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A polymer based fluorescent sensor for Zn^{2+} detection and its application for constructing logic gates

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ABSTRACT

A polymer-based fluorescent sensor was synthesized by polymerization of (*S*)-6,6'-dibutyl-3,3'-(di-5-salicylde-ethynyl)-2,2'-binaphthol (**M-1**) with (*R*,*R*)-1,2-diaminocyclohexane (**M-2**) via nucleophilic addition—elimination reaction. The responsive optical properties of the polymer on transition metal ions were investigated by fluorescence and UV–vis spectra. The polymer (1.0×10^{-5} mol/L in THF) could emit fluorescence at 550 nm and exhibit high selectivity for sensing Zn²⁺ with 36.1-fold fluorescence enhancement. Three logic gates were designed according to the different fluorescence responses of this polymer sensor to Zn²⁺ and Cu²⁺.

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1. Introduction

As is known to all, Zn^{2+} is the second most abundant transition metal ion in human body and plays a great role in many biology processes, such as DNA binding, gene expression, metalloenzyme catalysis, apoptosis, neurotransmission, brain function and pathology, immune function, and mammalian reproduction [1]. Disorders of zinc metabolism could lead to an increasing risk of several diseases, such as Alzheimer's disease, Parkinson's disease, prostate cancer, epilepsy, ischemic stroke, and infantile diarrhea [2]. In addition, high concentration of Zn²⁺ has a detrimental effect on biological systems, as well as natural environment [3]. Therefore, developing a highly selective detection method for Zn^{2+} is of considerable importance and in great need. In the past few years, many analytical methods have been developed for the detection of zinc, including atomic absorption spectrometry [4], UV-vis spectrometry [5], electrochemical [6], and potentiometry [7]. The superiority of fluorescent sensor over other type sensors lies in its sensitivity, selectivity, rapid response and high spatial resolution via microscopic imaging [8].

To the best of our knowledge, most of the fluorescent sensors for Zn^{2+} are based on small molecules, which contain DPA [9], quinoline [10], bipyridine [11], acyclic and cyclic polyamines [12], triazole [13], or Schiff-base [14]. However, very few polymer-based fluorescence sensors have been reported [15]. An advantage of fluorescent conjugated polymers over small molecules is that signal amplification occurs from electronic communication along the polymer backbone. Swager et al. [16] reported that the delocalizable π -electronic conjugated "molecular wire" polymer can greatly amplify the fluorescence responsive change due to facile energy migration along the polymer backbone upon light excitation.

Molecular logic gates were developed to meet the need of miniaturization in computer industry [17]. It is such a hot research field that various logic gates have been designed and fabricated recently [18]. Normally, an excellent chemosensor that can respond differently to the stimuli from external environment changing can be used for constructing molecular logic gate. In this research, three logic gates were developed *via* carefully modulating the "Inputs", which show distinct functions with the fluorescent polymer sensor.

2. Experiment part

2.1. Materials and methods

All solvents and reagents were commercially available and analytical-reagent-grade. THF was purified by distillation from sodium in the presence of benzophenone and Et₃N was newly distilled before using. NMR spectra were collected on 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. MS was determined on a Micromass GCT. FT-IR spectra were taken on a Nexus 870 FT-IR spectrometer. Fluorescence spectra were



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obtained from an RF-5301PCspectrometer. Ultraviolet–visible (UV–vis) spectra were obtained using a Perkin–Elmer Lambda 25 spectrophotometer. 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. Molecular weight was measured by GPC with Waters-244 HPLC pump and THF was used as solvent and relative to polystyrene standards. TGA was conducted on a Perkin–Elmer Pyris-1 instrument under N₂ atmosphere.

2.1.1. Metal ion titration

Each metal ion titration experiment was started with a 3.0 mL polymer with a known concentration $(1.0 \times 10^{-5} \text{ mol/L corresponding to the ($ *R*,*R* $)-salen moiety in THF solution). Zn(NO₃)₂ salt and other various metal salts (nitrate, <math>1.0 \times 10^{-3} \text{ mol/L}$, 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 sensor.

