn²⁺ detection

ABSTRACT

(*R*,*R*)-salen-based polymer fluorescence sensor **P-1** could be synthesized by the polymerization of 5,5′- (isoquinoline-5,8-diylbis(ethyne-2,1-diyl))-bis(3-tert-butyl-2-hydroxybenzaldehyde) (**M-1**) with (*R*,*R*)-1,2-diaminocyclohexane (**M-2**) *via* nucleophilic addition—elimination reaction, and (*R*,*R*)-salan-based polymer sensor **P-2** could be obtained by the reduction reaction of **P-1** with NaBH₄. The fluorescence response behaviors of two chiral polymers **P-1** and **P-2** on Zn^{2+} were investigated by fluorescence spectra. The fluorescence intensities of **P-1** and **P-2** can exhibit gradual enhancement upon addition of Zn^{2+} . Compared with other cations, such as Na⁺, K⁺, Mg²⁺, Ca²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Ag⁺, Cd²⁺, Cr³⁺ and Pb²⁺, Zn²⁺ can lead to the pronounced fluorescence enhancement as high as 22.8-fold for **P-1** and 3.75-fold for **P-2**, respectively. The results show that **P-1** and **P-2** incorporating (*R*,*R*)-salen/salan moieties as receptors in the polymer main chain backbone can exhibit high sensitivity and selectivity for Zn^{2+} detection.

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1. Introduction

Fluorescent sensors have witnessed a tremendous rise in the number of monitoring biologically relevant species such as metal ions in the past few years [1]. Especially, optical imaging with fluorescent sensors for Zn^{2+} detection has attracted great attention due to the biological significance of zinc [2-9]. As the second most abundant transition metal ion in the human body, Zn(II) ion plays an essential role in cellular metabolism, gene expression, apoptosis and neurotransmission [10-12]. The ability to track Zn(II) release in cell requires the highly selective and sensitive detector in a realtime and quantitative fashion [13,14]. Moreover, Zn(II) has no optical spectroscopic signal due to its closed-shell 3d¹⁰ electronic configuration, which limits the kinds of methods on its study and detection. Optical detection, following changes in solution fluorescence arising from a Zn(II)-induced perturbation of a chromophore, is best suited for monitoring Zn(II) in either biological contexts or living systems [2,15,16]. These problems have promoted numerous efforts on the design of sensitive chemosensors that can effectively detect zinc (II) ion without interference from other metal ions, especially Cd^{2+} .

Recently, many fluorescence sensors for Zn(II) detection have been reported, but most of them are based on organic small

molecules [17-27], only a few are polymer-based sensors [28-33]. In particular, fluorescence polymer sensors incorporating molecular recognition moieties are that they can make use of the high sensitivity of conjugated polymers to external structural perturbations and to electron density changes of the conjugated polymer backbone, when they can interact and form complexes with transition metal ions [34.35]. Conjugated polyelectrolytes (CPEs) as fluorescent chemosensors for metal ion detection based on the photoinduced-electron-transfer and energy migration mechanism have several advantages over small molecule sensors, such as fluorescent enhancement associated with electronic interaction between receptors and analytes within the conjugated π -electronic polymer main backbone. Swager reported that the delocalizable π electronic conjugated "molecular wire" polymer can greatly amplify the fluorescence response signal due to facile energy migration along the polymer backbone upon light excitations. As a result, a single CP can provide the enhanced fluorescence response behavior relative to one of its monomer units [36,37]. Therefore, the extended π -conjugated polymer, coupled with the chelation site, is expected to provide unique response toward selected metal ions.

