

# A Highly Selective Fluorescence-Based Polymer Sensor Incorporating an (*R,R*)-Salen Moiety for Zn<sup>2+</sup> Detection

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**Abstract:** A chiral polymer incorporating an (*R,R*)-salen moiety was synthesized by the polymerization of (*R,R*)-1,2-diaminocyclohexane with 2,5-dibutoxy-1,4-di(salicylaldehyde)-1,4-diethynyl-benzene by a nucleophilic addition–elimination reaction. The fluorescence responses of the (*R,R*)-salen-based polymer toward various metal ions were investigated by fluorescence spectra. Compared with other cations,

such as Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Ag<sup>+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, and Pb<sup>2+</sup>, Zn<sup>2+</sup> can lead to a pronounced fluorescence enhancement as high as 7.8-fold together with an obvious blue-shift change of the

chiral polymer. More importantly, the fluorescent color of the polymer changed to bright blue instead of weak yellow after addition of Zn<sup>2+</sup>, which can be easily detected by the naked eye. The results indicate that this kind of chiral polymer, incorporating an (*R,R*)-salen moiety as a receptor in the main chain backbone, can exhibit high sensitivity and selectivity for Zn<sup>2+</sup> recognition.

**Keywords:** diaminocyclohexane • chiral polymer • fluorescence • sensors • zinc detection

## Introduction

As the second most abundant transition-metal ion in the human body, the Zn<sup>2+</sup> ion plays an essential role in cellular metabolism, gene expression, apoptosis, and neurotransmission.<sup>[1]</sup> Disorder of Zn<sup>2+</sup> homeostasis is involved in a number of diseases, such as Alzheimer's disease,<sup>[2]</sup> prostate cancer,<sup>[3]</sup> and diabetes.<sup>[4]</sup> Consequently, the detection of Zn<sup>2+</sup> has attracted increasing interest in the areas of chemical and biological sciences. Zn<sup>2+</sup> has no optical spectroscopic signature due to its closed-shell 3d<sup>10</sup> configuration, which limits the kinds of methods that can be applied to its study and detection. Optical detection, following changes of fluo-

rescence or UV/Vis spectroscopy arising from a Zn<sup>2+</sup>-induced perturbation of a chromophore, is best suited for Zn<sup>2+</sup> detection in biological contexts or living systems. A number of analytical techniques have been reported for Zn<sup>2+</sup> detection, such as electrochemical,<sup>[5]</sup> UV/Vis,<sup>[6]</sup> fluorescence,<sup>[7]</sup> and atomic absorption spectra methods.<sup>[8]</sup> Among them, fluorescent sensors are of great practical value because of their advantages of simplicity, high sensitivity, and low cost. A typical fluorescence sensor contains a receptor (the recognition site) linked to a fluorophore (the signal source), which translates the recognition event into the fluorescence signal.<sup>[9]</sup> Therefore, an ideal fluorescence sensor must meet two basic requirements. First, the receptor must have the strongest affinity with species of interest (binding selectivity), which is the central processing unit of a sensor. Second, the fluorescence signal should not be perturbed by the environment (signal selectivity). Investigation into the development of highly sensitive and selective fluorescent sensors has received much attention in recent years. In particular, numerous efforts have focused on the design of chemosensory systems with unique electrical and optical properties that are capable of detecting metal ions in both a real-time and reversible fashion.

A number of fluorescence sensors containing quinoline,<sup>[10]</sup> fluorescein,<sup>[11]</sup> and peptides<sup>[12]</sup> for Zn<sup>2+</sup> detection have been reported in the literature, but most of them are based on small molecules, and reports of polymer-based chemosensors

