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In Situ Generated 1:1 Zn(II)-Containing Polymer Complex Sensor for Highly Enantioselective Recognition of N-Boc-Protected Alanine

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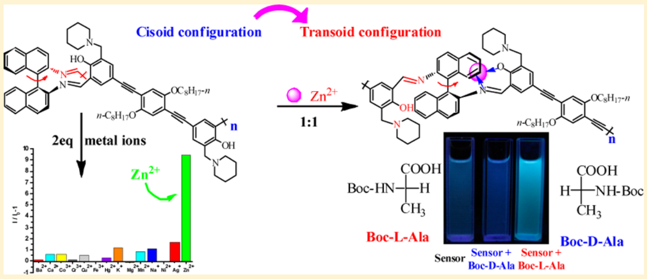
Supporting Information



ABSTRACT: A novel chiral (*S*)-BINAM-based fluorescence polymer sensor was designed and synthesized by the polymerization of 5,5′-((2,5-dioctyloxy-1,4-phenylene)bis(ethyne-2,1-diyl)bis(2-hydroxy-3-(piperidin-1-ylmethyl)-benzaldehyde (**M-1**) with (*S*)-2,2′-binaphthyldiamine (*S*-**BINAM**, **M-2**) via Schiff's base formation. The resulting chiral polymer sensor shows very weak fluorescence but exhibits the obvious fluorescence enhancement response toward Zn^{2+}. The *in situ* generated 1:1 Zn(II)-containing complex of chiral polymer can serve as a fluorescence sensor for highly enantioselective recognition of N-Boc-protected alanine, and the value of enantiomeric fluorescence difference ratio (*ef*) can reach as high as 6.90. This is the first report on the *in situ* generated chiral polymer complex used as a fluorescence sensor for highly enantioselective recognition of N-Boc-protected alanine.

■ INTRODUCTION

Investigations on highly sensitive and selective enantioselective recognition of chiral organic molecules have received increasing attention in recent years. In particular, numerous efforts have been devoted to the design of novel chiral fluorescence sensors with unique electrical and optical properties that are capable of detecting chiral molecule enantioselectivity in a both real time and reversible fashion[1−11] due to its importance for understanding the interactions of biological molecules, developing useful separation processes, designing of asymmetric catalysis systems, and screening high-throughput chiral catalyst.[12−20] Moreover, chiral fluorescence sensors can not only greatly facilitate rapid determination of enantiometric composition of chiral compounds with high sensitivity and waste reduction but also easily achieve high-throughput screening (HTS) determination.[19,21−23] In the past 10 years, many works have been reported on the design and synthesis of the fluorescent sensors for the amino acids and their derivatives.[24−31] But only some examples were focused on metal-containing complexes as chiral fluorescence sensors. Pu and co-workers designed a chiral BINOL−terpyridine−Cu(II) complex as fluorescence sensor for enantioselective recognition of chiral amino alcohols.[32] Feng also developed a chiral *N*,*N*′-dioxide−Ni(II) complex-based fluorescence sensor for enantioselective recognition of α-hydroxycarboxylic acids, amino alcohols, amino acids, and their derivatives.[27,28] Recently, our group reported the *in situ* generated perazamacrocycle−Cu(II) complex as chiral floresence sensor and successfully realized enantioselective recognition of unmodified α-amino acids in protic solution via a ligand displacement mechanism.[26]

Although there have been some works on enantioselective recognition based on metal ion containing complexes as chiral fluorescence sensors, most of them are based on chiral small molecules, and fluorescence polymer sensors are very few.[33−40] The fluorescence polymer sensors incorporating chiral recognition moieties are that they can make use of the high sensitivity of the conjugated polymers to external structural perturbations and to electron density changes within the conjugated polymer main backbone when they interact with chiral organic molecules.[41−43] Sensitive detection methods for sensing chiral molecules involve the exquisite design of "turn-on" fluorescence sensors based on the photoinduced electron transfer and energy migration mechanism within the conjugated polymer main backbone. Moreover, these chiral fluorescence-based polymers can also be systematically modified by the introduction of the different functional groups with steric and electronic properties at the well-defined molecular level.

The chirality of 2,2′-binaphthyldiamine (BINAM) is derived from the restricted rotation of the two naphthalene rings. The rigid structure and C_2 symmetry of the chiral binaphthyl molecules can play an important role in inherently chiral induction.[33,44−52] In our previous work we reported the chiral fluorescence polymer sensor incorporating (*S*)-2,2′-binaphthol (BINOL) and (*S*)-2,2′-BINAM moieties in the main chain of the polymer backbone for enantioselective recognition of phenylalaninol.[33] In this paper, we designed a novel

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fluorescence polymer sensor incorporating (*S*)-BINAM-based Schiff base moieties in the polymer main-chain backbone. The resulting polymer sensor can form *in situ* 1:1 Zn(II)-containing chiral polymer complex which can serve as a fluorescence sensor for highly enantioselective recognition of N-Boc-protected alanine. More importantly, the *in situ* Zn(II)-containing chiral polymer complex sensor solution can appear bright blue fluorescence color change upon addition of (L)-N-Boc-protected alanine under a commercially available UV lamp, which can be clearly observed by the naked eye.