2.2. 5-ethynylsalicylaldehyde (2)

Compound (1) was prepared according to a reported method [19a]. To a mixture of 5-bromo- salicylaldehyde (5.0 g, 24.87 mmol), Pd (PPh₃)₂Cl₂ (174 mg, 0.25 mmol), and CuI (47 mg, 0.25 mmol) in 80 mL of Et₃N (newly distilled), trimethylsilylacetylene (17.7 mL, 124.3 mmol) was added. The mixture was stirred for 12 h at 85–90 °C. After cooling, the resulting ammonium salt was filtered though a celite pad, and the filtrate was concentrated, following purified by chromatography on silica gel with petroleum ether and acetate as eluent (30: 1). Removal of solvent under vacuum afforded a yellow powder, and the product was identified as 5-trimethylethynylsilylsalicylaldehyde (4.0 g, 74%). Mp: 96-97 °C; ¹H NMR (300 MHz, CDCl₃): δ 11.12 (s, 1H), 9.87 (s, 1H), 7.72 (d, J = 2.1 Hz, 1H), 7.64-7.60 (d, J = 8.7 Hz, 1H), 6.97-6.93 (d, J = 8.7 Hz, 1H), 0.27 (s, 9H).

5-Trimethylethynylsilylsalicylaldehyde (4.36 g, 20.0 mmol) was dissolved in 30 mL CH₂Cl₂. KOH (1.12 g, 20.0 mmol) was dissolved in 15 mL MeOH and added to the CH₂Cl₂ solution. The reaction mixture was stirred at room temperature for 3 h, and then the solvent was concentrated under reduced pressure. To the residue was added a mixture of H₂O (40 mL) and CH₂Cl₂ (50 mL) to afford a two-phase solution. The aqueous layer was further extracted with CH₂Cl₂ (2 × 50 mL), and the combined CH₂Cl₂ layers were washed with H₂O twice, and dried over anhydrous Na₂SO₄. The solution was filtered, and the solvent was removed by rotary evaporation to obtain a light yellow powder identified as 5-ethynylsalicylaldehyde (**2**) (2.6 g, 88%). Mp: 121-122 °C; ¹H NMR (300 MHz, CDCl₃): δ 11.15 (s, 1H), 9.89 (s, 1H), 7.75 (d, *J* = 2.0 Hz, 1H), 7.66 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 1H), 3.06 (s, 1H).

2.3. Model compound 3 [19b]

A mixture of 5-ethynylsalicylaldehyde (584.6 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 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); ¹H NMR (300 Hz, CDCl₃): δ 13.54 (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 (m, 8H). ¹³C NMR (75 Hz, CDCl₃): δ 163.9, 161.5, 135.9, 135.3, 118.2, 117.3, 112.2, 83.0, 75.7, 72.4, 32.8, 24.0. FT-IR (KBr, cm⁻¹): 3299, 3281, 2941, 2863, 1633, 1587, 1486, 1286, 826,585. MS (FAB): m/z 370.2 (M⁺+1). Anal.

Calcd. for C₂₄H₂₂N₂O₂: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.81; H, 6.01; N, 7.58.

2.4. (S)-6,6'-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl (5)

(S)-6.6'-Dibromo-2.2'-bis(methoxymethoxy)-1.1'-binaphthyl (4) (5.9 g. 11.1 mmol) was dissolved in anhydrous THF (50 mL). n-BuLi (15.0 mL 2.5 mol/L in hexanes, 37.5 mmol) was added by syringe injection at -78 °C under a N₂ atmosphere. After the reaction mixture was stirred for 20 min, n-C₄H₉Br (5.3 g, 38.7 mmol) was added to the above solution at -78 °C under a N₂ atmosphere. The reaction mixture was gradually warmed to room temperature and stirred overnight. The reaction was quenched by adding saturated NH₄Cl solution, and the mixture was extracted with ethyl acetate (2 \times 50 mL). The combined organic layers were washed with water and brine respectively, and then dried over anhydrous Na₂SO₄. After removal of solvent under reduced pressure, the crude product was purified by column chromatography (petroleum ether/ethyl acetate) (30: 1, v/v) to afford a colorless viscous oil product (S)-6,6'-dibutyl-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl (**5**) in 70.4% yield (3.8 g). $[\alpha]_D^{25} = -38.0^{\circ}$ (c = 0.5, CH₂Cl₂). ¹H NMR (300 MHz, CDCl₃): δ 7.90 (d, 2H, J = 9.0 Hz), 7.65 (s, 2H), 7.56-7.52 (d, 2H, J = 9.0 Hz), 7.09 (s, 4H), 5.08-5.05 (d, 2H, J = 6.9 Hz), 4.98-4.95 (d, 2H, J = 6.6 Hz), 3.16 (s, 6H), 2.73 (t, 4H, J = 7.5 Hz), 1.69-1.64 (m, 4H), 1.43-1.35 (m, 4H), 0.98-0.92 (t, 6H, I = 7.2 Hz); ¹³C NMR (75 MHz, CDCl₃): 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. FT-IR (KBr, cm⁻¹): 2956, 2929, 2857, 1596, 1500, 1480, 1241, 1151, 1028, MS (EI, m/z); 486 (Mt, 7%), 410 (100%), 382 (48%), 339 (34%).