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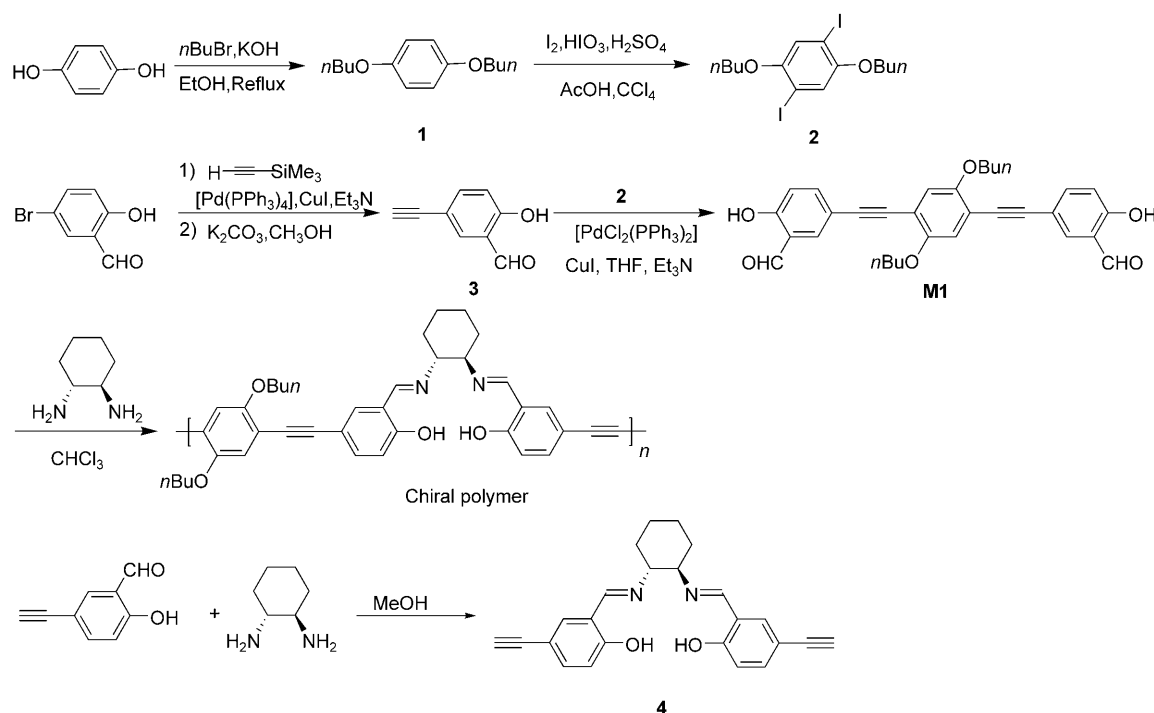
are few.<sup>[13]</sup> An advantage of fluorescent conjugated polymers over small molecules is that signal amplification occurs from electronic communication along the polymer backbone. Swager and co-workers<sup>[14]</sup> reported that the delocalizable  $\pi$ -electronic conjugated “molecular-wire” polymer can greatly amplify the fluorescence responsive change due to facile energy migration along the polymer backbone upon light excitation. As a result, a single conjugated polymer provides an enhanced optical response relative to one of its monomer units, and conjugated polymers can be used as optical platforms in highly sensitive chemical and biological sensors. Additionally, to the best of our knowledge, some available  $\text{Zn}^{2+}$  sensors have difficulty in distinguishing  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ ,<sup>[15]</sup> since  $\text{Cd}^{2+}$  is in the same group of the periodic table and has similar properties to  $\text{Zn}^{2+}$ . Therefore, the design of highly selective and sensitive fluorescence sensor for  $\text{Zn}^{2+}$  detection without interference from other metal ions, especially  $\text{Cd}^{2+}$ , is one of the most important objectives.

Salen, a particular chelating Schiff base, can be synthesized by the condensation of salicylaldehydes or salicylaldehyde derivatives with 1,2-diamines. Salen-based ligands can form stable complexes with various metal ions due to the potentially tetradentate  $\text{N}_2\text{O}_2$  donor.<sup>[16]</sup> In consideration of the reported fluorescence properties of salen- $\text{Zn}$ ,<sup>[17]</sup> we designed a novel optically active (*R,R*)-salen-based polymer and used it as fluorescence sensor for  $\text{Zn}^{2+}$  recognition. In this paper, the fluorescence response of the chiral polymer toward various metal ions is fully investigated. Compared with other cations, such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ , and  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  can lead to a pronounced fluorescence enhancement

together with an obvious blue-shift change of the chiral polymer. More importantly, the fluorescent color of the polymer changed to bright blue instead of weak yellow after addition of  $\text{Zn}^{2+}$ , which can be easily detected by the naked eye. The results indicate that this kind of chiral polymer incorporating (*R,R*)-salen moiety as a receptor in the main chain backbone can exhibit high sensitivity and selectivity for  $\text{Zn}^{2+}$  recognition.

## Results and Discussion

**Syntheses and features of the chiral polymer sensor:** 1,4-Diiodo-2,5-dibutoxybenzene (**2**) was synthesized from the starting material hydroquinone in a two-step reaction according to reported procedures.<sup>[18,19]</sup> 5-Ethynylsalicylaldehyde (**3**) was synthesized in a two-step reaction from the starting material 5-bromosalicylaldehyde.<sup>[20]</sup> Monomer, 2,5-dibutoxy-1,4-di(salicylaldehyde)-1,4-diethynylbenzene (**M1**), was synthesized by a typical Sonogashira reaction from **2** and **3**. The chiral polymer incorporating the (*R,R*)-salen moiety was obtained by Schiff base formation between the dialdehyde **M1** and (*R,R*)-1,2-diaminocyclohexane as a yellow powder in 72.4% yield (Scheme 1). The specific rotation value ( $[\alpha]_{\text{D}}^{25}$ ) of the model compound **4** is  $-0.059$  ( $c = 0.49$ , THF), and the  $[\alpha]_{\text{D}}^{25}$  of the polymer is  $+10.62$  ( $c = 0.20$ , THF). The molecular weight was determined by GPC by using a Waters-244 HPLC pump with THF as the solvent and relative to polystyrene standards. GPC analysis shows the high molecular weight corresponding to approximately a 71 repeating unit ( $M_w = 91080$ ,  $M_n = 41700$ , polydispersity



