A Helical Chiral Polymer-Based Chromo-Fluorescence and CD Response Sensor for Selective Detection of Trivalent Cations

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ABSTRACT: A novel chiral (*S*)-BINAM-based fluorescent polymer sensor was designed and synthesized by the polymerization of 4,4'-((2,5-dibutoxy-1,4-phenylene)bis(ethyne-2,1-diyl))-dibenzaldehyde (**M-1**) with (*S*)-2,2'-binaphthyldiamine (*S*-BINAM, **M-2**) via Schiff's base formation. The resulting helical chiral polymer sensor exhibited remarkable "turn-on" bright blue fluorescence color upon the addition of trivalent metal ions under a commercially available UV lamp; this change can be clearly observed by the naked eye for direct visual discrimination at low concentration. More importantly, the addition of trivalent metal cations can lead to a most pronounced change of CD spectra of the chiral polymer indicating this kind chiral sensor can also be used as a sole probe for selective recognition of trivalent metal cations based on CD spectra. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *00*, 000–000

KEYWORDS: chiral; CD spectra; fluorescence; helical polymer; helical chiral polymer; sensor; trivalent metal cations

INTRODUCTION Detection and quantification of metal cations especially trivalent metal cations (M^{3+}) at low concentrations is an active area of research due to their well-known impact on the environment and human health.¹ Traditional methods like atomic emission spectrometry, atomic absorption spectrometry, and mass spectrometry (MS) depend on expensive instruments and need rigorous testing requirements, meanwhile sometime they cannot distinguish metals with different valence states, such as Fe^{3+} and Fe^{2+} , these disadvantages limit their extensive application. Recently, due to the simplicity, high sensitivity and tenability, fluorescence chemosensors have been widely used as tools in chemistry, biology, medicine, and material science.² Fluorescent probes for detection of biologically relevant metal cations not only in vitro detection but also can in vivo with imaging applications,³ which could not be realized by traditional methods. The most general strategy for the fluorescent sensor design is to combine fluorescent dye molecules with the arranged receptors for specific analytes, the recognition event between receptors and analytes can lead to a fluorescent property change of the dye moiety.⁴ So according to different requirements, the researchers can design and synthesize variety of fluorescent sensors with diversified structure and apply them to multifarious system.

To the best of our knowledge, recently, most of the fluorescent sensors specific for trivalent metal cations (M^{3+}) were mainly

focused on small molecules,⁵ few studies were devoted to the development of conjugated polymers as fluorescence chemosensors. Conjugated polymers as fluorescence chemosensors have several advantages over small molecule sensors, such as enhancements associated with electronic interaction between receptors and analytes within the conjugated π -electronic polymer backbone, processability, and ease of structural modification. Furthermore, another advantage of conjugated polymer-based sensor over organic small molecules is that the fluorescence responsive signal amplification can be arisen from facile energy migration along the delocalizable π -electronic conjugated polymer backbone upon light excitation.⁶ More importantly, there has been no report on CD response behavior of chiral fluorescence sensor as a sole probe for selective recognition of trivalent metal cations from a variety of mono- and divalent metal cations up to now. As part of our research on chiral polymers fluorescence chemosensors in metal cations recognition'; herein, we firstly described a novel chiral (S)-BINAM-based polymer with helical configuration in the main chain backbone, which exhibited remarkable "turn-on" fluorescence enhancement response toward trivalent metal cations. The chiral polymer sensor solution can appear bright blue fluorescence color upon the addition of M^{3+} under a commercially available UV lamp at low concentration, the color change can be clearly observed by the naked eye. Moreover, trivalent metal cations can lead to obvious change of CD spectra of the chiral

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SCHEME 1 Synthesis procedure of chiral polymer sensor.

polymer indicating this kind chiral polymer can be used as a sole CD spectra sensor for selective recognition of M^{3+} .

