BODIPY-based fluorescent polymeric probes for selective detection of Fe³⁺ ions in aqueous solution

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Abstract

It is of scientific and practical significance to sense and to remove heavy metal ions in the environment. In this work, four BODIPY-based fluorescent polymeric probes with the ability to sense and separate Fe³⁺ ions have been prepared via thiol-ene click reaction. The polymers have good thermal stability. Meanwhile, the results show that they have selective recognition capabilities only for Fe³⁺, which are mainly manifested as significant quenching of fluorescence and color modulation under visible light. The sensitivity is good, and the limit of detection reaches as low as 0.14 μM. They can also be used as reversible chemical probes to detect Fe³⁺. Therefore, the click reaction provides us with a facile method for preparing fluorescent polymer probes.

Keywords BODIPY-based polymer probes · Thiol-ene click reaction · Sensing metal · High sensitivity

1 Introduction

Heavy metals have become serious pollutants due to their difficulty in treatment [1]. Therefore, the identification and separation of heavy metal ions are still of great significance. Researchers have developed many methods for detecting heavy metal ions [2]. Commonly employed detection methods are time-consuming, expensive analytical instruments, which are difficult to meet increasing needs [3]. Fluorescent probes are organic indicator molecules that can bind and signal the presence of an analyte [4]. Among the common fluorescent dyes, floral and coumarin fluorescent dyes have short absorption wavelengths, which is not conducive to improving the sensitivity of detection in chemical analysis [5]. However, Boron dipyrromethene (BODIPY) fluorescent dyes can overcome these shortcomings. And, they have attracted enormous

interest due to high fluorescence quantum yield, stable spectral properties, and large extinction coefficient [6]. Due to the excellent physical and chemical properties, a wide range of applications have been demonstrated, such as in fluorescent probes, environmental management, and fluorescent labeling of biomolecules [7].

Compared with small molecules, polymeric probes exhibit many advantages, including excellent processability, simple separation and purification process and high selective recognition sensitivity [8], while retaining most of the advantages of corresponding small molecules. There are two methods to introduce fluorophore as building module into polymers, i.e., to the main chain and the side chain. Moreover, polymers constructed by these two ways have certain applications in detecting and removing heavy metal ions [9, 10]. Haldar et al. [11] have synthesized a water-soluble BODIPY side-chain polymer integrated

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with thiosemicarbazone units, which can be used to detect and separate Hg^{2+} in pure aqueous solutions simultaneously. It exhibited bright yellow emission upon exposure to Hg^{2+} , with a limit of detection as low as $0.37 \mu\text{M}$. Bozdemir et al. [12] have designed and synthesized novel BODIPY materials, and then, they are functionalized to further synthesize metal ion-mediated BODIPY backbone supramolecular polymers. These polymers are responsive to Fe^{3+} . At present, most fluorescent probes only focus on the detection performance of heavy metal ions [13, 14], and new methods to synthesize fluorescent polymers still should be developed.

The traditional polymerization methods of organic macromolecules materials include condensation polymerization, free radical polymerization, ionic polymerization and coordination polymerization [15, 16]. Shortcomings in traditional free radical polymerization and step polymerization are also notable. For example, it is difficult to obtain well-defined polymer chains, and the by-products in condensation polymerization are also an adverse problem.

However, the newly developed methods for synthesizing polymers include: Sonogashira reaction [17], acid-catalyzed Schiff base formation reaction [18] and click reaction [19]. In order to introduce sulfur elements and unsaturated bonds that can bind metal ions into the main chain, click reaction is a good method. And the click reaction can easily and efficiently obtain well-defined polymers [20]. The characteristics of an ideal click reaction include high yield, mild reaction conditions, harmless by-products, and insensitivity to oxygen and water [21]. In the click chemistry, compared with the copper-catalyzed azide-alkyne cycloaddition, thiol-ene click reaction that does not require heavy metal catalysis is favored [22]. Schlaad et al. [23] used polybutadiene and sulfhydryl compounds with different functional groups as raw materials and then synthesized a series of polymers with excellent physical and chemical properties through the thiol-ene click reaction. Liras et al. [24] have reported a new method of synthesizing acrylic polymers after modifying bromine end groups into thiol functional groups for the first time. It was confirmed that this terminal functionalization was achieved through the thiol-ene click reaction. Although these methods can be used to prepare ordered polymers, it is still a challenge to synthesize fluorophore containing polymeric probes. Moreover, there are not many related BODIPY iron probes dealing with sulfur binding or selenium binding [25].