Scheme 1. Synthesis procedures of the chiral polymer and the model compound **4**.

index (PDI)=2.18). The chiral polymer is an air-stable solid, yellow in color and shows good solubility in common organic solvents, such as toluene, THF,  $\text{CHCl}_3$ , and  $\text{CH}_2\text{Cl}_2$ , which can be attributed to the nonplanarity of the twisted polymer backbone and the flexible *n*-butoxy substituent. According to thermal analysis of the polymer (Figure 1), it

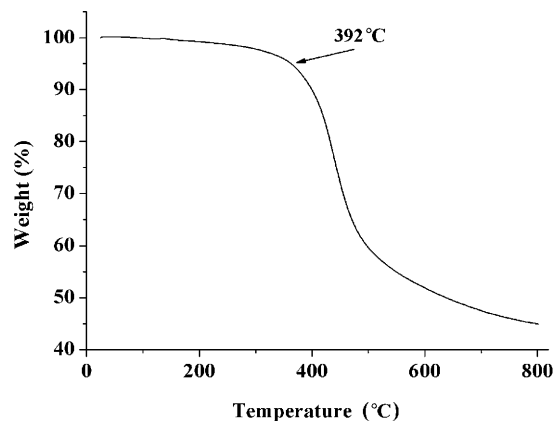


Figure 1. TGA curve of the chiral polymer.

has a high thermal stability without loss of weight below 390°C. An apparently one-step degradation was observed at temperatures ranging from 390°C to 700°C. The polymer tends to complete decomposition at 800°C. A total loss of about 46% was observed when it was heated to 800°C. Therefore, the chiral polymer is stable and can provide desirable thermal property for practical application as a fluorescence sensor.

**Optical properties:** Figure 2 illustrates the UV/Vis absorption spectra and fluorescence spectra of the model compound **4** and the chiral polymer ( $1.0 \times 10^{-5} \text{ mol L}^{-1}$  corresponding to the (*R,R*)-salen moiety in THF). As shown in

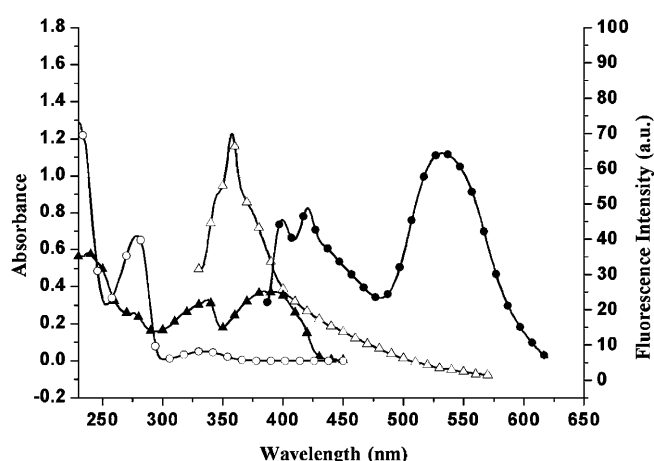


Figure 2. UV/Vis spectra and fluorescence spectra of the model compound **4** ( $1.0 \times 10^{-5} \text{ mol L}^{-1}$ ) and the chiral polymer ( $1.0 \times 10^{-5} \text{ mol L}^{-1}$ ) in THF.  $\circ$  = UV (model compound **4**),  $\blacktriangle$  = UV (polymer),  $\triangle$  = PL (model compound **4**,  $\lambda_{\text{ex}} = 324 \text{ nm}$ ),  $\bullet$  = PL (polymer,  $\lambda_{\text{ex}} = 375 \text{ nm}$ ).

Figure 2, the UV/Vis spectrum of compound **4** exhibits a maximal absorption at 234 nm, the polymer shows a strong and broad absorption in the region from 350 to 430 nm, which is associated with a  $\pi$ - $\pi^*$  transition of the conjugated segment. The chiral polymer has fluorescent emissions at 400, 420, and 530 nm upon excitation at 375 nm. Compared with the model compound **4**, the polymer shows a large red shift due to the extended  $\pi$ -electronic structure in the main chain backbone. Figure 3 illustrates the circular dichroism