■ EXPERIMENTAL SECTION

Instruments and Materials. All solvents and reagents were commercially available and analytical reagent grade. THF and Et_3N were purified by distillation from sodium in the presence of benzophenone. NMR spectra were collected on a Bruker 300 spectrometer (300 MHz for ^1H NMR and 75 MHz for ^{13}C NMR) and reported as parts per million (ppm) from the internal standard TMS. Electrospray ionization mass spectra (ESI-MS) were measured on a Thermo Finnigan LCQ Fleet system, and time-of-flight mass spectra (TOF-MS) were determined on a Micromass GCT. FT-IR spectra were taken on a Nexus 870 FT-IR spectrometer. Fluorescence spectra were obtained from an RF-5301PC spectrometer. The circular dichroism (CD) spectrum was determined with a Jasco J-810 spectropolarimeter. Specific rotation was determined with a Ruololph Research Analyfical Autopol I. C, H, and N of elemental analyses were performed on an Elementar Vario MICRO analyzer. Thermogravimetric analyses (TGA) were performed on a PerkinElmer Pyris-1 instrument under a N_2 atmosphere. Molecular weight was determined by gel permeation chromatography (GPC) with a Waters 244 HPLC pump, and THF was used as solvent relative to polystyrene standards.

*Synthesis of 2,5-Diiodo-1,4-dioctyloxybenzene (**1**).* A solution of hydroquinone (10 g, 90 mmol), *n*-bromooctane (35 g, 181 mmol), and K_2CO_3 (33.8 g, 245 mmol) in 250 mL of ethanol was reflexed for 12 h. Then the solvent was removed by a rotary evaporator, and the result mixture was diluted by water and extracted by CH_2Cl_2. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The crude product was obtained as an oil liquid without further purified and directly used for next reaction. A mixture of 1,4-dioctyloxybenzene (**1**) (5.0 g, 14.9 mmol), KIO_3 (1.3 g, 6.2 mmol), and iodine (3.2 g, 12.5 mmol) in acetic acid (50 mL), sulfuric acid (1.3 mL), and water (5 mL) was refluxed for 15 h. A precipitate formed. The suspension was cooled with an ice bath and filtered. The isolated solid was washed with saturated aqueous Na_2SO_3 solution and finally with water and dried in vacuo. Recrystallization from ethanol give 2,5-diiodo-1,4-dioctyloxybenzene (7.6 g, 87%) as a slightly beige crystals. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.19 (s, 2H), 3.94 (t, *J* = 6.5 Hz, 4H), 1.82 (m, 4H), 1.57−1.31 (m, 24H), 0.91 (t, *J* = 6.6 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 152.7, 122.7, 86.2, 70.3, 31.7, 29.18, 29.15, 29.07, 26.0, 22.6, 14.1. TOF-MS: *m*/*z* 586.0. FT-IR (KBr, cm^{-1}): 2921, 2850, 1635, 1486, 1459, 1400, 1352, 1214, 1051, 846, 786. Anal. Calcd for $C_{22}H_{36}I_2O_2$: C, 45.07; H, 6.19. Found: C, 46.02; H, 6.38.

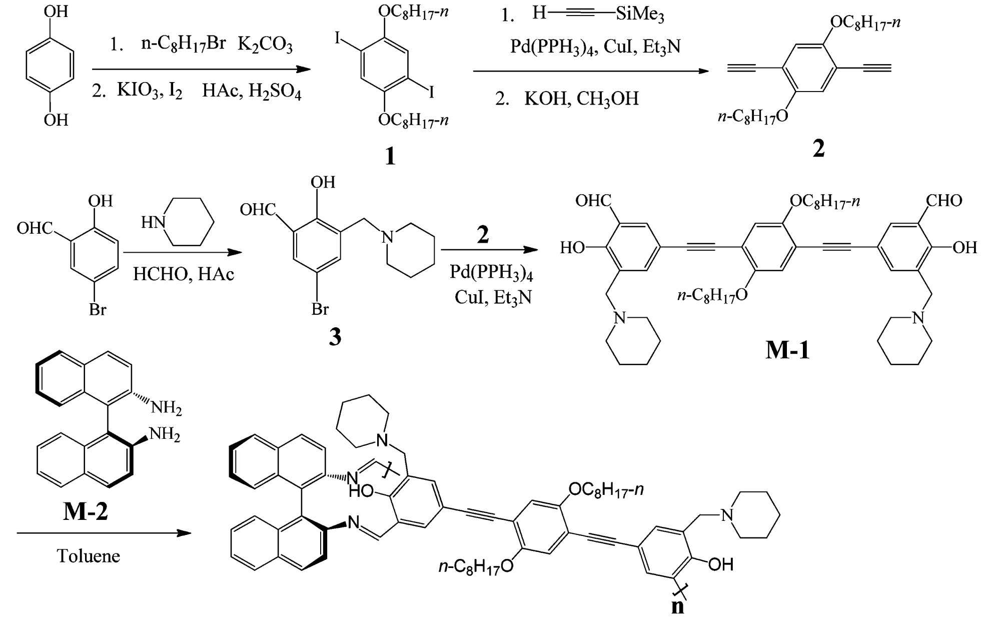
*Synthesis of 2,5-Diethynyl-1,4-dioctyloxybenzene (**2**).* A mixture of 2,5-diiodo-1,4-dioctyloxybenzene (5.86 g, 10 mmol), $Pd(PPh_3)_4$ (300 mg, 0.25 mmol), CuI (10 mg, 0.05 mmol), and trimethylsilylacetylene (2.4 mL, 20 mmol) was dissolved in 30 mL of Et_3N. The reaction mixture was stirred at 40 °C for 24 h under a N_2 atmosphere. After cooling, the resulting ammonium salt was filtered off, and the residue was purified by chromatography on a short plug of silica gel with petroleum ether as eluent. Removal of solvent under vacuum afforded a gray solid, and the obtained crude product was then dissolved in 10 mL of THF. KOH (1.12 g, 20.0 mmol) was dissolved in 5 mL of MeOH and added to the THF solution. The reaction mixture was stirred at room temperature for 4 h, and then the solvent was concentrated under reduced pressure. To the residue was added a mixture of H_2O (20 mL) and CH_2Cl_2 (20 mL) to afford a two-phase solution. The aqueous layer was further extracted with CH_2Cl_2 (2 × 20 mL), and the combined CH_2Cl_2 solutions were washed with H_2O and dried over $MgSO_4$. The solution was filtered, and the solvent was removed by rotary evaporation. The crude product was purified by silica gel column chromatography (ethyl acetate−petroleum ether, 1:30, v/v) to give the compound (2,5-diethynyl-1,4-dioctyloxybenzene) as a light yellow crystal after removal of the solvent (2.48 g, 64%). ^1H NMR (300 MHz, $CDCl_3$): δ 5.97 (s, 2H), 3.99 (t, *J* = 6.8 Hz, 4H), 3.35 (s, 2H), 1.82 (m, 4H), 1.50−1.30 (m, 24H), 0.91 (t, *J* = 6.6 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.9, 117.6, 113.1, 82.3, 79.7, 69.5, 31.7, 29.22, 29.15, 29.03, 25.8, 22.6, 14.1. TOF-MS: *m*/*z* 382.2. FT-IR (KBr, cm^{-1}): 3285, 2924, 2851, 1501, 1470, 1385, 1218, 1039, 860, 671, 646. Anal. Calcd for $C_{26}H_{38}O_2$: C, 81.62; H, 10.01; Found: C, 80.32; H, 11.00.