In this paper, BODIPY is selected as a construction block. In order to prevent overcrowding of the groups in the BODIPY-based polymer structure, we use the thiol-ene click reaction to introduce the softer segment as the other building block into the polymer chain, achieving the effect of rigid-flexible combination. A series of fluorescent

polymer probes have been successfully constructed by BODIPY derivatives with 1, 3-propanedithiol or 1, 2-benzenedithiol molecules through thiol-ene click reactions. In addition, structure, optical properties, thermodynamic properties and sensing mechanism of them have been studied. Experimental results show that these polymer probes not only have good thermal stability, but also have a high fluorescence quantum yield, and Φ of PY4 is as high as 0.56. It is worth noting that the four polymers only have sensitive and highly selective recognition effect on Fe^{3+} , which is manifested as the color change under visible light and the significant quenching of fluorescence intensity. Moreover, even in the presence of interference from other metal ions, these probes can still detect Fe^{3+} and can be seen with the naked eye.

2 Experimental

2.1 Materials

Protocatechualdehyde, 1, 3-propanedithiol, 1, 2-benzenedithiol, allyl bromide, 3-bromopropyne, 2, 4-dimethylpyrrole, trifluoroacetic acid (TFA), 2, 3-dichloro-5, 6-dicyano-1, 4-benzoquinone (DDQ), and boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{Et}_2\text{O}$) were purchased from J&K China Chemical Ltd. Bovine serum albumin was purchased from Biosharp. Toluene, NaHCO_3 , potassium carbonate (K_2CO_3), 2,2'-Azobis(2-methylpropionitrile) (AIBN), Na_2EDTA , tetrahydrofuran (THF), triethylamine (TEA) and N, N-dimethylformamide (DMF) were bought from Aladdin Chemical Co., Ltd. Dichloromethane (DCM), ethanol (EtOH), ethyl acetate (EA), petroleum ether (PE) and acetone were bought from Sinopharm Chemical Reagent Co., Ltd. Toluene, THF, TEA, and acetone were purified by distillation for further use.

All metal salts (Fe^{3+} , Mn^{2+} , K^+ , Ni^{2+} , Co^{2+} , Ag^+ , Pd^{2+} , Zn^{2+} , Pb^{2+} , Cu^{2+} , Na^+ , Ca^{2+} , Fe^{2+} , Ba^{2+} , Mg^{2+} , Hg^+ , Sn^{4+} , Sn^{2+} , Cd^{2+} , Au^{3+} , and Hg^{2+}) were purchased from Aladdin Chemical Co., Ltd. and used as received. Ultrapure water ($> 17 \text{ M}\Omega \cdot \text{cm}^{-1}$) from a Milli-Q water system was used throughout the experiments.

2.2 Instrumentation

Fourier transform infrared spectra (FTIR, $4000\text{--}500 \text{ cm}^{-1}$) were performed on a Nicolet NEXUS 470 spectrometer. ^1H NMR was measured by AVANCE III 400 MHz (Bruker). Mass spectrometry (LC-MS) is measured on Varian Pro MALDI instrument. The microscopic morphologies were obtained by scanning electron microscopy (SEM, JSM-5510LV, Japan). Fluorescence spectra were performed on a Shimadzu F-4500 fluorescence spectrophotometer. The element diagram and band diagram were performed by

XPS (PHI-5300; ESCA). A variety of samples were measured on a UV-5900PC spectrophotometer (METASH) for UV-Vis measurement. Thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) were acquired by German STA449F3 instrument. Gel permeation chromatography (GPC) was performed in a Polymer Laboratories PL-GPC 50 Plus integrated GPC system (Wyatt Technology, USA) to obtain the molecular weight.