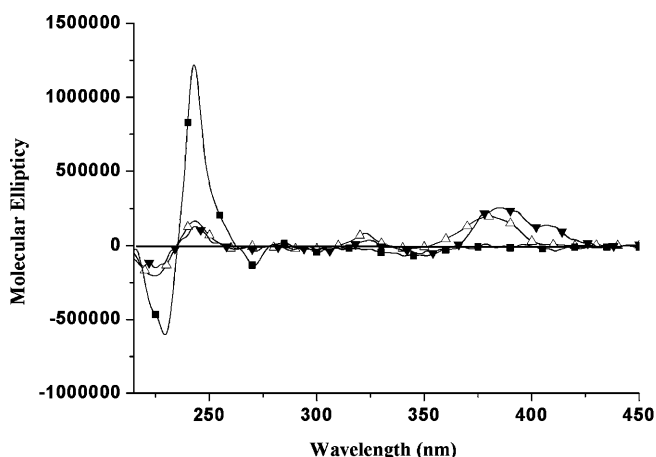


Figure 3. CD spectra of the model compound **4** ( $\blacksquare$ ) and the polymer in the absence ( $\triangle$ ) and presence of 1.0 equiv  $\text{Zn}^{2+}$  ( $\blacktriangledown$ ) in THF.

(CD) spectra of the model compound **4** and the chiral polymer in the absence and presence of  $\text{Zn}^{2+}$  (1.0 equiv) in THF. The molecular ellipticity of **4** is  $[\theta]_{\lambda(\text{max})} = -6.06 \times 10^5$  (229.5 nm),  $1.22 \times 10^6$  (243.0 nm),  $-1.37 \times 10^5$  (270.8 nm),  $-6.56 \times 10^4$  (348.4 nm); and that of the chiral polymer is  $[\theta]_{\lambda(\text{max})} = -2.06 \times 10^5$  (224.7 nm),  $1.62 \times 10^5$  (243.4 nm),  $-2.36 \times 10^4$  (262.1 nm),  $2.55 \times 10^4$  (297.6 nm),  $8.04 \times 10^4$  (322.6 nm),  $-2.16 \times 10^4$  (343.4 nm),  $1.95 \times 10^5$  (380.2 nm), respectively. The model compound **4** and the chiral polymer exhibit similar CD signals with negative and positive Cotton effects at short wavelengths in their CD spectra. But the CD intensity of the model compound **4** is much stronger than that of the chiral polymer. On the contrary, the chiral polymer has the longer wavelength CD effect at about 380 nm, which is attributed to the extended conjugated structure in the repeating unit. In addition, the CD spectrum of the  $\text{Zn}^{2+}$  polymer exhibits little change except a 6 nm red shift at long wavelength, which is consistent with the changing features of the UV/Vis absorption spectra (Figure 4).

**UV/Vis titration of the chiral polymer on  $\text{Zn}^{2+}$ :** As shown in Figure 4, the UV/Vis spectra of the polymer exhibit a maximal absorption at 240 nm and two broad bands around 337 and 391 nm before titrations in THF. Upon addition of  $\text{Zn}^{2+}$  (0–1.2 equiv), the absorbance peaks at 240 and 337 nm show a little reduction with increasing amounts of  $\text{Zn}^{2+}$ . On the contrary, the strongest broad-band absorption peak at 395 nm arising from the conjugated structure exhibits a

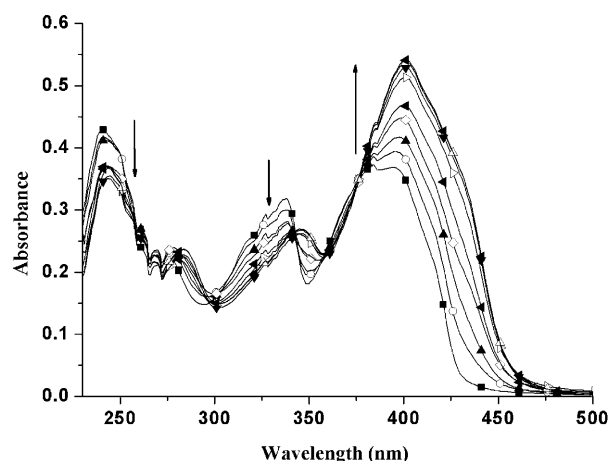


Figure 4. UV/Vis spectra of the polymer ( $1.0 \times 10^{-5} \text{ mol L}^{-1}$ ) in THF with increasing amounts of  $\text{Zn}^{2+}$  (Polymer/ $\text{Zn}^{2+}$  = 1:0 (■), 1:0.1 (○), 1:0.2 (▲), 1:0.3 (◇), 1:0.4 (◀), 1:0.6 (▷), 1:0.8 (▼), 1:1.0 (△), 1:1.2 (◄)).

gradual enhancement and an obvious bathochromic shift. Meanwhile, a new absorption peak at 284 nm can be observed. Moreover, there are four isosbestic points at 298, 343, 362, and 376 nm, which indicate the formation of the UV active zinc complex.<sup>[15b]</sup>