Salen, as a well-known building block, has widely used as a chelation-enhanced fluorescence sensor for transition metal ions detection due to the potentially tetradentate N_2O_2 donor [38–42]. Moreover, very few salen-based fluorescence polymer sensors for zinc ion detection have been reported [28,29,43–45]. To the best of our knowledge, there has been no report on salan-based



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^{0032-3861/\$ —} see front matter @ 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.polymer.2011.11.017

fluorescence polymer sensors for metal ions detection so far. In this paper, we reported the synthesis of two novel (R,R)-salen/salanbased polymers **P-1** and **P-2** as fluorescent sensors for Zn²⁺. Compared with other cations, such as Na⁺, K⁺, Mg²⁺, Ca²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Ag⁺, Cd²⁺, Al³⁺ and Pb²⁺, Zn²⁺ can lead to the most pronounced fluorescence enhancement response without interference from other metal ions, especially Cd²⁺. More importantly, **P-1** and **P-2** turn to be bright yellow after addition of Zn²⁺, which can be easily detected by naked eyes. The results indicate that two chiral polymers incorporating (R,R)-salen/salan moieties as receptors in the main chain backbone can exhibit highly selective and sensitive fluorescence responses for sensing zinc ion.

2. Experimental part

2.1. Measurements and materials

NMR spectra were obtained using a 300-Bruker spectrometer 300 MHz for ¹H NMR and 75 MHz for ¹³C NMR and reported as parts per million (ppm) from the internal standard TMS. FT-IR spectra were taken on a Nexus 870 FT-IR spectrometer. UV–vis spectra were obtained from a Perkin–Elmer Lambda 25 spectrometer. Fluorescence spectra were obtained from an RF-5301PC spectrometer. Thermogravimetric analyses (TGA) was performed on a Perkin–Elmer Pyris-1 instrument under N₂ atmosphere. MS was determined on a Micromass GCT. C, H and N of elemental analyses were performed on an Elementar Vario MICRO analyzer. Circular dichroism (CD) spectrum was determined with a Jasco J-810 spectropolarimeter. Molecular weight was determined by GPC with Waters-244 HPLC pump and THF was used as solvent and relative to polystyrene standards. All solvents and reagents were commercially available and analytical-reagent-grade. Isoquinoline, 2-tert-butylphenol and (R,R)-1,2-diaminocyclohexane were purchased from Aldrich and directly used without purification. THF and Et₃N were purified by distillation from sodium in the presence of benzophenone.

2.2. Preparation of 3-tert-butyl-2-hydroxy-5-iodobenzaldehyde (4)

3-tert-butyl-2-hydroxybenzaldehyde **(3)** was synthesized according to a reported method [46]. A mixture of 3-tert-butyl-2-hydroxybenzaldehyde (2.6 g, 14.6 mmol) and iodine (5.56 g, 21.9 mmL) was dissolved in anhydrous THF (20 mL), a solution of NaHCO₃ (1.84 g, 21.9 mmol in 5 mL H₂O) was added to the above solution. The mixture was refluxed 12 h, and the reaction was quenched by saturated NaS₂SO₃ solution (15 mL). Upon being evaporated to dryness, the residue was extracted with ethyl acetate (3 × 30 mL) and washed with aqueous Na₂SO₂ and brine twice and then dried over anhydrous Na₂SO₄. The solution was recrystallized by petroleum ether to afford a white solid 3-tert-butyl-2-hydroxy-5-iodobenzaldehyde (4.2 g, 79%). ¹H NMR (300 Hz, CDCl₃): δ 11.76 (s, 1H), 9.82 (s, 1H), 7.73 (dd, *J* = 9.0, 2.3 Hz, 2H), 1.42 (s, 9H) (Scheme 1).

2.3. Preparation of the model compounds (**5** and **6**) (Scheme 1) [47,48]

A mixture of 3-tert-butyl-2-hydroxybenzaldehyde **(3)** (712.9 mg, 4.0 mmol) and (R,R)-1,2-diaminocyclo- hexane (228.4 mg, 2.0 mmol) was dissolved in 20 mL methanol. The obtained yellow solution was heated at reflux for 1 h. After cooling to room temperature, the solvent was removed by a rotary evaporator. The crude product was recrystallized by the mixed solvents of ethyl acetate and petroleum ether to afford a yellow solid **5** (692 mg, 80%)