*Synthesis of 5-Bromo-2-hydroxy-3-(piperidin-1-ylmethyl)-benzaldehyde (**3**).* Piperidine (2.0 mL, 20 mmol) was added to a solution of paraformaldehyde (0.6 g, 20 mmol) dissolved in HAc (30 mL) and stirred for 12 h at room temperature. Then 5-bromo-2-hydroxybenzaldehyde (4.02 g, 20 mmol) was added, and the mixture was heated at reflux for 24 h. After cooling to room temperature, the mixture was brought to pH ∼ 8 with saturated Na_2CO_3, extracted with $CHCl_3$, dried over anhydrous Na_2SO_4, and concentrated. The crude product was purified by silica gel column chromatography (ethyl acetate−petroleum ether, 2:1, v/v) to yield 4.61 g (77%) of the product as a pale yellow solid after removal of the solvent. ^1H NMR (300 MHz, $CDCl_3$) δ: 10.36 (s, 1H), 7.78 (d, *J* = 2.1 Hz, 1H), 7.32 (d, *J* = 2.1 Hz, 1H), 3.72 (s, 2H), 2.58 (br, 4H), 1.73−1.65 (m, 4H), 1.55 (br, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 152.6, 138.5, 132.9, 130.4, 129.0, 128.1, 126.6, 125.9, 121.7, 117.5, 95.3, 55.7, 35.9, 33.8, 22.8, 14.3. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 189.2, 161.3, 136.7, 129.7, 125.4, 124.4, 110.7, 60.6, 53.7, 25.5, 23.5. ESI-MS: $[M + 1]^+$ 298.25. FT-IR (KBr, cm^{-1}): 3417, 2935, 2864, 1674, 1594, 1448, 1385, 1238, 1110, 989. Anal. Calcd for $C_{13}H_{16}BrNO_2$: C, 52.36; H, 5.41; N, 4.70. Found: C, 52.29; H, 5.41; N, 4.80.

*Synthesis of 5,5′-((2,5-Dioctyl-1,4-phenylene)bis(ethyne-2,1-diyl))bis(2-hydroxy-3-(piperidin-1-ylmethyl)benzaldehyde (**M-1**).* The mixture of 5-bromo-2-hydroxy-3-(piperidin-1-ylmethyl)-benzaldehyde (2.52 g, 8.4 mmol), 1,4-dioctyloxy-2,5-diethynylbenzene (1.61 g, 4.2 mmol), $Pd(PPh_3)_2Cl_2$ (121.2 mg, 0.17 mmol), and CuI (33.1 mg, 0.17 mmol) was dissolved in 50 mL of anhydrous Et_3N and was stirred for 24 h at 70 °C under N_2. After being cooled to room temperature, the solvent was removed by a rotary evaporator. The residue was purified by flash chromatography on silica gel (ethyl acetate−triethylamine, 5:1, v/v) by using CH_2Cl_2 as eluent. The solvent was removed and washed by ethyl acetate to afford 5,5′-((2,5-dioctyl-1,4-phenylene)bis(ethyne-2,1-diyl))bis(2-hydroxy-3-(piperidin-1-ylmethyl)benzaldehyde (**M-1**) as a yellow powder (930 mg, 27%). ^1H NMR (300 M Hz, $CDCl_3$) δ: 10.70 (br, 2H), 10.41 (s, 2H), 7.87 (s, 2H), 7.40 (s, 2H), 6.98 (s, 2H), 4.03 (t, *J* = 6.6 Hz, 4H), 3.76 (s, 4H), 2.60 (br, 8H), 1.86 (m, 4H), 1.71−1.29 (m, 32H), 1.04 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 189.9, 162.4, 153.4, 137.0, 131.2, 123.3, 123.1, 116.8, 113.73, 113.67, 93.8, 85.0, 69.5, 60.8, 53.7, 31.8, 29.33, 29.28, 29.22, 26.0, 25.5, 23.6, 22.6, 14.1. ESI-MS: $[M + 1]^+$ 817.50. FT-IR (KBr, cm^{-1}): 3428, 2932, 2857, 2358, 1671, 1607, 1465, 1388, 1206, 1110. Anal. Calcd for $C_{52}H_{68}N_2O_6$: C, 76.44; H, 8.39; N, 3.43. Found: C, 78.69; H, 9.02; N, 3.80.