2.5. (S)-6,6'-dibutyl-2,2'-binaphthol (model compound 6) [19c]

Compound (5) was dissolved in the mixed solvents of 10 mL ether and 10 mL methanol. 15 mL of hydrochloric acid (12 mol/L) solution was added to the above solution. The solution was stirred at room temperature for 8 h. After removal of all solvents under reduced pressure, the residue was extracted with ethyl acetate $(2 \times 30 \text{ mL})$. The combined organic layers were washed with 2 mol/ L NaHCO₃ solution and brine twice, and then dried over anhydrous Na₂SO₄. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) (20:1 v/v) to afford a white solid product (0.71 g, 93.4% yield). Mp: 72~74 $^\circ\text{C}$ $[\alpha]_{D}^{20} = +82.9$ (c = 0.31, CH₂Cl₂). ¹H NMR (300 MHz, CDCl₃) δ 7.94–7.90 (d, J = 9.0 Hz , 2H), 7.68 (s, 2H), 7.38-7.35 (d, J = 8.9 Hz , 2H), 7.20-7.16 (dd, J = 8.6 Hz , 2H), 7.12-7.09 (d, J = 8.6 Hz , 2H,), 4.98 (s, 2H), 2.77-2.72 (t, J = 7.7 Hz , 4H), 1.70-1.67 (m, 4H), 1.44-1.36 (m, 4H), 0.98-0.93 (t, I = 7.3 Hz , 6H). ¹³C NMR (75 MHz, CDCl₃) δ 152.5, 139.0, 132.1, 131.2, 130.0, 129.4, 127.3, 124.6, 118.0, 111.3, 35.9, 33.9, 22.8, 14.4. FT-IR (KBr, cm⁻¹): 3503.4, 3421.9, 2950.1, 2921.8. 1598.1, 1507.3, 1474.1, 1363.7, 1214.1, 1142.6, 1124.5, 952.2, 880.6, 827.1 cm⁻¹.

2.6. (S)-6, 6'-dibutyl-3, 3'-diiodo-2, 2'-binaphthol (7)

Compound (**5**) (3.69 g, 7.58 mmol) was dissolved in 30 mL of anhydrous THF. 10.6 mL of *n*-BuLi (2.5 mol/L in hexane, 26.53 mmol) was added by syringe injection to the above solution at room temperature under N₂ atmosphere. The solution was stirred for 6 h at room temperature, and then the solution of iodine (7.7 g, 30.32 mmol in 30 mL of THF) was slowly injected to the mixed solution at -78 °C. The mixture was then stirred overnight while the temperature was gradually warmed to room temperature. The reaction was quenched with 10% aqueous Na₂S₂O₃ (30 mL). After removal of the solvent under reduced

pressure, the residue was extracted with ethyl acetate (2×50 mL), the combined organic layers were washed with water and brine twice. The solution was concentrated to give a crude product of (S)-6,6'-dibutyl-3,3'-diiodo-2,2'-bismethoxymethoxy-11'binaphthyl which was directly used without purification. The crude product was dissolved in the mixed solvents of 30 mL of ether and 30 mL of methanol, and then 35 mL of HCl (12 mol/L) solution was added to the above solution. The solution was stirred at room temperature for 8 h. After the removal of the solvent under reduced pressure, the residue was extracted with ethyl acetate (2 \times 50 mL). The combined organic layers were washed with 8% aqueous NaHCO3 and brine twice, and then dried over anhydrous Na₂SO₄. After removal of solvent, a yellow viscous product (S)-6,6'-dibutyl-3,3'-diiodo-2,2'-binaphthol was obtained in the yield of 38.8% (1.91 g). $[\alpha]_D^{25} = -65.0$ (c = 0.3, CH₂Cl₂). Mp: 58–60 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.45 (s, 2H), 7.57 (s, 2H), 7.19 (dd, 2H, J = 8.7 Hz, 1.5 Hz), 7.03 (d, 2H, J = 8.7 Hz), 5.36 (s, 2H), 2.74 (t, 4H, J = 7.5 Hz), 1.69-1.61 (m, 4H), 1.43-1.34 (m, 4H), 0.98-0.92 (m, 6H); ¹³C NMR (75 MHz, CDCl₃): δ149.5, 139.7, 139.3, 131.5, 130.8, 129.5, 125.6, 124.3, 112.5, 86.3, 35.4, 33.3, 22.3, 13.9. FT-IR (KBr, cm⁻¹): 3476, 2925, 2854, 1572, 1500, 1441, 1362, 1143. MS (EI, m/z): 650 (Mt, 100%), 607 (100%).