yield). $[\alpha]_D^{25} = -431.00$ (*c* 0.29, THF). ¹H NMR (300 Hz, CDCl₃): δ 13.87 (br, 2H), 8.32 (s, 2H), 7.27 (d, 2H), 7.03 (d, *J* = 7.5 Hz, 2H), 6.74 (t, *J* = 7.7 Hz, 2H), 3.36–3.38 (m, 2H), 1.06–2.02 (m, 6H), 1.49–1.53 (m, 2H), 1.46 (s, 18H). FT-IR (KBr, cm⁻¹): 3292, 3058, 2997, 2945, 2860, 1631, 1486, 1438, 1269, 1139, 1087, 852, 754, 680.

The model compound (5) (200 mg, 0.46 mmol) was dissolved in the solvent of 20 mL MeOH, and then NaBH₄ (44.0 mg, 1.16 mmol) was added portionwise at room temperature over a period of 30 min to the above solution. The reaction mixture was stirred at room temperature until the yellow color disappeared. The colorless solution was stirred for another 30 min, and then 10 mL water was added to stop the reduction reaction. The mixture was extracted with CH_2Cl_2 (3 \times 20 mL). The combined organic layers were dried with anhydrous Na₂SO₄ and evaporated under re cduced pressure to yield the model compound (6) (200 mg, 100% yield) as a white solid. $[\alpha]_{D}^{25} = -46.77$ (*c* 0.29, THF). ¹H NMR (300 Hz, CDCl₃): δ 7.21 (d, J = 8.1 Hz, 2H), 6.89 (d, J = 7.5 Hz, 2H), 6.74 (t, J = 7.5 Hz, 2H). 4.03(dd, J = 36.6, 13.5 Hz, 4H), 2.46 (t, J = 4.2 Hz, 2H), 2.20 (d, J = 12 Hz, 2H), 1.73 (d, J = 4.2 Hz, 2H), 1.393–1.470 (m, 20H), 1.25 (d, J = 8.1 Hz, 2H). FT-IR (KBr, cm⁻¹): 3298, 3051, 2997, 2945, 2858, 1591, 1440, 1240, 1089, 781, 746.

2.4. Preparation of M-1 (Scheme 1)

To a mixture of 5,8-bis(ethynyl)isoquinoline (2) (177.2 mg, 1.0 mmol), 3-tert-buty-2-hydroxy-5- iodobenzaldehyde (4) (608.2 mg, 2.0 mmol), Pd(PPh₃)₄ (74.7 mg, 0.06 mmol), and CuI (11.4 mg, 0.06 mmol), 30 mL Et₃N was added. The reaction mixture was heated to 45 °C for 4 h under a N₂ atmosphere. After cooled to room temperature, the solvent was removed by a rotary evaporator. The residue was purified by silica gel column chromatography to yield 460 mg (87%) of the product as a yellow powder after removal of the solvent. ¹H NMR (300 Hz, CDCl₃): δ 12.05 (s, 1H), 12.04 (s, 1H), 9.95 (s, 2H), 9.87 (s, 1H), 8.74 (d, J = 5.0 Hz 1H), 8.24 (d, J = 5.7 Hz 1H), 7.94 (d, J = 7.5 Hz 1H), 7.83 (d, J = 7.8 Hz 1H), 7.75-7.79 (m, 4H), 1.49 (s, 18H). ¹³C NMR (75 Hz, CDCl₃): δ 196.5, 161.7, 161.6, 151.4, 144.5, 139.2, 136.9, 135.9, 135.5, 135.3, 133.3, 130.6, 121.6, 120.5, 120.2, 113.6, 113.4, 96.6, 96.1, 84.9, 84.6, 35.0, 29.0. FT-IR (KBr, cm⁻¹): 3437, 2958, 2871, 2210, 1652, 1598, 1450, 1407, 1269, 1151, 765, 713. MS (FAB): *m*/*z* 528.3 (M⁻-1). Anal. Calcd for C₃₅H₃₁NO₄: C, 79.37; H, 5.90; N, 2.64; O, 12.08. Found: C, 79.31; H, 5.88; N, 2.66; O, 12.15.