Synthesis of the Chiral Polymer Sensor. A mixture of **M-1** (163.4 mg, 0.2 mmol) and (*S*)-2,2′-binaphthyldiamine (56.8 mg, 0.2 mmol) was dissolved in toluene (5 mL) and kept refluxing for 72 h. The solvent was removed under reduced pressure, and the residue was dissolved in a small quantity of CH_2Cl_2; 50 mL of methanol was added to precipitate the polymer. A dark yellow solid was filtered off and washed with methanol several times. The polymer was dried under vacuum at room temperature for 24 h. The final yield was 50% (0.105 mg). $[\alpha]_D^{25}$ = +290.9 (*c* 0.3, THF). M_w = 32 590, M_n = 18 180, PDI = 1.79. ^1H NMR (300 M Hz, $CDCl_3$) δ: 8.63 (s, HC═N), 8.10−7.96 (m, ArH), 7.61−7.25 (m, ArH), 6.93 (s, ArH), 6.68 (s, ArH), 4.00−3.91 (m, CH_2N), 3.51−3.37 (m, CH_2O), 2.38 (br, CH_2N), 1.91−1.26 (m), 0.90−0.84 (m, CH_3). IR (KBr): 3415, 2956, 2862, 2361, 1615, 1572, 1505, 1442, 1392, 1261, 1105, 1022, 803.

Scheme 1. Synthesis Procedures of the Chiral Polymer Sensor



Fluorescence Measurements. The concentrations of the stock solution of metal salts (nitrate) and N-boc-protected amino acids are 1.0×10^{-3} mol/L in H_2O and 1.0×10^{-2} mol/L in CH_3CN, respectively. Each experiment was started with a 3.0 mL of polymer in THF solution with a known concentration (1.0×10^{-5} mol/L). The adding amount of each experiment example of metal salt and N-boc-protected amino acids is shown in the figure and the graphical interpretation. All the fluorescence measurements were taken at λ_{ex} = 362 nm (slit 3/5) except for Boc-L-Phg and Boc-D-Phg. The slit has been changed to 3/3 because the fluorescence intensity of complex sensor upon Boc-L-Phg and Boc-D-Phg overran the measuring range of the RF-5301PC spectrometer at slit 3/5, and all the other measurements were carried out under the same conditions.

■ RESULTS AND DISCUSSION

Synthesis and Structure of the Chiral Polymer Fluorescence Sensor. The synthesis procedures of chiral polymer sensor are outlined in Scheme 1. 1,4-Dioctyloxy-2,5-diethynylbenzene (**2**) was synthesized by four-step reaction in 64% yield according to reported literatures.[53−55] 5-Bromo-2-hydroxy-3-(piperidin-1-ylmethyl)benzaldehyde (**3**) could be obtained by the Mannich reaction from the starting material 5-bromosalicylaldehyde in 77% yield.[56] The monomer **M-1** was synthesized by the reaction of 1,4-dioctyloxy-2,5-diethynylbenzene with 5-bromo-2-hydroxy-3-(piperidin-1-ylmethyl)-benzaldehyde via Pd-catalyzed Sonogashira coupling reaction. The chiral BINAM-based polymer could be obtained by Schiff-base formation via nucleophilic addition−elimination reaction between **M-1** and (*S*)-2,2′-BINAM (**M-2**) to afford a yellow powder in 50% yield.[36,47,54] The specific rotation value ($[\alpha]_D^{20}$) of (*S*)-BINAM-based chiral polymer is +290.9° (*c* 0.3, THF). M_w, M_n, and PDI of the chiral polymer were determined by gel permeation chromatography using polystyrene standards in THF, and the values of them are 32 590, 18 180, and 1.79, respectively. The GPC result of the chiral polymer shows the moderate molecular weight. The chiral polymer sensor is an air-stable powder and shows high solubility in common organic solvents, such as THF, toluene, CH_2Cl_2, $CHCl_3$, and CH_3CN, which can be attributed to the nonplanarity of the twisted framework and the flexible *n*-octyl substituents. TGA result shows that polymer sensor has high thermal stability without weight loss before 260 °C and tends to complete decomposition at 650 °C, indicating that it has a desirable thermal property for application as a fluorescence sensor (Supporting Information Figure SI 1).

UV−vis and Fluorescence Behavior of Chiral Polymer Sensor upon Zn^{2+}. As shown in Figure 1, UV−vis spectra of the chiral polymer sensor exhibit a maximal absorption at 243 nm and two broad bands around 328 and 387 nm before titrations in THF. Upon addition of Zn^{2+} (0−2.4 equiv), the absorbance peaks at 243 nm show a little reduction and hypsochromic shift with increasing amounts of Zn^{2+}. One the contrary, the strongest broad-band absorption peak at 387 nm arisen from the conjugated structure exhibits the gradual enhancement and an obvious hypsochromic shift. Meanwhile, a new absorption peak at 278 nm can be observed. Moreover, there are two isosbestic points at 269 and 390 nm, which indicate the formation of the UV active zinc complex.[54,57] It can be found that UV−vis absorption spectra of the chiral polymer sensor can reach the saturated situation with a Zn^{2+} concentration change from 0.2 to 2.0×10^{-5} mol/L, indicating

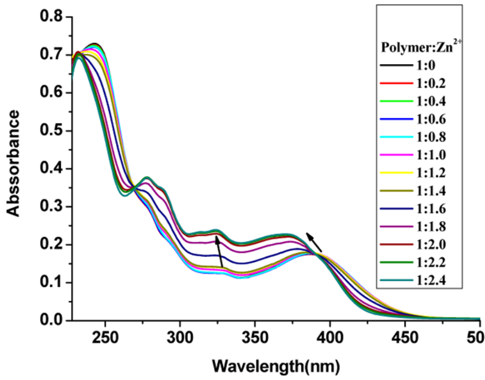


Figure 1. UV−vis spectra of the chiral polymer (1.0×10^{-5} mol/L) in THF with increasing amounts of Zn^{2+} (0−2.4 equiv).

that the polymer sensor can form a 1:2 $(Zn^{2+})_2$–sensor polymer complex .