EXPERIMENTAL

Instrumentation 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. Fluorescence spectra were obtained from a RF-5301PC spectrometer. UV-vis spectra were obtained from a PerkineElmer Lambda 25 spectrometer. Specific rotation was determined with a Ruololph Research Analytical Autopol IV-T/V. Electrospray ionization mass spectra were measured on a Thermo Finnigan LCQ Fleet system and time-of-flight mass spectrometry (TOF-MS) was determined on a Micromass GCT. C, H, N of elemental analyses were performed on an Elemental Vario MICRO analyzer. The gel permeation chromatography (GPC) analysis of the polymers was conducted on a Shimadzu 10 Å with THF as the eluent and polystyrene as the standard. The data were analyzed by using the software package provided by Shimadzu Instruments. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer Pyris-1 instrument under N₂ atmosphere. Circular dichroism (CD) spectra were carried out on a JACSCO J-810 CD Spectrophotometer. All solvents and reagents were commercially available A.R. grade. THF and Et₃N were purified by distillation from sodium in the presence of benzophenone.

The concentrations of the stock solution of metal salts (nitrate) are $1 \times 10^4 \ \mu\text{M}$ in H₂O. Initially, each experiment was started with a 3.0 mL polymer with a known concentration (10 μ M). The adding amount of each experiment example of metal salt is shown on the figure interpretation.

Synthesis of the Chiral Polymer

A mixture of $M-1^8$ (100.0 mg, 0.19 mmol) and (S)-2,2'-BINAM (M-2, 21.0 mg, 0.19 mmol) was dissolved in 2 mL of toluene. The solution was stirred at 80 °C for 48 h. 20 mL of methanol was added to precipitate the yellow solid polymer. The resulting polymer was filtrated and washed with methanol several times and dried in the yield of 85.0% (90.0 mg). GPC results: $M_{\rm w} = 26,560$; $M_{\rm n} = 12,650$; PDI = 2.1 [α]_D²⁵ = +299.0 (*c* 0.20, THF). ¹ H NMR (300 Hz, CDCl₃) δ 8.25 (s, HC=N), 8.19-6.92 (m, ArH), 4.30-3.92 (t, CH₂O), 1.92-1.75(m, CH₂), 1.67-1.50(m, CH₂), 0.87-1.21 (m, CH₃). FT-IR (KBr, cm⁻¹): 2955, 2869, 1599, 1512, 1412, 1277, 813.

RESULTS AND DISCUSSION

Synthesis and Structure Feature of Chiral Polymer

The synthetic routes of the polymer sensor are illustrated in Scheme 1. The monomer M-1, 4,4'-((2,5-dibutoxy-1,4phenylene)bis(ethyne-2,1-diyl))dibenzaldehyde was prepared according to reported literatures,8 which reacted with the monomer (S)-2,2'-BINAM (M-2) afforded the corresponding polymer as a yellow solid in 86.7% yield. M_w , M_n , and PDI of the chiral polymer were determined by GPC using polystyrene standards in THF, and the values of them are (26,560, 12,650, and 2.1), respectively, indicating moderate molecular weight. The chiral polymer is air stable solid and has good solubility in common organic solvents, such as toluene, THF, CHCl₃, and CH₂Cl₂, which can be attributed to the nonplanarity of the twisted polymer backbone and the flexible *n*-butoxy group substituents. In addition, the ethynyl linker can reduce steric hindrance between phenyl groups and also have a beneficial influence on the stability of the resulting chiral polymers. TGA result of the polymer suggested that the chiral polymer has high thermal stability without loss weight before 440 °C (Fig. 1). Therefore, the resulting chiral polymer can provide a desirable thermal property for practical application as a stable fluorescence sensor material.

The Selective Fluorescence Recognition of the Chiral Polymer Sensor on Metal Ions

The fluorescence spectra of the chiral polymer sensor were carried out in a solution of THF. The concentration of the



FIGURE 1 TGA curves of the chiral polymer.

chiral polymer was 10 μ M corresponding to 1,1'-binaphthyl moiety. The polymer sensor shows weak fluorescence situated at 457 nm with fluorescence quantum yield of 0.02. The fluorescence response behaviors of the polymer sensor on various metal ions have been investigated by fluorescence spectra with the excitation at 375 nm. As evident from Figure 2. it was found that the fluorescence strength of the polymer sensor has almost no change upon the addition of metal ions, such as Ag^+ , Ba^{2+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Cu^{2+} , Fe^{2+} , Hg^{2+} , K^+ , Mg^{2+} , Mn^{2+} , Na^+ , Ni^{2+} , Pb^{2+} , Zn^{2+} , and the fluorescent emission wavelengths of the metal-polymer complexes do not show an obvious difference from the metalfree polymer. Interestingly, upon the addition of trivalent cations, such as Al^{3+} , Cr^{3+} , and Fe^{3+} (30 μ M), the fluorescence intensities of the mixtures show gradual enhancement as high as 63-fold, 57-fold, and 70-fold, respectively (Fig. 2). Quantum yields of 0.32, 0.24, and 0.57 were determined for