2.3 Synthesis

Small molecules and BODIPY-based polymers are prepared by solvothermal synthesis. The synthetic route is shown in Scheme 1.

2.3.1 General procedure 1: synthesis of compounds OA and AA

The starting materials are dissolved in acetone and 5.2 equivalents K_2CO_3 are added. The reaction mixture is stirred vigorously at 50 °C for 5 h and then poured into water. The aqueous layer is extracted with ethyl acetate. The combined organic extracts are washed with saturated brine, dry over anhydrous $MgSO_4$, and the solvent is removed under reduced pressure. Purification by column chromatography on silica gel:

3,4-bis(allyloxy)benzaldehyde (OA) TLC (PE/EA = 30:1, v/v). White oil, yield (85 %). 1H NMR (400 MHz, DMSO)

δ 9.80 (s, 1 H), 7.49 (d, 1 H), 7.38 (d, 1 H), 7.11 (d, 1 H), 6.12–5.90 (m, 2 H), 5.41 (d, 2 H), 5.30–5.15 (m, 2 H), 4.63 (d, 4 H). ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{13}H_{14}O_3$: 219.1016, found 219.1014 (Figure S1a).

3,4-bis(prop-2-yn-1-yloxy) benzaldehyde (AA) TLC (PE/EA = 22:1, v/v). White solid, yield (78 %). 1H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1 H), 7.60–7.54 (m, 1 H), 7.26 (s, 1 H), 7.18 (d, 1 H), 4.85 (d, 4 H), 2.57 (d, 2 H). ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{13}H_{10}O_3$: 215.0630, found 215.0705 (Figure S1b).

2.3.2 General procedure 2: synthesis of precursor compounds O-BODIPY and A-BODIPY

OA/AA (1 mmol) and 2, 4-dimethylpyrrole (2.25 mmol) are dissolved in THF (40 mL) and purge with nitrogen in a 250-mL flask before TFA (30 μ L) is added as a catalyst, and the mixture is stirred 6 h. DDQ (1 mmol) is added to the reaction solution under ice bath; then, Et_3N (2.7 mL) and $BF_3 \cdot Et_2O$ (3 mL) are added sequentially and stirred vigorously for 6 h. The organic phase is spin-dried and then dissolved in DCM. The organic phase is separated, dried ($NaHCO_3$), filtered, and concentrated. Purification by column chromatography on silica gel:

4, 4-difluoro-8- [3, 4-diallyloxy]-1, 3, 5, 7-tetramethyl-4-bora-3a, 4a-diaza-s-indacene (O-BODIPY). TLC (PE/EA = 40:1, v/v) Orange red solid, yield (48.5 %). 1H NMR (400 MHz, DMSO) δ 7.11 (d, 1 H), 6.93 (d, 1 H), 6.81 (d, 1 H), 6.15 (s, 2 H), 6.05–5.93 (m, 2 H), 5.44–5.32 (m, 2 H), 5.22

Scheme 1 Synthesis route for preparation of small molecules and BODIPY-based polymers

(d, 2 H), 4.59 (d, 4 H), 2.36 (d, 6 H), 1.31 (d, 6 H). ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{25}H_{27}BF_2N_2O_2$: 437.2206, found 437.2210 (Figure S2a).