**The selective and sensitive recognition of the chiral polymer on  $\text{Zn}^{2+}$ :** The fluorescence titration of the polymer with  $\text{Zn}^{2+}$  was presented in Figure 5. The polymer displayed a

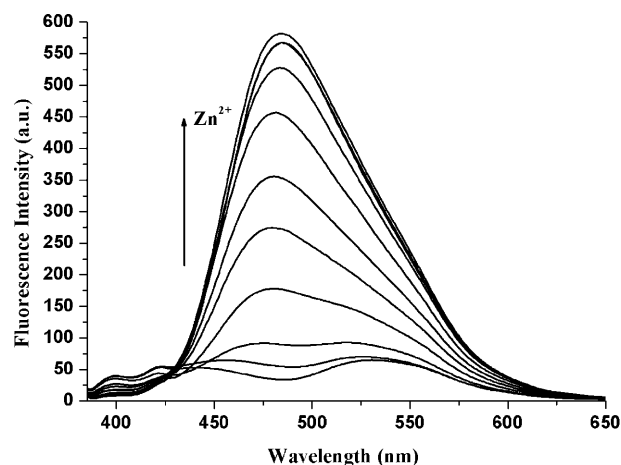


Figure 5. Fluorescence spectra of the polymer ( $1.0 \times 10^{-5} \text{ mol L}^{-1}$ ) in THF with increasing amounts of  $\text{Zn}^{2+}$  (0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 8.0, 10.0, 11.0,  $12.0 \times 10^{-6} \text{ mol L}^{-1}$ ) ( $\lambda_{\text{ex}} = 375 \text{ nm}$ ).

weak and broad emission band situated at 530 nm due to the extended  $\pi$ -electronic structure. The fluorescence intensities of the  $\text{Zn}^{2+}$ -containing polymer complex show gradual enhancement, as high as 7.8-fold, upon the concentration molar ratio addition of  $\text{Zn}^{2+}$  from 0.1 to 1.2. It can also be found that the addition curve keeps a nearly linear correla-

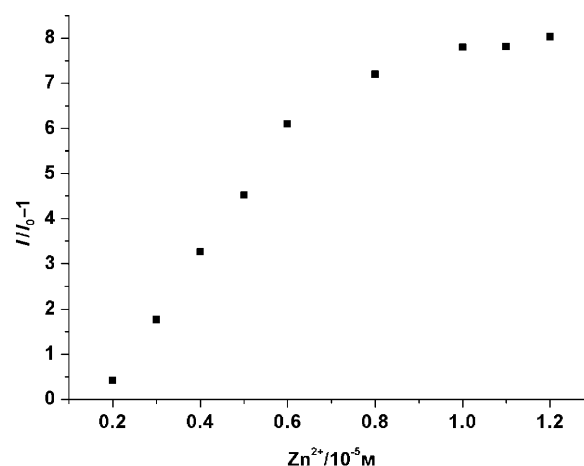


Figure 6. Plot of the concentration of  $\text{Zn}^{2+}$  versus  $I-I_0/I_0$ , in which  $I$  is the fluorescence intensity of the polymer ( $1.0 \times 10^{-5} \text{ mol L}^{-1}$ ) with addition of  $\text{Zn}^{2+}$  at  $\lambda_{\text{em}} = 480 \text{ nm}$  and  $I_0$  is the fluorescence intensity of the polymer without  $\text{Zn}^{2+}$  at  $\lambda_{\text{em}} = 530 \text{ nm}$ .

tion with the concentration molar ratio of  $\text{Zn}^{2+}$  from 0.2 to 0.6 (Figure 6). Moreover, the maximum emission wavelength of the polymer was remarkably blue shifted from 530 to 480 nm along with a dramatic enhancement of fluorescence intensity. The  $\text{Zn}^{2+}$ -polymer solution can emit blue fluorescence and was easily detected by the naked eye (Inset; Figure 5). The obvious fluorescent enhancement can be attributed to two reasons.<sup>[23]</sup> One is suppressed PET (photoinduced-electron-transfer) quenching when  $\text{Zn}^{2+}$  coordinates with the nitrogen atoms of the (*R,R*)-salen-based moiety in the chiral polymer main chain. Upon complexation, the lone pair of electrons on the nitrogen atom is no longer available for PET, thus leading to an enhancement of the emission. On the other hand, the formation of  $\text{Zn}^{2+}$ -polymer can enhance the planarity and rigidity of the conjugated segment of the chiral polymer, which can reduce the nonradiative decay of the excited state and lead to the pronounced fluorescence enhancement. As shown in Figure 5, we also found that when the salen-based  $\text{N}_2\text{O}_2$  receptor in the main chain backbone of the chiral polymer coordinates with  $\text{Zn}^{2+}$ , a large blue shift of about 50 nm for the emission spectrum peak of the polymer is observed, which may be attributed to a decrease of the HOMO of the conjugated segment of the chiral polymer.<sup>[24]</sup>