2.5. Preparation of the polymers P-1 and P-2 (Scheme 1)

A mixture of **M-1** (0.11 g, 0.21 mmol) and (*R*,*R*)-1,2diaminocyclohexane (23.7 mg, 0.21 mmol) was dissolved in 10 mL of chloroform. The obtained solution was stirred at 40 °C for 4 h. Methanol was added precipitate the yellow (*R*,*R*)-salen-based polymer. The resulting polymer was filtrated and washed with methanol several times, and then dried in the yield of 75% (95 mg). GPC: $M_w = 10840$, $M_n = 6300$, PDI = 1.7. [α]_D²⁵ = +917.03 (*c* 0.21, THF). ¹H NMR (300 Hz, CDCl₃): δ 14.33 (br, 2H), 9.79 (s, 1H), 8.66 (d, J = 5.8 Hz, 1H), 8.33 (s, 2 H), 8.14 (d, J = 5.7 Hz, 1H), 7.82 (d, J = 7.6 Hz, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.52 (d, J = 4.7 Hz, 4H), 7.35 (d, J = 8.4 Hz, 2H), 1.80–2.08 (m, 8H), 1.46 (d, J = 2.1 Hz, 18H). FT-IR (KBr, cm⁻¹): 3439, 2935, 2860, 2198, 1631, 1450, 1386, 1363, 1278, 1203, 1161, 1001, 563, 487. Anal. Calcd for C₄₂H₄₅N₃O₂: C, 80.86; H, 7.27; N, 6.74; O, 5.13. Found: C, 79.79; H, 7.32; N, 6.78; O, 6.11.

100 mg polymer **P-1** was dissolved in the mixed solvents of 10 mL THF and 10 mL MeOH, and then NaBH₄ was added in batches to the above solution. The reaction mixture was stirred at room temperature for 2 h, and 10 mL water was added to stop the reduction reaction. The mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried with

anhydrous Na₂SO₄, and evaporated under reduced pressure to afford **P-2** as a yellow powder (85 mg, 85.3% yield). GPC: $M_w = 8980$; $M_n = 5060$; PDI = 1.7. $[\alpha]_D^{25} = +178.36 (c 0.21, THF)$. ¹H NMR (300 Hz, CDCl₃): $\delta = 9.85$ (s, 1H), 8.67 (d, J = 5.1 Hz, 1H), 8.20 (d, J = 5.4 Hz, 1H), 7.83 (s, 1H), 7.74 (s, 1H), 7.50 (s, 3H), 7.23 (d, J = 9.6 Hz 1H), 4.05 (dd, J = 29.7, 11.7 Hz 4H), 2.53–2.66 (m, 2H), 2.21 (s, 2H), 1.75 (s, 4H), 1.42 (s, 18H), 1.37 (s, 2H). FT-IR (KBr, cm⁻¹): 3427, 2947, 2860, 2198, 1598, 1556, 1471, 1257, 1139,1076, 883, 840, 786. Anal. Calcd for C₄₂H₄₉N₃O₂: C, 80.34; H, 7.87; N, 6.69; O, 5.10 Found: C, 80.45; H, 7.91; N, 6.66; O, 4.98.

2.6. Metal ion titration

Each metal ion titration experiment was started with a 3.0 mL polymer in THF solution with a known concentration $(1.0 \times 10^{-5} \text{ mol L}^{-1} \text{ corresponding to } (R,R)$ -salen or (R,R)-salan moiety). Zn(NO₃)₂ salt and other various metal salts (nitrate, $1.0 \times 10^{-3} \text{ mol L}^{-1}$, H₂O) were used for the titration. Polymer-metal complexes were produced by adding aliquots of a solution of the selected metal salt to a THF solution of the polymer. All kinds of measurements were monitored 30 min after addition of the metal salt to the polymer solutions.