4, 4-difluoro-8-[3, 4-diprop-2-yn-1-yloxy]-1, 3, 5, 7-tetramethyl-4-bora-3a, 4a-diaza-s-indacene (A-BODIPY). TLC (PE/EA = 25:1, v/v). Bright red solid, yield (52 %). 1H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, 1 H), 6.98 (d, 1 H), 6.89 (d, 1 H), 5.98 (s, 2 H), 4.80 (d, 4 H), 2.59–2.50 (m, 6 H), 2.43 (t, 2 H), 1.48 (s, 6 H). ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{25}H_{23}BF_2N_2O_2$: 433.1821, found 433.1898 (Figure S2b).

2.3.3 General procedure 3: synthesis of BODIPY-based polymers PY1, PY2, PY3 and PY4

First, 1,3-propanedithiol (1.2 mmol) is dissolved in anhydrous toluene and protected by nitrogen. Second, O-BODIPY (1 mmol) is added slowly. Last, AIBN (0.05 mmol) is added to the above mixture. After stirring at 80 °C for 3 d, the precipitate is filtered and washed successively with hexane, toluene, acetone and methanol. Finally, the crude product is purified by Soxhlet extraction with methanol for 24 h to obtain polymer product.

BODIPY-based polymer 1 (PY1) black powder, yield (61 %). 1H NMR (400 MHz, DMSO) δ 7.93 (s, 1 H), 7.33 (d, 1 H), 7.14 (d, 1 H), 6.16 (s, 2 H), 4.06 (d, 4 H), 2.79 (d, 6 H), 2.65 (s, 2 H), 2.31 (s, 6 H), 2.27–2.15 (m, 2 H), 1.98 (s, 2 H), 1.61–1.21 (m, 6 H), 1.22 (s, 2 H).

BODIPY-based polymer 2 (PY2) 1,2-benzenedithiol is used as the other alternative raw material to synthesize PY2 with O-BODIPY. Black powder, yield (52 %). 1H NMR (400 MHz, DMSO) δ 7.38 (s, 2 H), 7.21 (s, 2 H), 6.96 (s, 3 H), 5.73 (s, 2 H), 3.99 (s, 4 H), 3.08 (s, 2 H), 2.70 (d, 3 H), 2.31 (s, 3 H), 1.96 (s, 2 H), 1.70 (d, 2 H), 1.32 (s, 2 H), 1.36–1.06 (m, 6 H).

BODIPY-based polymer 3 (PY3) Using 1,3-propanedithiol and A-BODIPY as raw materials, PY3 is synthesized in

the same way. Red black powder, yield (68 %). 1H NMR (400 MHz, DMSO) δ 7.27–7.11 (m, 3 H), 6.65 (s, 1 H), 6.00 (s, 2 H), 5.74 (d, 3 H), 5.31 (d, 4 H), 2.87 (d, 2 H), 2.81–2.59 (m, 6 H), 2.31 (s, 2 H), 1.98 (d, 2 H), 1.43 (d, 6 H).

BODIPY-based polymer 4 (PY4) 1,2-benzenedithiol, as the other material to replace 1,3-propanedithiol, is reacted with A-BODIPY to synthesize PY4 (yield: 55 %). Purple black powder, yield (54 %). 1H NMR (400 MHz, DMSO) δ 7.14 (d, 6 H), 6.10–5.87 (m, 3 H), 5.50 (s, 2 H), 4.09 (d, 4 H), 2.66 (s, 3 H), 2.31 (s, 3 H), 2.00–1.92 (m, 2 H), 1.21 (d, 6 H).

3 Results and discussions

The structure of small molecule compounds is characterized by 1H NMR, FTIR and HR-MS. The structure of polymers is characterized by 1H NMR, FTIR and GPC. At the same time, the microstructure of the fluorescent polymers is observed by SEM, and its thermal stability is studied. UV-Vis and fluorescence spectroscopies are used to determine the performance of the polymers to selectively recognize Fe^{3+} . In order to better compare with the sensing properties of polymers, the corresponding properties of small molecules have also been studied. Data for small molecules are shown in supplementary materials (SI).