The above studies prompted us to select the polymer for further evaluation aimed at determining its selectivity. The fluorescence titration of the polymer with various metal ions exhibits high selectivity to  $\text{Zn}^{2+}$  (Figure 7). Addition of 1.0 equiv of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  slightly enhanced fluorescence ( $I/I_0 - 1 < 0.5$ ). And  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Hg}^{2+}$  caused limited quenching of the fluorescence intensity under the same conditions. Meanwhile,  $\text{Fe}^{3+}$  and  $\text{Co}^{2+}$  can effectively quench fluorescence of the chiral polymer, but  $\text{Mn}^{2+}$  and  $\text{Cu}^{2+}$  lead to almost complete quenching of the chiral polymer (Figure 7). Most importantly, based on the fluorescence image of the chiral polymer in the absence and presence of 1.0 equiv of a metal ion, we can

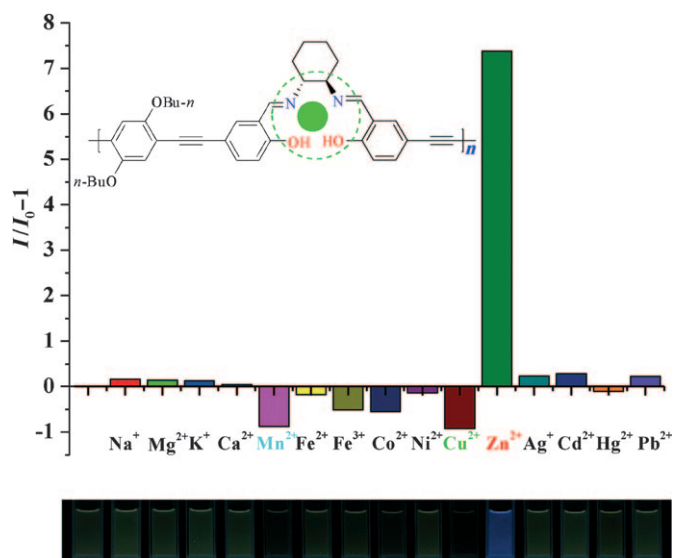


Figure 7. The selectivity of the polymer toward  $\text{Zn}^{2+}$  and other metal ions. In these experiments, the fluorescence measurement was taken at  $\lambda_{\text{ex}} = 375 \text{ nm}$  from  $10 \mu\text{M}$  of the polymer in THF at room temperature and in the absence and presence of 1.0 equiv of a metal ion. The fluorescence intensity at  $\lambda_{\text{em}} = 530 \text{ nm}$  is plotted against the analyte. Bottom: The fluorescence image of a solution of the polymer ( $1 \times 10^{-5} \text{ mol L}^{-1}$ ) plus 1.0 equiv metal ion excited by a commercially available UV lamp ( $\lambda = 365 \text{ nm}$ ).

easily distinguish  $\text{Zn}^{2+}$  by the distinctive bright blue fluorescence from use of a UV lamp ( $\lambda = 365 \text{ nm}$ ) with the naked eye. In this paper, we further investigated the selectivity of the polymer for  $\text{Zn}^{2+}$  using a solution of Zn-polymer complex treated with other metal ions. The fluorescence intensities of the chiral polymer do not appear to have obvious differences in the presence of other metal ions, or the mixture of the chosen metal ions even at a higher concentration except that the coexisting ions ( $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Fe}^{3+}$ ) showed interference in  $\text{Zn}^{2+}$  detection to some extent. The results indicate that the resulting chiral polymer can be used as  $\text{Zn}^{2+}$  selective probe that was hardly affected by coexisting ions (see the Supporting Information, Figures S7 and S8).

## Conclusion

A chiral polymer incorporating an (*R,R*)-salen moiety was synthesized, which exhibits excellent fluorescent sensor properties for the detection of  $\text{Zn}^{2+}$ . Compared with other cations, such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ , and  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  can produce a pronounced fluorescence enhancement as well as a large blue shift of the polymer fluorescence. Most importantly, we can identify  $\text{Zn}^{2+}$  with the naked eye by using a commercially available UV lamp ( $\lambda = 365 \text{ nm}$ ). This work can be applied to the detection of  $\text{Zn}^{2+}$  by a simple, rapid, sensitive, and selective method.