the M^{3+} -containing polymer solution, respectively. This kind chiral polymer in THF solution can exhibit bright blue "turnon" fluorescence change in the presence of Al^{3+} , Cr^{3+} , or Fe^{3+} under the excitation of 375 nm, and visual sensing response could be clearly observed by the naked eye (Fig. 2, inset). Based on the pronounced fluorescence difference, our polymer can be used as an effective chromo-fluorescence sensor for direct discrimination of trivalent metal cations (M^{3+} , M = Al, Cr, Fe) over a variety of monovalent and divalent metal cations at low concentration.

To more announcing the detail of the M^{3+} on the fluorescent behavior of our chiral polymer, Fe³⁺ was chosen as the representative and fluorescence responses of the polymer with different concentration of Fe³⁺ was showed in Figure 3. Before the addition of Fe³⁺, the color of the solution of the free polymer itself emits weak blue. When Fe³⁺ is added into the solution, the color turns to light blue. The color began to be obviously observed at [Fe³⁺] of 20 μ M and it becomes brilliant blue when [Fe³⁺] is higher than 30 μ M.

CD and UV-vis Response Behaviors of the Chiral Polymer toward Trivalent Metal Cations

The chirality of 2,2'-binaphthyldiamine 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.⁹ 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.¹⁰ Herein our synthesized (*S*)-BINAM-based chiral polymer can adopt a stable helical conformation since the same configuration of chiral (*S*)-binaphthyl unit is connected through rigid group and a highly ordered structure of the main chain backbone are twisted to one-direction by the chiral binaphthyl



FIGURE 2 Fluorescence responses of the chiral polymer (10 μ M in THF, λ ex = 375 nm) to various metal ions (30 μ M). [Inset: the photograph of the fluorescence color of polymer sensor to various metal ions (30 μ M)].



FIGURE 3 Fluorescence spectra of the chiral polymer (10 μ M in THF, $\lambda ex = 375$ nm) with increasing amounts of Fe³⁺ from 3 to 30 μ M. [Inset: the photo of the fluorescence color of polymer sensor to different concentration of Fe³⁺ (μ M)].

linker.¹¹ The helical conformation can be also confirmed by the opposite specific rotations of (*S*)-BINAM (-157°) and (*S*)-BINAM-based polymer ($+299.0^{\circ}$).¹² In our previous work, we have reported this kind of chiral BINAM-based helical polymer can exhibit as an excellent fluorescence sensor for enantioselective recognition of phenylalaninol enantiomers^{9(a)} and N-Boc-protected alanine.¹³

Here, the CD spectra of the chiral polymer sensor in the absence/ presence of metal ion have been measured in THF [Fig. 4(a,b), Supporting Information Fig. S3-S5]. Before addition of metal ion, it can be found that the free polymer has the band centered at 326 nm which is arisen from chiral binaphthyl-imine base moiety, and another strong negative Cotton effect at wavelengths of 375 nm, which can be regarded as the extended conjugated structure in the repeating unit and a high rigidity of polymer backbone.¹⁴ In addition, it can also be clearly observed that the chiral polymer shows a strongest positive Cotton effect at long wavelength of 425 nm, which is attributed to the significant chiral amplification arisen from the helical conformation backbone.¹⁵ After the addition of trivalent metal cations, such as Fe^{3+} , we found that the negative Cotton effect of the chiral polymer sensor at 326 nm gradually turns the positive Cotton effect with 20 nm blue shift; moreover, the negative Cotton effect at 375 nm and the positive Cotton effects of long wavelength at 425 nm show gradual reduction to complete disappearance as the increase concentration of Fe^{3+} from 5 to 35 μ M, which can be attributed to the break of the rigid chain backbone and helical conformation of the chiral conjugated polymer structure. As shown in Supporting Information, other trivalent metal cations, Al³⁺ and Cr³⁺ showed similar response