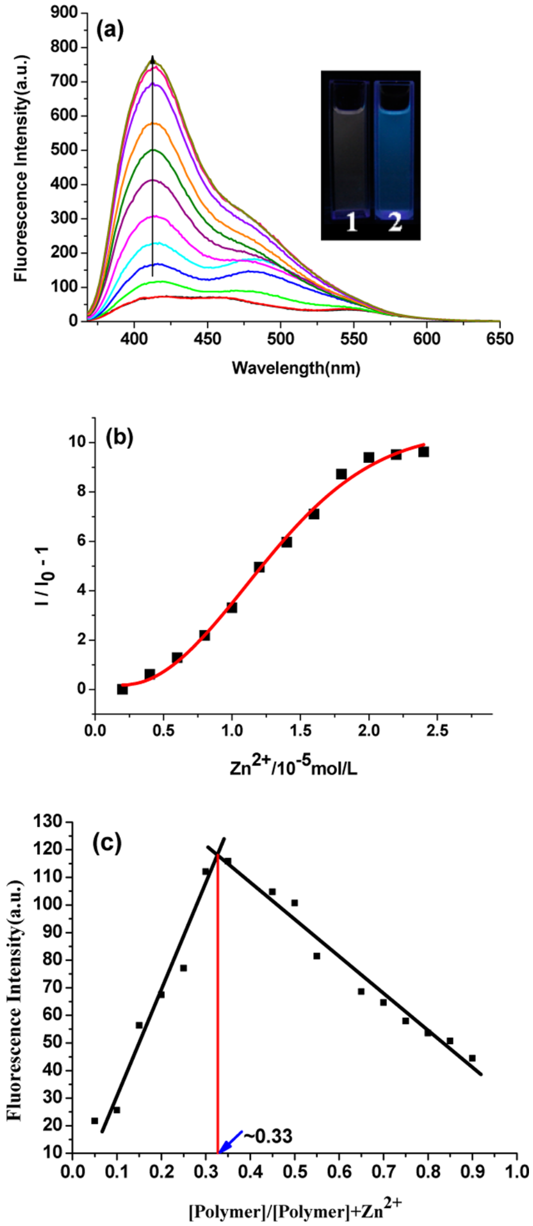


Figure 2. (a) Fluorescence spectra of polymer sensor with increasing concentration Zn^{2+} from 0.0 to 2.4×10^{-5} mol/L (inset: the photo of the fluorescent color of polymer sensor (1) and 1:2 Zn^{2+}-containing polymer complex (2)). (b) Profile of the fluorescent enhancement value $(I/I_0 - 1)$ vs the increasing concentration of Zn^{2+} from 0.0 to 2.4 $\times 10^{-5}$ mol/L. (c) Fluorescence Jobs plot of chiral polymer and Zn^{2+}. The total concentrations of polymer sensor and Zn^{2+} are 1.0 μM. The fluorescence emission spectra were measured at 25 °C and in THF solution.

Figure 2a illustrates the fluorescence titration of chiral polymer (1.0×10^{-5} mol/L corresponding to (*S*)-binaphthyl moiety in THF) toward Zn^{2+}. The polymer sensor can emit the weak fluorescence situated at 414 and 543 nm, which can be attributed to the strong intramolecular hydrogen bond between imine and hydroxyl of phenol. The fluorescence intensities of the chiral polymer show gradual enhancement as high as 10.3-fold upon the concentration molar ratio addition of Zn^{2+} from 0.2 to 2.0. The fluorescence curve of the polymer sensor with Zn^{2+} reveals that the fluorescent enhancement value $(I/I_0 - 1)$ exhibited a good linear response to a Zn^{2+} concentration change from 0.2 to 2.0×10^{-5} mol/L, indicating that the polymer sensor can form a 1:2 $(Zn^{2+})_2$–sensor polymer complex (Figure 2b). The Job plot analysis also confirmed the binding number of the chiral polymer is 2 for Zn^{2+} (Figure 2c). Moreover, the bright blue color of the polymer sensor can be observed under a commercially available UV lamp (inset, Figure 2a). The obvious fluorescence enhancement for the Zn(II)-containing polymer sensor can be regarded as two reasons. One is suppressed PET (photoinduced electron transfer) quenching when Zn^{2+} coordinates with the nitrogen atoms of the Schiff-base 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 Zn^{2+}-containing polymer complex can break the intramolecular hydrogen bonding between imine and hydroxyl of phenol and promote 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.[54,58−60]

The experiment of the polymer sensor interacted with other various metal ions (Ba^{2+}, Ca^{2+}, Co^{3+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, K^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, and Ag^+) was also carried out under the same determination conditions to reveal the selective fluorescence response behavior. As shown in Figure 3, almost no fluorescence response can be observed upon the addition of Ba^{2+}, Hg^{2+}, Mg^{2+}, and Ni^{2+} at 1:2 molar ratio. But Ca^{2+}, Cu^{2+}, Co^{3+}, K^+, Na^+, Ag^+, and Mn^{2+} can cause the limited fluorescent enhancement change. Meanwhile, the fluorescent peak situated at 543 nm appears a slight enhancement upon addition of Fe^{3+} and Cr^{3+}, but no obvious change at 414 nm (Supporting Information Figure SI 2). It indicates that the resulting chiral polymer can act as a "turn-on" fluorescence sensor only for Zn^{2+}.