2.7. (S)-6,6'-dibutyl-3,3'-di-(salicylal-5-ethynyl)-2,2'-binaphthol (M-1) [20]

An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with Pd(PPh₃)₂Cl₂ (4.31 mg, 6.15 umol), and CuI (1.17 mg, 6.15 µmol), and 5-ethynylsalicylaldehyde (2) (89.89 mg. 615 µmol). After the flask was capped with a rubber septum, the flask was evacuated and backfilled with nitrogen for three circles. Then (*S*)-6,6'-dibutyl-3,3'-diiodo-2,2'-binaphthol (**7**) (200 mg, 308 µmol) was added by syringe in THF, followed by TEA (5 mL) and THF (5 mL). The Schlenk flask was then sealed and stirred at ambient temperature for 20 h. Diluted with THF, and filtered through a celite pad, then the crude product was purified by column chromatography (30: 1-10: 1, v/v) to afford a white powder (30.7 mg) in 30.0% yield. $[\alpha]_D^{25} = -83.1$ (c = 0.5, THF). Mp: 132–134 °C. ¹H NMR (300 MHz, CDCl₃): δ 11.03 (s, 2H), 9.56 (s, 2H), 8.09 (s, 2H), 7.78 (s, 2H), 7.76 (s, 2H), 7.71 (s, 2H), 7.33-7.29 (d, 2H, J = 9.0 Hz), 7.11 (s, 2H), 7.08 (s, 2H), 6.93-6.90 (d, 2H, J = 9.0 Hz), 2.81-2.75 (t, 4H, J = 7.5 Hz), 1.76-1.65 (m, 4H, J = 7.5 Hz), 1.47-1.39 (m, 4H, J = 7.5 Hz), 1.00-0.95 (t, 6H, J = 7.5 Hz); ¹³C NMR (75 MHz, CDCl₃): *b* 196.2, 161.8, 156.4, 152.0, 138.6, 133.5, 131.3, 130.1, 129.7, 129.2, 127.0, 126.3, 125.7, 122.3, 120.1, 118.5, 118.1, 112.1, 100.4, 35.5, 33.3, 22.4, 13.9. FT-IR (KBr, cm⁻¹): 2923, 1661, 1478, 1282. MS (EI, *m*/ *z*): 685.7 (M⁺-1). Anal. Calcd. for C₄₆H₃₈O₆: C, 80.45; H, 5.58. Found: C, 80.37; H, 5.37.

2.8. Polymer sensor [21]

A mixture of M-1 (0.15 g, 0.22 mmol) and (*R*,*R*)-1, 2diaminocyclohexane (24.9 mg, 0.22 mmol) was dissolved in 8 mL of chloroform. The obtained solution was stirred at 50 °C for 6 h concentrated to 1 ml and the residual was dropped into methanol (15 mL) to precipitate the yellow Salen polymer. The resulting polymer was filtrated and washed with methanol several times, and then dried in vacuo to afford 70 mg light yellow powder in the yield of 70.0%. GPC results: Mw = 12090, Mn = 10310, PDI = 1.17; $[\alpha]_D^{25} = -723.7$ (*c* = 0.10, THF); ¹H NMR (300 Hz, CDCl₃): δ 8.34-7.58 (8H), 7.01-6.63 (10H), 3.35-2.74 (4H), 1.89-1.62 (4H), 1.41-1.27 (10H), 0.95-0.92 (10H). FT-IR (KBr, cm⁻¹): 2927, 2360, 1688, 1635, 1629, 1525, 1491, 1487 , 1285. Anal. Calcd. for C₅₂H₄₈N₂O₄: C, 81.65; H, 6.32; N, 3.66. Found: C, 81.38; H, 6.31; N, 3.64.