3. Results and discussion

3.1. Synthesis and structure feature of the polymers

The synthesis procedures of the monomer (M-1), model compounds (5, 6) and the chiral polymers P-1. P-2 are outlined in Scheme 1. 5,8-Bis(ethynyl)isoquinoline (2) was synthesized by a three-step reaction from the starting product isoquinoline according to the literature [49]. 3-Tert-butyl-2-hydroxy-5iodobenzaldehyde (4) could be synthesized from 2-tert-butylphenol [46]. Monomer M-1, 5,5'-(isoquinoline-5,8-diylbis(ethyne-2,1diyl))bis(3-tert-butyl-2-hydroxybenzaldehyde), was synthesized by the reaction of **2** with **4** via a typical Pd-catalyzed Sonogashira cross-coupling reaction. Chiral salen-based polymer P-1 was obtained by Schiff base formation between M-1 and (R,R)-1,2- diaminocyclohexane (M-2) as a yellow powder in 75% yield, and chiral salan-based polymer P-2 could be obtained by reduction of P-1 with NaBH₄ in 85.3% yield. (R,R)-salen/salan moieties as the metal chelating ligands can orient in a well-defined spatial arrangement in the chiral polymer main chain backbones and also directly coordinate with different transition metal ions to form the corresponding metal-polymer complexes. Furthermore, we also chose an electron-deficient heterocyclic unit 5,8-bis(ethynyl)isoquinoline as the conjugated molecular bridge linker into the polymer main chain. Quinoline, isoquinoline, guinoxaline and oxadiazole derivatives have been widely used as electron transporting/hole blocking materials in LED devices and LED blends because these units have many excellent properties on the better chromophore, high electron affinity, high thermal and oxidative stability, and the good charge injection and transporting building blocks [49-61]. 5,8-Bis(ethynyl)isoquinoline can maintain conjugation between the isoquinoline and salen/salan moieties so that the electron transporting properties of the chiral polymers can be improved. In addition, the ethynyl linker can reduce steric hindrance between isoquinoline and phenyl groups and also have a beneficial influence on the stability of the resulting chiral polymers.

The GPC results of two chiral polymers **P-1** and **P-2** show moderate molecular weights. **P-1** and **P-2** are air stable solid and show good solubility in common solvents, such as toluene, THF, CHCl₃ and CH₂Cl₂, which can be attributed to the nonplanarity of the twisted polymer backbone and the flexible *t*-butoxy substituents on phenyl units as side chains of the polymers. TGA of **P-1** and



Fig. 1. TGA curve of the chiral polymers.

P-2 were carried out under a N₂ atmosphere at a heating rate of 10 °C/min. As shown in Fig. 1, **P-1** show an apparently one-step degradation at temperature ranging from 350 to 550 °C. **P-2** exhibits a two-step degradation process: the first step degradation is observed at temperature ranging from 200 to 300 °C, and the second step degradation appears at temperature ranging from 360 °C to 700 °C. There is a total loss of about 50%, 45% for **P-1**, **P-2** when heated to 700 °C. Therefore, the herein described materials can provide desirable thermal properties for practical applications as fluorescent chemosensors.

3.2. CD spectra

The specific rotation values $([\alpha]_D^{25})$ of the model compounds **5** and **6** are $-431.00 (c \ 0.29, \text{THF})$ and $-46.77 (c \ 0.29, \text{THF})$. And $[\alpha]_D^{25}$ of the chiral polymers **P-1** and **P-2** are $+917.03 (c \ 0.21, \text{THF})$ and $+178.36 (c \ 0.21, \text{THF})$, respectively. But the absolute values of the specific rotation $([\alpha]_D^{25})$ of two polymers are much larger than their corresponding model compounds and have opposite specific rotation signal, which can be attributed to the counteracting result of the repeating chiral unit upon the formation of helical chiral polymer configuration [62–68]. Fig. 2 illustrates the CD spectra of the model compound **5**, compound **6** and the chiral polymers **P-1** and **P-2** ($1.0 \times 10^{-5} \text{ mol/L}$) in THF. The model compound **5** and the chiral polymer **P-1** exhibit different CD signals with negative and



Fig. 2. CD spectra of the model compounds 5, 6, P-1 and P-2 in THF.