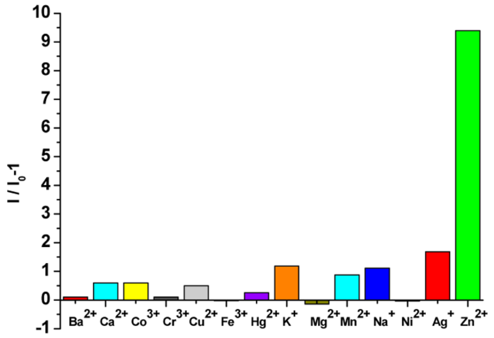


Figure 3. Selectivity of the polymer sensor (1.0×10^{-5} mol/L in THF, λ_{ex} = 362 nm, λ_{em} = 414 nm) toward Zn^{2+} and other metal ions (2.0×10^{-5} mol/L): relative fluorescence intensity of the chiral polymer sensor−metal ion complexes.

CD Spectra of the Chiral Polymer and Zn(II)-Containing Polymer Complexes. The CD spectra of the polymer sensor in the absence/presence of Zn^{2+} have been measured in THF (Figure 4 and Supporting Information Table SI 1). Compared with the chiral polymer, the CD spectra of its corresponding *in situ* generated 1:1 and 1:2 Zn(II)-containing polymer complexes show great difference from the reversed Cotton effects. As is evident from Figure 4, we found that the

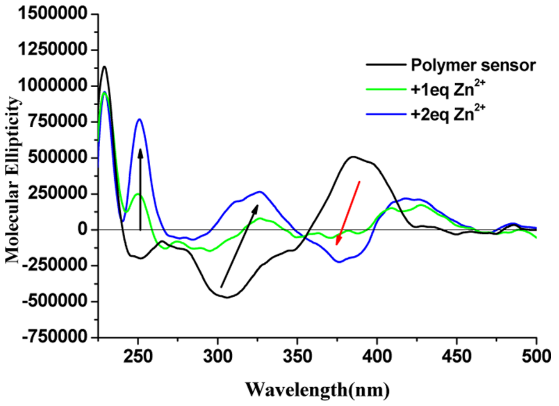


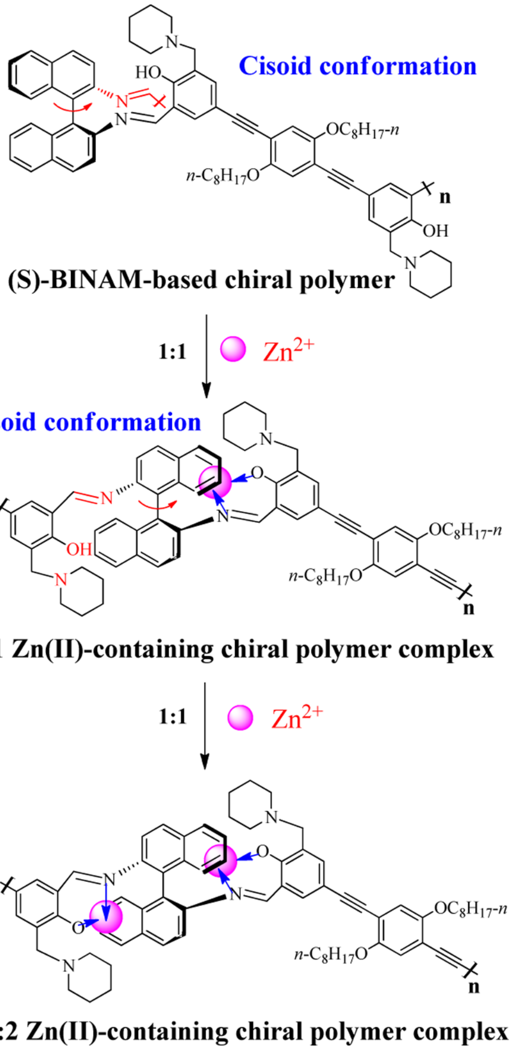
Figure 4. CD spectra of the polymer sensor and *in situ* generated 1:1 and 1:2 Zn(II)-containing complexes (1.0×10^{-5} mol/L in THF).

negative Cotton effects of the chiral polymer centered at 250 nm appears the positive Cotton effect upon addition of Zn^{2+}, and the intensities gradually enhance as the increase of Zn^{2+} molar ratios from 1:1 to 1:2, but the Cotton effect at 306 nm shows a larger red-shift to 326 nm. Moreover, the positive Cotton effect of the long wavelength at 384 nm gradually turns the negative Cotton effect with 45 nm blue shift in CD spectra of the *in situ* Zn(II)-containing polymer complexes.

The chirality of 1,1′-BINAM is derived from the restricted rotation of the two naphthalene rings. The rigid structure and C_2 symmetry of the chiral binaphthyl molecules can play an important role in inherently chiral induction. The dihedral angle between two naphthalene rings of a binaphthyl molecule ranges from 60° to 120° which leads to the kinked or twisted polymer main chain backbone.[44,61] According to the Pu Lin and Mason's reports, the binaphthyl derivatives have two kind configurations based on the substituted groups.[44,62−64] If the 2,2-substituents of the 1,1-binaphthyl molecules are either small or capable of intramolecular hydrogen bonding, the compounds would prefer the cisoid conformation. If the two groups are of large sizes in binaphthyl molecular, the compounds prefer transoid conformation in order to reduce the steric interaction. In this paper the resulting BINAM-based chiral polymer can adopt a stable ciscoid conformation due to the small groups of two imine substituents. The reversed Cotton effect can be attributed to the increase of the dihedral angle between two naphthalene rings of a binaphthyl molecule from cisoid to transoid conformation after the formation of the Zn(II)-containing polymer complexes. As is evident from CD spectra at long wavelengths, we assumed that the chiral polymer chain conformation appears reverse change from ciscoid to tanscoid upon the formation of the Zn(II)-containing complex polymer. It can be well understood that the whole polymer chain backbone reverse need very high energy. The coordination bond between the chelating imine base ligand and Zn^{2+} is strong enough to cause the conformation reverse. Moreover, it can be concluded that the dihedral angle gradually enlarges as the increase of Zn^{2+} molar ratios from 1:1 to 1:2 (Scheme 2), leading to greater Cotton effect change of the 1:2 Zn(II)-containing polymer complex than the corresponding 1:1 Zn(II)-containing polymer complex.