3. Results and discussion

3.1. Syntheses and feature of the polymer sensor

5-Ethynylsalicylaldehyde (2) was synthesized by a two-step reaction from the starting material 5-bromosalicylaldehyde [19a]. Model compound 3 could be synthesized in 80.0% vield according to the reported literatures [19b]. Model compound 6 could be obtained in 93.4% yield [19c]. (S)-6,6'-Dibutyl-3,3'-diiodo-2,2'binaphthol (7) was obtained by a five-step reaction from (S)-BINOL in 27.3% yield according to literatures [19d]. Monomer M-1, (S)-6,6'dibutyl-3,3'-di-(salicylal-5-ethynyl)-2,2'-binaphthol, was synthesized through a typical Sonogashira reaction from (7) and (2) in 30.0% yield. The polymer could be obtained by Schiff base formation between dialdehyde (M-1) and (R,R)-1,2-diaminocyclohexane (M-2) under a mild condition in 70.0% yield (Fig. 1). Mw, Mn and PDI of the polymer were determined by gel permeation chromatography using polystyrene standards in THF, and the values of them are 12090, 10310 and 1.17, respectively. The GPC result of the polymer shows the moderate molecular weight. The polymer is an air stable powder with light yellow color and shows good solubility in common organic solvents, such as toluene, THF, CHCl₃, CH₂Cl₂, and DMF, which can be attributed to the nonplanarity of the twisted polymer backbone and the flexible *n*-butoxy group. The (S)-BINOL and (R,R)-salen moieties can orient a well-defined spatial arrangement in the main chain backbone of the polymer, meanwhile salen-based moieties can form stable complexes with various metal ions due to the potentially tetradentate N₂O₂ donor [22].

3.2. UV-vis titration of the polymer sensor on Zn^{2+}

As can be seen from Fig. 2, UV—vis spectra of the polymer exhibit a maximal absorption at 262 nm and a broad band situated at 353 nm. Upon addition of Zn^{2+} , the absorbance peaks at 262 and 284 nm show a significant reduction with the increasing amount of Zn^{2+} . Simultaneously, the absorbance peak at 353 nm appears redshift to 368 nm. Moreover, there are three isosbestic points at 275, 297 and 355 nm, which indicate the formation of a stable complex with a certain stoichiometric ratio.

3.3. The selective and sensitive recognition of the polymer sensor on $\mathbb{Z}n^{2+}$

The fluorescence titration of the polymer sensor with Zn²⁺ was presented in Fig. 3. The polymer sensor can lead to a specific response toward Zn²⁺, and the fluorescent intensity of Zn²⁺-containing polymer complex shows gradual enhancement as high as 36.1-fold upon the concentration molar ratio addition of Zn^{2+} from 0.1 to 1.5 (Fig. 3). Moreover, the maximum emission wavelength of the polymer is remarkably blue shifted from 550 to 485 nm along with a dramatic enhancement of fluorescence intensity. The Zn²⁺polymer solution can emit green fluorescence and is readily detected by naked eyes (Fig. 3, inset). The obvious fluorescence enhancement response and blue shift can be attributed to three reasons: Firstly, a relatively high-energy non-bonding electron pair of the nitrogen atom arisen from the imine group transfers an electron to the excited fluorophore, which results in the fluorescence quenching. But when the electron pair is bound by coordination of Zn^{2+} , the redox potential of the receptor is raised so that the HOMO of the receptor becomes lower in energy than that of the fluorophore. Thus, the PET process from the receptor to the fluorophore is suppressed, and the fluorescence is switched on [8a]. Secondly, the formation of Zn²⁺-polymer complex can enhance the planarity and rigidity of the polymer and tend to produce fluorescence enhancement [23]. Thirdly, when salen-based N₂O₂ receptor



Fig. 1. Synthesis procedures of model compounds 3, 6 and polymer sensor.

in the main chain backbone of the polymer sensor coordinates with Zn^{2+} , a large blue shift of 50 nm for the emission spectrum of the polymer is observed (Fig. 5a), which suggests that an ICT process is also involved in. The donating character of the salen-based receptor containing cyclohexyl electron-donating group is reduced when the binding event occurs, which leads to a blue shift of the fluorescence sensor [8a].