Table 1				
CD spectra data of compounds 5 and 6	, P-1	and	P-2 in	THF

	•			
	$\textbf{5} \times 10^5$	$\pmb{6}\times 10^5$	$\textbf{P-1} \times 10^5$	$\textbf{P-2}\times10^{5}$
$[\theta](\lambda_{\max})$	-0.45 (222.0)	+0.016 (219.1)	-1.95 (228.8)	+0.80 (218.6)
in nm)	+0.71 (231.4)	-0.075 (221.0)	+0.81 (260.4)	-0.64 (222.5)
	+0.86(250.8)		-0.69 (361.0)	+0.40 (416.8)
	-0.83 (268.2)		+1.87 (413.6)	
	-0.67 (330.5)			

positive Cotton effects at short wavelengths in their CD spectra. The reason may be contributed to the (R.R)-salen moietie can orient a well-defined spatial arrangement in the regular polymer backbone. That is, each unit in the polymer P-1 acts independently with an organized helical chain structure. The polymer P-2 exhibits relatively weak positive and negative Cotton effect at the wavelength less than 230 nm and one strong positive Cotton effect band centered at 417 nm, respectively. However, the model compound 6 almost appears no Cotton effect signal in the CD spectrum (Table 1). Compared to the rigid chain backbone structure P-1, the flexible chain backbone P-2 shows weaker Cotton effect although P-2 should generate chiral secondary helical structure. It could be contributed to another reason that the chiral (R,R)-1,2diaminocyclohexane unit is no longer available for the conjugated system of model compound 6 and P-2. It can also be found that P-1 and P-2 have strong Cotton effect at long wavelengths of 414 nm and 417 nm, which can be regarded as the extended conjugated structure [43,49,69-71].

3.3. UV-vis titration of the chiral polymers on Zn^{2+}

Fig. 3 illustrates the UV–vis absorption spectra of model compounds **5**, **6**, and **P-1**, **P-2** $(1.0 \times 10^{-5} \text{ mol L}^{-1})$ in THF. UV–vis spectra of the polymers **P-1**, **P-2** are similar due to the similar repeating units of the conjugated polymer backbone. UV–vis absorption maxima λ_{max} of model compounds **5** and **6** appear at 331 nm and 292 nm, respectively. But the conjugated polymers **P-1** and **P-2** display great red shifts and show the strong and broad absorption wavelengths λ_{max} of **P-1** and **P-2** and appear at 389 nm and 394 nm. A large red shifts in the electronic absorptions of the conjugated polymers can be attributed to the effective π - π^* conjugated segments of the polymer main chain backbone [49,71].

The UV-vis responses of the chiral polymers **P-1** and **P-2** on transition Zn^{2+} ions were tested in THF solution (Fig. 4). Upon



Fig. 3. UV-vis spectra of model compounds 5, 6, P-1 and P-2 in THF.



Fig. 4. UV-vis spectra of P-1 (a) and P-2 (b) with increasing amounts of Zn^{2+} (0-2.0 equiv).



Fig. 5. Fluorescence spectra of model compound 5, model compound 6, P-1 and P-2 in THF.

addition of Zn^{2+} (0–2.0 equiv), the main absorbance peak of the chiral polymer **P-1** at 389 nm appears the obvious reduction, meanwhile a shoulder peak in the wavelength region at 453 nm can be observed and show gradual enhancement with increasing amounts of Zn^{2+} . However, the crest band of the polymer **P-1** at 306 nm shows a little enhancement (Fig. 4a). Moreover, there are two isosbestic points at 338 and 411 nm, which indicate the formation of the UV active zinc complex [72]. In view of **P-2**, the main absorbance peak of **P-2** also appears the obvious decrease, and the gradual enhancement of a shoulder peak at 454 nm can be

observed with increasing addition of Zn^{2+} (Fig. 4b). In addition, the weak absorption band of the polymer **P-2** at 275 nm shows a little enhancement. There are three isosbestic points located at 281, 340 and 414 nm, which also indicate the formation of the UV active zinc complex [72].