Enantioselective Recognition of *in Situ* Generated 1:1 Zn(II)-Containing Chiral Polymer Complex Sensor toward N-Boc-Protected Amine Acid. Considering the significant discrepancy of the CD spectra of (*S*)-BINAM-based chiral polymer induced by the addition amount of Zn^{2+} shown above, we further investigated the fluorescence response behaviors of chiral polymer sensor toward Boc-D-Ala and Boc-L-Ala by using (*S*)-BINAM-based chiral polymer and *in situ* generated 1:2 Zn(II)-containing polymer complex. No obvious fluorescence response changes and enantioselectivities can be observed by adding Boc-D-Ala and Boc-L-Ala (Supporting Information Figure SI 3). But while using *in situ* generated 1:1 Zn(II)-containing polymer complex as a fluorescence senor, a remarkable difference in fluorescent enhancement response behaviors between these two enantiomers could be detected as demonstrated in Figure 5. Boc-L-ala causes a large increase on the fluorescent intensity of the polymer complex sensor; on the contrary, D-isomer only has little influence on the fluorescence intensity under the same conditions. Interestingly, the chiral polymer complex sensor solution can appear bright blue fluorescence color change upon addition of (L)-N-Boc-protected alanine under a commercially available UV lamp, which can be clearly observed by the naked eye for directly visual discrimination in a lower concentration (Figure 5, inset). It can also be found that the fluorescent emission wavelengths do not show an obvious difference between guest-free sensor and guest sensor. The obvious fluorescence enhancement of chiral polymer complex sensor with N-boc-protected alanine

Scheme 2. Dihedral Angle Changes of Chiral Polymer with the Increase of Zn^{2+} Molar Ratios



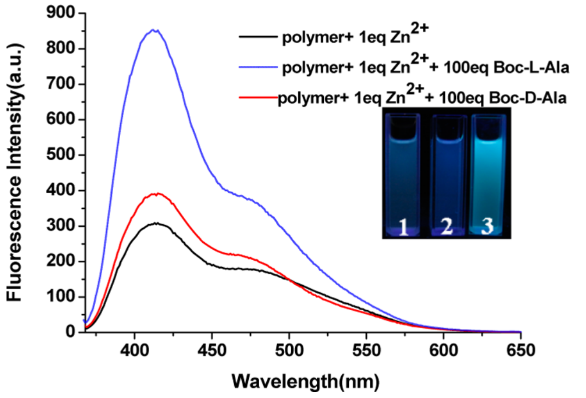


Figure 5. Fluorescent spectra of *in situ* 1:1 Zn^{2+}-containing sensor with Boc-L-ala or Boc-D-ala (inset: the photo of the fluorescence color changes of complex sensor (1) when it interacted with Boc-D-ala (2) and Boc-L-ala (3)) (polymer sensor: 1.0×10^{-5} mol/L in THF; Zn^{2+}: 1×10^{-5} mol/L; λ_{ex} = 362 nm; λ_{em} = 414 nm).

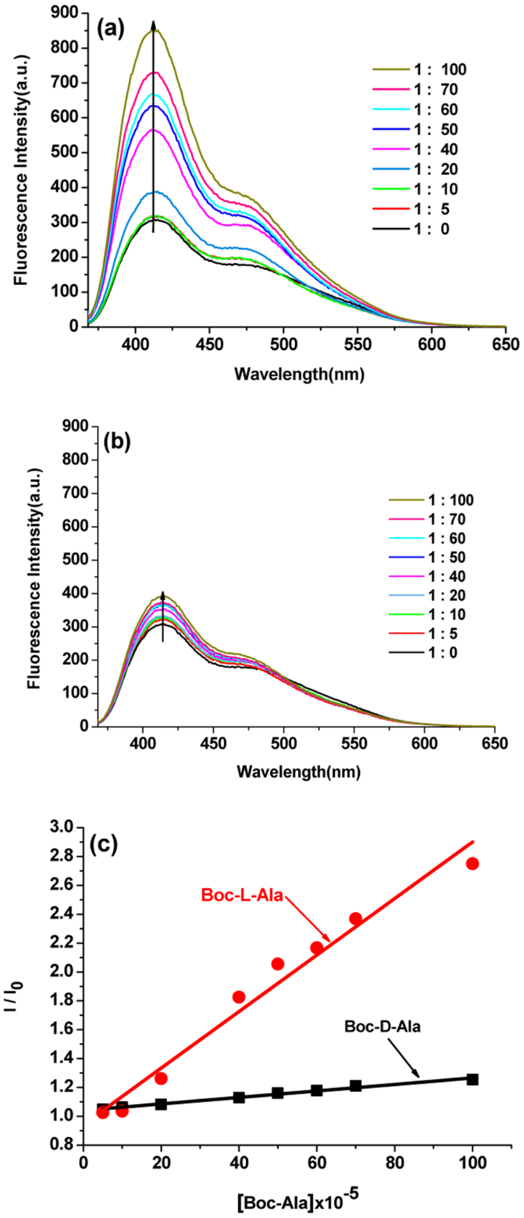
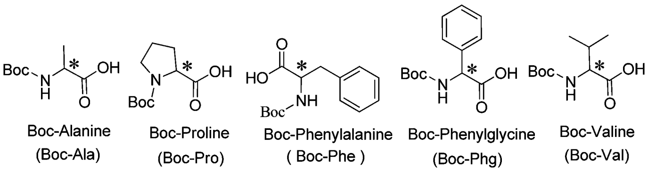