changes as Fe^{3+} . On the contrary, CD spectrum of the chiral polymer has almost no response for Fe^{2+} , as shown in Figure 4(b), Supporting Information Figure S5. Other monovalent or divalent cations, such as Ag^+ , Ba^{2+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Cu^{2+} , Hg^{2+} , K^+ , Mg^{2+} , Mn^{2+} , Na^+ , Ni^{2+} , Pb^{2+} , Zn^{2+} , showed similar results as Fe^{2+} [Fig. 4(b)]. The obvious highly selective CD effect changes suggest that only trivalent metal cations M^{3+} can produce an induced circular dichroism, which indicated that the chiral BINAM-based polymer can be used as a sole probe for selective recognition of trivalent metal cations (Al³⁺, Cr³⁺, and Fe³⁺) over monovalent and divalent metal cations according to CD spectra.

In this article, the UV-vis responses of the chiral polymer sensor on metal cations were also carried out in THF solution. As a result, the intensity of UV-vis absorption maxima of the chiral polymer shows the gradual reduction, and the absorption wavelength arising from the conjugated structure of the polymer main-chain backbone appears the gradual blue shift from 399 to 390 nm upon the additions of Fe³⁺ concentration from 10 to 40 μ M [Fig. 4(c)]. In contrast, UV-vis spectra of the polymer appear little change upon the additions of various molar ratio of Fe²⁺ and other metal cations [Fig. 4(d) and Supporting Information Fig. S9].

Then we turned our attention to why our chiral polymer with binaphthyl-imine base moiety show selective recognition of M^{3+} rather than the metal cations like Zn^{2+} and Cu^{2+} , which have strong affinity to imine base moiety. As well known, the trivalent metal cations M^{3+} (Al³⁺, Cr³⁺, and Fe³⁺) intensively hydrolyzed in water and made aqueous solution acidic with different extent. Thus the addition of M^{3+} aqueous solution



FIGURE 4 (a,b) CD spectra of the chiral polymer (10 μ M in THF) with the increasing amounts of Fe³⁺ or Fe²⁺. (c,d) UV–vis spectra of the chiral polymer (10 μ M in THF) with the increasing amounts of Fe³⁺ or Fe²⁺.

into our polymer THF solution is equivalent to the addition of acid, and the H⁺ may be the key role leading to the enhancement of the fluorescence and change of CD spectra. Meanwhile, the order of Ksp for Fe(OH)₃, Al(OH)₃, and Cr(OH)₃ is completely consistent with the order of I₄₅₇ shown in Figure 2. So we further studied with the fluorescence response of the polymer towards trifluoroacetic acid (CF₃COOH). The result shows that the fluorescence grows up as the addition of CF₃COOH, which coincide with our hypothesis (Fig. 5). Tang and coworkers just reported a similar result using Py-TPE as a fluorescent chemosensor for selective recognition of trivalent metal cations based on the M³⁺ hydrolyzed mechanism.^{5(j)} After the addition of CF₃COOH, the CD spectra of the chiral polymer show the similar tendency as M³⁺ (Supporting Information Fig. S6).

CONCLUSIONS

In summary, we have developed a novel BINAM-based helical chiral polymer, which exhibited remarkable "turn-on" fluorescence enhancement response toward trivalent metal cations (M^{3+} , M = Al, Cr, Fe) over monovalent and divalent metal cations. The solution of the polymer turns on bright blue fluorescence color upon the addition of trivalent metal cations under a commercially available UV lamp, this change can be clearly observed by the naked eyes for direct visual discrimination at low concentration. More importantly, the addition of trivalent metal cations lead to the most pronounced change of CD spectra indicating this kind chiral polymer can be used as a sole probe for selective recognition



FIGURE 5 Fluorescence spectra of the chiral polymer (10 μ M in THF, λ ex = 375 nm) with increasing amounts of trifluoroacetic acid from 5 to 30 μ M.

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of trivalent metal cations according to CD spectra. Further study on the mechanism announced that the different fluorescence and CD response of the chiral polymer between trivalent metal cations and monovalent and divalent metal cations due to the higher hydrolyzing ability of the M^{3+} in water and the H^+ might play an important role in the recognition process.

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