3.4. The selective and sensitive recognition of the polymer sensors on Zn^{2+}

Fluorescence spectra of model compounds **5**, **6** and **P-1**, **P-2** are shown in Fig. 5. The two chiral polymers **P-1** and **P-2** can emit yellow light under ultraviolet light (361 nm) in low concentration $(1 \times 10^{-5} \text{ mol L}^{-1})$. On excitation at 280 nm, fluorescence maxima λ_{max} of model compounds **5**, **6** appear at 304 and 322 nm. On the contrary, the emission wavelengths λ_{max} of **P-1**, **P-2** ($\lambda_{\text{ex}} = 420 \text{ nm}$) exhibit large red shifts as high as 234 nm and 237 nm due to the extended π -electronic structure in the main chain backbone [69,73–75].

The fluorescence response behaviors of two chiral polymers **P-1** and **P-2** $(1.0 \times 10^{-5} \text{ mol L}^{-1} \text{ in THF})$ on Zn^{2+} have been investigated by fluorescence spectra with the common excitation at 420 nm (Fig. 6a and b). As is evident from Fig. 6, obvious fluorescence enhancement could be observed upon the addition of Zn^{2+} . Zn^{2+} can lead to fluorescence enhancement as high as 22.8-fold for **P-1** and 3.75-fold for **P-2** at a concentration of 1:1 M ratio. More importantly, **P-1** and **P-2** turns to be bright yellow after addition of Zn^{2+} , which can be easily detected by naked eyes (Seen the inset figure of Fig. 6). It can also be found that the addition curves keep nearly linear correlation with the concentration molar ratio of Zn^{2+} from 0.1 to 0.9 for **P-1** and **P-2** (Fig. 7). Normally, the fluorescent



Fig. 6. Fluorescence spectra of **P-1** (a) and **P-2** (b) with increasing amounts of Zn^{2+} ($\lambda_{ex} = 420$ nm).



Fig. 7. Fluorescence enhancement values (I/I_0-1) vs the increasing concentration of Zn^{2+} for P-1 (a) and P-2 (b).

enhancement for salen/salan-based polymers can be attributed to two reasons [19,43,76,77]. One is suppressed PET (photoinducedelectron-transfer) quenching when Zn^{2+} coordinates with the nitrogen and oxygen atoms of (*R*,*R*)-salen/(*R*,*R*)-salan-based moieties in the chiral polymer main chain. On complexation, the lone pair of electrons on the nitrogen and oxygen atom is no longer available for ICT (intramolecular charge transfer) or PET (photoinduced-electron-transfer), thus leading to an enhancement of the emission. On the other hand, the formation of Zn^{2+} -polymer complexes can enhance the planarity and rigidity of the conjugated segment of the chiral polymer, which can reduce the non-radiative decay of the excited state and lead to the pronounced fluorescence enhancement. However, we found that **P-1** bearing salen unit can exhibit more pronounced fluorescence response on Zn^{2+} than salan-based polymer **P-2**. One reason may result from the steric hindrance on the complex formation of the flexible salan-based unit with Zn^{2+} . The other reason is due to the fact that the lone pair of electrons on the nitrogen atom is no longer available for conjugated system of Zn^{2+} -**P-2** complex, leading to the disappearence of suppressed PET quenching. As shown in Fig. 6, we also found that a short red shift of about 10 nm is observed when salen-based receptor in the main chain backbone of the polymer **P-1** coordinates with Zn^{2+} , while salan-based **P-2** shows a larger blue shift as high as 20 nm, which may be attributed to the changes of HOMO of the conjugated segment of the chiral polymer [78,79].