Figure 6. (a) Fluorescent spectra of complex sensor with increasing concentration Boc-L-ala from 0 to 100×10^{-5} mol/L. (b) Fluorescent spectra of complex sensor with increasing concentration Boc-D-ala from 0 to 100×10^{-5} mol/L. (c) Fluorescent enhancement (I/I_0) of complex sensor versus the increasing concentration of Boc-L-ala or Boc-D-ala (complex sensor: 1.0×10^{-5} mol/L in THF; λ_{ex} = 362 nm; λ_{em} = 414 nm).

can be attributed to the suppressed PET (photoinduced electron transfer) quenching[65−68] when the protons of N-Boc-protected alanine interact with the nitrogen atoms of imine moieties of Schiff base in the chiral polymer main chain. On complexation, the lone pair of electrons on the nitrogen atom is no longer available for PET, leading to the fluorescence enhancement.[69−74] Herein, we further investigated the interaction of *in situ* 1:1 generated Zn(II)-containing chiral polymer complex sensor with N-boc-protected alanine at a much broader concentration range. In regard to the fluorescence signal changes of this chiral polymer complex sensor on Boc-D-Ala and Boc-L-Ala, the fluorescence intensities appear gradual enhancement upon addition of Boc-D-Ala and Boc-L-Ala in the range from 1:5 to 1:100 molar ratios (Figure 6a,b). Meanwhile, it can also be found that the fluorescent enhancement ratio (I/I_0) displays a nearly linear correlation with concentrations of Boc-L-ala change from 10 to 70×10^{-5} mol/L and Boc-D-ala change from 5 to 100×10^{-5} mol/L, respectively (Figure 6c). The enantiomeric fluorescence difference ratio ef (ef = $(I_L - I_0)/(I_D - I_0)$ in this case is 6.90 at 1:100 molar ratio, which indicates that this *in situ* generated 1:1 Zn(II)-containing chiral polymer complex can exhibit highly enantioselective response toward Boc-L-ala. The reason may be attributed to an inherent chiral recognition based on the steric repulsion of polymer complex precursor for Boc-L-ala. The building block of 1:1 Zn(II)-containing complex receptor composed of Schiff base, Zn(II) complex of Schiff base, and the piperidyl groups, which is also controlled by the dihedral angle of binaphthyl, can well fit for the formation of a more stable *S*-L complex as compared to the *S*-D diastereomeric complex. As shown in Scheme 2, we can also draw the conclusion that either (*S*)-BINAM-based chiral polymer or *in situ* generated 1:2 Zn(II)-containing polymer complex cannot exhibit fluorescence response and enantioselective recognition toward Boc-L-Ala or Boc-D-Ala. Therefore, the explanation can be made as the following reasons: N-Boc-protected alanine guest molecules cannot enter the small steric space of the building block in (*S*)-BINAM-based chiral polymer due to cisoid configuration. On the other hand, as for *in situ* generated 1:2 Zn(II)-containing polymer complex, N-boc-protected alanine guest cannot directly interact with the chiral unit centers because two (*S*)-BINAM-based Schiff bases have been completely occupied by two Zn^{2+} ions and form 1:2 $(Zn^{2+})_2$−Schiff base complex.

In order to ascertain the significance of the presence of Zn^{2+} for this polymer complex sensor, we further investigated *in situ* 1:1 other metal ion-containing polymer complexes as fluorescence sensors for enantioselective recognition toward Boc-D-Ala and Boc-L-Ala, such as Mg^{2+}, Cu^{2+}, Ni^{2+}, Hg^{2+}, Cr^{3+}, and Ag^{+} to replace Zn^{2+} under the same conditions. As shown in Supporting Information Figure SI 4, none of these metal-containing chiral polymer complexes show obvious fluorescence response and enantioselectivity toward Boc-D-Ala and Boc-L-Ala. In a set of comparable experiments, we also studied the interaction of 1:1 Zn(II)-containing chiral polymer complex sensor with other N-Boc-protected amino acids including N-Boc-Phe, N-Boc-Phg, N-Boc-Pro, and N-Boc-Val (Scheme 3); almost no enantioselective recognition effect could be detected even the obvious fluorescence enhancement responses can be observed (Supporting Information Figures SI 5−8).

Scheme 3. Guest Molecules Used in the Enantioselective Recognition with the Complex Sensor



CONCLUSIONS

In summary, we first designed a kind (*S*)-BINAM-based chiral polymer which can show the "turn-on" fluorescent sensor only for Zn^{2+}. The *in situ* generated 1:1 Zn(II)-containing polymer complex used as the fluorescence sensor can exhibit the remarkable fluorescence enhancement response and high enantioselectivite recognition toward N-Boc-L-protected alanine, which indicates that the building block of Zn(II)-containing complex receptor containing Schiff base, Zn(II) complex of Schiff base, and the piperidyl groups, which is also controlled by the dihedral angle of binaphthyl, can well fit for the formation of a more stable *S*-L complex as compared to the *S*-D diastereomeric complex. Interestingly, the chiral polymer complex sensor solution can appear bright blue fluorescence color change upon addition of (L)-N-Boc-protected alanine under a commercially available UV lamp, which can be clearly observed by the naked eye for direct visual discrimination in a lower concentration. This work can be applied for detection of chiral enantiomers by a simple, rapid, and sensitive method.

ASSOCIATED CONTENT

Supporting Information

Fluorescence and data mentioned in the text; ^{1}H and ^{13}C NMR spectra of all new compounds as well. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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