## Experimental Section

**Measurements and materials:** All solvents and reagents were commercially available and analytical reagent grade. THF and  $\text{Et}_3\text{N}$  were purified by distillation from sodium in the presence of benzophenone. NMR spectra were obtained by using a 300-Bruker spectrometer 300 MHz for  $^1\text{H}$  NMR spectroscopy and 75 MHz for  $^{13}\text{C}$  NMR spectroscopy and are reported as parts per million (ppm) from the internal standard TMS. FTIR spectra were taken on a Nexus 870 FTIR spectrometer. Fluorescence spectra were obtained from an RF-5301PC spectrometer. UV/Vis spectra were obtained by using a Perkin-Elmer Lambda 25 spectrophotometer. Specific rotation was determined with a Ruolph Research Analytical Autopol I. MS was determined on a Micromass GCT. Elemental analyses for C, H, and N were performed on an Elementar Vario MICRO analyzer. Molecular weight was determined by GPC with Waters-244 HPLC pump and THF was used as solvent and relative to polystyrene standards.

**Metal ion titration:** Each metal ion titration experiment was started with polymer (3 mL) of known concentration ( $1.0 \times 10^{-5} \text{ mol L}^{-1}$  with respect to the (*R,R*)-salen moiety in THF solution).  $\text{Zn}(\text{NO}_3)_2$  salt and other various metal salts (nitrate,  $3.0 \times 10^{-4} \text{ mol L}^{-1}$  in  $\text{H}_2\text{O}$ ) 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 chiral polymer. All types of measurement were monitored 5 min after addition of the metal salt to the polymer solutions.

**Preparation of 5-ethynylsalicylaldehyde (3):** 1,4-diiodo-2,5-dibutoxybenzene (**2**) was synthesized from hydroquinone in a two-step reaction according to the reported procedure.<sup>[18,19]</sup> Compound **3** was prepared according to a reported method.<sup>[20]</sup> Trimethylsilylacetylene (17.7 mL, 124.3 mmol) was added to a mixture of 5-bromosalicylaldehyde (5.00 g, 24.87 mmol),  $[\text{PdCl}_2(\text{PPh}_3)_2]$  (873 mg, 1.24 mmol), and CuI (474 mg, 2.48 mmol) in  $\text{Et}_3\text{N}$  (80 mL). The mixture was stirred for 12 h at  $80^\circ\text{C}$ . After cooling, the resulting ammonium salt was filtered off, and the residue was purified by chromatography on silica gel with petroleum ether as eluent. Removal of solvent under vacuum afforded a yellow powder, and the product was identified as 5-trimethylethynylsilylsalicylaldehyde (4.0 g, 74%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 11.11$  (s, 1H), 9.85 (s, 1H), 7.70 (d,  $J = 2.1 \text{ Hz}$ , 1H), 7.60 (dd,  $J = 8.7, 2.1 \text{ Hz}$ , 1H), 6.94 (d,  $J = 8.7 \text{ Hz}$ , 1H), 0.25 ppm (s, 9H). 5-Trimethylethynylsilylsalicylaldehyde (2.18 g, 10.0 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (10 mL). KOH (561 mg, 10.0 mmol) was dissolved in MeOH (5 mL) and added to the  $\text{CH}_2\text{Cl}_2$  solution. The reaction mixture was stirred at room temperature for 4 h, and then the solvent was concentrated under reduced pressure. A mixture of  $\text{H}_2\text{O}$  (20 mL) and  $\text{CH}_2\text{Cl}_2$  (20 mL) was added to the residue to afford a two-phase solution. The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 20 \text{ mL}$ ), and the combined  $\text{CH}_2\text{Cl}_2$  solutions were washed with  $\text{H}_2\text{O}$  and dried over  $\text{MgSO}_4$ . The solution was filtered, and the solvent was removed by rotary evaporation to obtain a light yellow powder identified as 5-ethynylsalicylaldehyde (**3**) (1.3 g, 88%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 11.15$  (s, 1H), 9.89 (s, 1H), 7.75 (d,  $J = 2.0 \text{ Hz}$ , 1H), 7.65 (dd,  $J = 8.6, 2.1 \text{ Hz}$ , 1H), 6.98 (d,  $J = 8.7 \text{ Hz}$ , 1H), 3.06 ppm (s, 1H).