In this paper, we further investigated the selectivity of the polymer to various metal ions. The fluorescence titration experiment was carried out under the conditions mentioned above. As can be seen from Fig. 4, the polymer sensor exhibits the highest sensitivity and selectivity to Zn^{2+} among tested metal ions. Addition of 1.0 equiv Na⁺, K⁺, Mg²⁺, Ca²⁺, Ag⁺, Cd²⁺, Hg²⁺, Pb²⁺, Cr³⁺, Fe³⁺ can only cause slight fluorescence enhancement (I/I_0 -1<1.2). Whereas Ni²⁺ and Cu²⁺ lead to nearly complete quenching for the polymer fluorescence on the ion addition at a concentration of 1:1 molar ratio, which can be attributed to the intramolecular photoinduced electron transfer (PET) or photoinduced charge transfer (PCT) between the polymer backbone and binding metal complexes. Moreover, we also found that Cd²⁺ gives no interference in the detection, which means that this polymer provides an alternative way to distinguish Zn²⁺ from Cd²⁺ under our reported



Fig. 2. UV–vis spectra of the polymer (1.0 \times 10 $^{-5}$ mol/L) with increasing amounts of Zn $^{2+}$ (0–1.5 equiv.).



Fig. 3. Fluorescence spectra of the polymer (1.0 \times 10⁻⁵ mol/L) with increasing amounts of Zn²⁺ (0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 8.0, 10.0, 15.0, 20.0, 25.0, 30.0, 40.0 \times 10⁻⁶ mol/L) (λ_{ex} = 350 nm).



Fig. 4. Relative fluorescence intensity of polymer-metal ions complex. In these experiments, the fluorescence measurement was taken at $\lambda_{ex}=350$ nm from 10 μM of the polymer in THF at room temperature and in the absence and presence of 1.0 equiv. of a metal ion.

procedure. Most importantly, based on the fluorescence image of the polymer sensor in the absence and presence of 1.0 equiv. of a metal ion, we can easily distinguish Zn^{2+} by the distinctive bright green fluorescence under the UV lamp ($\lambda = 365$ nm) by naked eyes. In addition, the competing experiment of the polymer towards Zn^{2+} was conducted by treating a solution of Zn-polymer complex with other metal ions. The fluorescence intensities of the polymer do not appear obvious difference in the presence of other metal ions even at a higher concentration. But the coexisted ions (Cr³⁺, Co²⁺, Ni²⁺ and Cu²⁺) showed interference in Zn²⁺ detection to some extent (SI2, Fig. 1).

3.4. Logic gate development

Based on the different fluorescence responses of this polymer sensor towards Cu^{2+} and Zn^{2+} , three logic gates were designed accordingly. EDTA was introduced into the process of constructing logic gates as a result of its strong chelating property for metal ions. Fig. 5 illustrated an INH logic gate that combine a NOT gate to an AND gate. The fundamental INH action was obtained with Zn^{2+} (10 μ M) and Cu^{2+} (10 μ M) as input. High FL intensity was observed only in the presence of 1.0 equiv. of Zn^{2+} and the absence of Cu^{2+} ,



Fig. 5. INH logic gate with Zn^{2+} (10 $\mu M)$ and Cu^{2+} (10 $\mu M)$ as "input".



Fig. 6. INH logic gate with Zn^{2+} (10 μ M) and EDTA (10 μ M) as "input".



Fig. 7. IMP logic gate with Cu^{2+} (100 μ M) and EDTA (100 μ M) as "input".

leading to the output as "1". Under other conditions fluorescence is quenched, resulting in output "0". The central metal displacement occurred when Cu^{2+} was added to a high fluorescence solution of polymer sensor and Zn^{2+} , which caused fluorescence quenching [24]. Fig. 6 also showed an INH logic gate with Zn^{2+} (10 μ M) and EDTA (10 μ M) as input. The mechanism for Fig. 6 is due to the strong chelating property of EDTA, which caught Zn^{2+} tightly and made the solution's fluorescence return to its initial state. Fig. 7 showed another type of logic gate that incorporating a NOT gate and an OR gate (Implication). It also can be basically understood as a reversed INH operation with the same mechanism as Fig. 6.

4. Conclusions

A novel polymer-based fluorescence sensor incorporating salen moieties in the main chain backbone was used as an excellent probe for the detection of Zn²⁺. Compared with other cations, such as Na⁺, K⁺, Mg²⁺, Ca²⁺, Cr³⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Ag⁺, Cd²⁺, Hg²⁺, and Pb²⁺, Zn²⁺ produced the most pronounced fluorescence enhancement response as well as a large blue shift of the polymer sensor. Most importantly, we can identify Zn²⁺ with naked eye under UV excitation (λ = 365 nm). Three logic gates were designed with two different interaction mechanisms. The results indicated that this polymer-based fluorescence sensor can be employed to selectively sensing Zn²⁺ and construct molecular logic gates to meet computing needs.

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Appendix. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2011.10.034.

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