In this paper we further investigated the fluorescence response behaviors of the chiral polymers on other various metal ions, including Na⁺, K⁺, Mg²⁺, Ca²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Ag⁺, Cd²⁺,



Fig. 8. The selectivity of the polymers toward Zn^{2+} and other metal ions. (a) Fluorescence spectra of **P-1** (1.0×10^{-5} mol L^{-1}) in THF with 1.0 equiv of a metal ion. (b) Relative fluorescence intensity of **P-1**-metal ions complex. (c) Fluorescence spectra of **P-2** (1.0×10^{-5} mol L^{-1}) in THF with 1.0 equiv of a metal ion. (d) Relative fluorescence intensity of **P-2**-metal ions complex.

 Cr^{3+} and Pb^{2+} . In these experiments, the fluorescence spectra of two polymers (1.0×10^{-5} mol L⁻¹ in THF) were determined at room temperature in the absence and presence of 1.0 equiv. of a metal ion with the excitation at 420 nm. As is evident from Fig. 8a and c, addition of Zn^{2+} ion to a THF solution of **P-1** or **P-2** can induce a remarked fluorescence enhancement. By contrast, the fluorescent enhancement response of the salan-based polymer P-1 are not almost affected by the addition of most of the other metal ions. especially Cd^{2+} (Fig. 8d). But addition of 1.0 equiv of Ag⁺ and Cd^{2+} can slightly enhance fluorescence for polymer **P-1** (I/I_0 -1 = 0.850, 0.456), and Na⁺, K⁺, Mg²⁺, Ca²⁺, Cr³⁺, Fe³⁺, Al³⁺ and Pb²⁺ caused limited quenching of the fluorescence intensity on the same condition. Meanwhile, Cu²⁺ and Ni²⁺ can effectively quench fluorescence of the chiral polymer (I/I_0 -1 = -0.848, -0.868), but Co²⁺ can lead to almost complete quenching of the chiral polymer (I/I₀-1 = -0.926). In view of **P-2**, the similar effect was observed (Fig. 8d). Addition of 1.0 equiv of Na⁺, Ni²⁺, Ag⁺, Pb²⁺ slightly enhanced fluorescence $(I/I_0-1 = 0.297, 0.297, 0.197, 0.719)$ for polymer **P-2**. And K⁺, Mg²⁺, Ca²⁺, Cr³⁺, Fe³⁺ and Al³⁺ caused limited quenching of the fluorescence intensity on the same condition. Meanwhile, Co^{2+} , Cu^{2+} and Cd^{2+} can effectively guench fluorescence of the chiral polymer $(I/I_0-1 = -0.965, -0.965, -0.928)$. These results confirmed the polymer P-1 and P-2 can exhibit high sensitivity and selectivity fluorescence enhancement response to Zn²⁺. In addition, the polymer chemosensors can also exhibit obvious fluorescence quenching response to Co^{2+} , Ni^{2+} and Cu^{2+} , which can be attributed to photoinduced charge transfer (PCT) between the polymer backbones and binding metal complexes. 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 a highly quenching response as in the case of Co^{2+} with $3d^7$, Ni^{2+} with $3d^8$ and Cu^{2+} with $3d^9$ electronic structure.

4. Conclusion

Chiral polymer **P-1** incorporating (R,R)-salen-type unit was synthesized via nucleophilic addition-elimination reaction, and chiral polymer **P-2** incorporating (R,R)-salan-type unit could be obtained by the reduction reaction of P-1 with NaBH₄. Compared with other cations, such as Na⁺, K⁺, Mg²⁺, Ca²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Ag⁺, Cd²⁺, Cr³⁺ and Pb²⁺, Zn²⁺ can lead to the pronounced fluorescence enhancement as high as 22.8-fold for P-1 and 3.75fold for P-2. The two chiral polymers P-1 and P-2 incorporating (R,R)-salen/salan as a receptor in the main chain backbone can exhibit high sensitivity and selectivity for Zn²⁺. And **P-1** exhibited more sensitive response signals for Zn^{2+} than **P-2**.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 21074054, 51173078), National Basic Research Program of China (2010CB923303), the Bureau of Science and Technology of Wenzhou (No. S20100007) and the Fundamental Research Funds for the Central Universities (1082020502).

Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2011.11.017.

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