**Preparation of 2,5-dibutoxy-1,4-di(salicylaldehyde)-1,4-diethynylbenzene (M1):**<sup>[21]</sup> The mixture of 5-ethynylsalicylaldehyde (438.3 mg, 3.0 mmol), 1,4-bis-dodecyloxy-2,5-diiodobenzene (474.1 mg, 1.0 mmol),  $[\text{PdCl}_2(\text{PPh}_3)_2]$  (70.6 mg, 0.1 mmol), and CuI (37.5 mg, 0.2 mmol) was dissolved in THF (10 mL), followed by addition of  $\text{Et}_3\text{N}$  (30 mL). The reaction mixture was heated to  $70^\circ\text{C}$  overnight. After cooling to room temperature, the solvent was removed by a rotary evaporator. The residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:3, v/v), then with ethyl acetate as eluent on a short plug of silica gel. The solvent was removed, and then washed by methanol to afford 2,5-dibutoxy-1,4-di(salicylaldehyde)-1,4-diethynylbenzene (**M1**) as a brown powder (294 mg, 57%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 11.15$  (s, 2H), 9.91 (s, 2H), 7.77 (d,  $J = 2.0 \text{ Hz}$ , 2H), 7.69 (dd,  $J = 8.6, 2.0 \text{ Hz}$ , 2H), 7.02 (t,  $J = 4.3 \text{ Hz}$ , 4H), 4.06 (t,  $J = 6.4 \text{ Hz}$ , 4H), 1.96–1.78 (m, 4H), 1.71–1.49 (m, 4H), 1.03 ppm (t,  $J = 7.4 \text{ Hz}$ , 6H);  $^{13}\text{C}$  NMR (75 Hz,  $\text{CDCl}_3$ ):  $\delta = 196.0, 161.4, 153.5, 139.7, 136.7, 120.5, 118.1, 116.7, 115.3, 113.6, 93.0, 85.4, 69.2, 31.3, 19.2, 13.8 \text{ ppm}$ ; MS (FAB):  $m/z$ : 510.3 [ $M+1$ ]<sup>+</sup>.

**Preparation of the model compound 4** (Scheme 1): A mixture of 5-ethynylsalicylaldehyde (584.6 mg, 4.0 mmol) and (*R,R*)-1,2-diaminocyclohexane (228.4 mg, 2.0 mmol) was dissolved in methanol (20 mL). The obtained solution was stirred at 40 °C for 12 h. After cooling to room temperature, the solvent was removed by a rotary evaporator. The crude product was recrystallized from ethyl acetate and petroleum ether to afford a yellow solid 4 (592 mg, 80% yield). Mp: 146–148 °C;  $[\alpha]_D^{25} = -0.059$  ( $c = 0.49$ , THF); <sup>1</sup>H NMR (300 Hz, CDCl<sub>3</sub>):  $\delta = 11.16$  (br, 2H), 8.23 (s, 2H), 7.39 (dd,  $J = 8.4$ , 1.8 Hz, 2H), 7.34 (d,  $J = 1.8$  Hz, 2H), 6.87 (d,  $J = 8.4$  Hz, 2H), 3.34–3.37 (m, 2H), 2.97 (s, 2H), 1.45–1.97 ppm (m, 8H); <sup>13</sup>C NMR (75 Hz, CDCl<sub>3</sub>):  $\delta = 163.9$ , 161.5, 135.9, 135.3, 118.2, 117.3, 112.2, 83.0, 75.7, 72.4, 32.8, 24.0 ppm; FTIR (KBr):  $\tilde{\nu} = 3299$ , 3281, 2941, 2863, 1633, 1587, 1486, 1286, 826, 585 cm<sup>-1</sup>; MS (FAB):  $m/z$ : 370.2 [ $M+1$ ]<sup>+</sup>; elemental analysis calcd (%) for C<sub>24</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>: C 77.81, H 5.99, N 7.56; found: C 77.81, H 6.01, N 7.58.

**Preparation of the chiral polymer** (Scheme 1):<sup>[22]</sup> A mixture of **M1** (0.1 g, 0.17 mmol) and (*R,R*)-1,2-diaminocyclohexane (20 mg, 0.17 mmol) was dissolved in chloroform (4 mL). The obtained solution was stirred at 40 °C for 4 h. Methanol was added to precipitate the yellow (*R,R*)-salen polymer. The resulting polymer was filtered and washed with methanol several times, and then dried resulting in a yield of 72.4% (70 mg). GPC results: Mw = 91080, Mn = 41700, PDI = 2.18;  $[\alpha]_D^{25} = +10.62$  ( $c = 0.20$ , THF); <sup>1</sup>H NMR (300 Hz, CDCl<sub>3</sub>):  $\delta = 13.59$  (br, 2H), 8.26 (s, 2H), 7.42 (dd,  $J = 8.7$ , 1.8 Hz, 2H), 7.38 (d,  $J = 1.8$  Hz, 2H), 6.97 (s, 2H), 6.88 (d,  $J = 8.7$  Hz, 2H), 4.01 (t,  $J = 6.3$  Hz, 2H), 3.36 (br, 2H), 1.75–1.92 (m, 10H), 1.46–1.62 (m, 8H), 0.99 ppm (t,  $J = 7.5$  Hz, 6H); FTIR (KBr):  $\tilde{\nu} = 3441$ , 2955, 2931, 2863, 1632, 1504, 1486, 1287, 1214 cm<sup>-1</sup>; elemental analysis calcd (%) for C<sub>38</sub>H<sub>40</sub>N<sub>2</sub>O<sub>4</sub>: C 77.52, H 6.85, N 4.76; found: C 77.48, H 6.73, N 4.59.

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