3.1 Structure characterization

3.1.1 FTIR analysis

First, infrared spectroscopy is used to characterize the structure of the synthesized compounds, as shown in Fig. 1. It can be seen from the OA spectra that the characteristic peaks of C=O, C–O–C and C=C bond are located at 1680 cm^{-1} , 1258 cm^{-1} and 1505 cm^{-1} , respectively. In the O-BODIPY spectra, the characteristic peak of C=O

Fig. 1 FTIR spectra of **a** OA, O-BODIPY, PY1 and PY2, and **b** AA, A-BODIPY, PY3 and PY4

disappeared, and the stretching vibration peak of C=N bond appeared at 1634 cm^{-1} . After PY1 and PY2 were synthesized, a new symmetrical stretching vibration peak of C-S-C appeared at 1090 cm^{-1} .

The C=O stretching vibration in the AA structure is observed at 1687 cm^{-1} . After A-BODIPY is synthesized, a new peak at 1555 cm^{-1} appeared due to its transformation into C=N. This result indicates that AA has been completely reacted. Meanwhile, in the infrared spectra of A-BODIPY, there are two obvious absorption peaks at 2109 cm^{-1} and 1140 cm^{-1} , which are attributed to the C $\equiv$ C stretching vibration peak and the C-O-C asymmetric stretching vibration peak, respectively. It can be seen from the infrared spectra of PY3 that the stretching vibration peak of C $\equiv$ C on A-BODIPY and the -SH on propylene dithiol disappear after polymerization, but the clear C=C stretching vibration is observed at 1622 cm^{-1} . Similar results are observed in the infrared spectra of PY4. Thus, these data prove the occurrence of the polymerization.

3.1.2 ^1H NMR analysis

In order to further confirm the structure of small molecules and polymers, Figures S3–S7 show the ^1H NMR spectra of each molecule. In Figure S3, the aldehyde hydrogen and the terminal olefin active hydrogen in the OA structure are at 9.80 ppm and 5.25–6.03 ppm, respectively. And the new methyl peak appears in the ^1H NMR spectra of O-BODIPY after the reaction. In Figure S7a, the peaks of H14–H15 are attributed to 1,3-propanedithiol. In Figure S7b, the peaks at 7.38 ppm and 7.21 ppm are designated as hydrogen on the benzene ring of 1,2-benzenedithiol.

Similarly, the aldehyde hydrogen of compound AA (Figure S5) resonates at 9.88 ppm, which completely disappear in the spectra of A-BODIPY (Figure S6), indicating that monomer AA has been completely used up. Furthermore, new peaks appear at 1.48 ppm (c), 2.55 ppm (a) and 5.98 ppm (b) in the spectra of A-BODIPY, corresponding to the resonances of the newly formed CH_3 , CH_3 and C=CH groups, respectively. Then, the proton resonance peaks of the CH_2 group (H15–H17) are observed at 2.86 ppm, 2.03 ppm and 2.42 ppm in the PY3 spectra (Figure S7c) after the reaction, respectively. The hydrogen on the benzene ring of 1,2-benzenedithiol is observed at 7.21–7.44 ppm in the spectra of PY4 (Figure S7d). In summary, the test results show that the position and number of hydrogens in each molecular structure are consistent with the experimental design.

3.1.3 GPC analysis

The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity (PDI) of BODIPY-based polymers are determined with gel permeation chromatography (GPC) using polystyrene as the standard. And “ n ” is the number of repeating units; the results are summarized in Table 1. All the four polymers reveal the M_n higher than 5000 g mol^{-1} , indicating that they have reached the polymer level.

3.1.4 SEM analysis

To further characterize the morphology of these polymer materials, scanning electron microscopy (SEM) is performed on them. The test results are shown in Fig. 2, and the partially enlarged photograph (upper right corner) is taken to assist in the analysis of their microstructure.

From these SEM image, it can be seen that the four BODIPY-based polymers, PY1, PY2, PY3, and PY4, all show a loose and porous morphology, like the honeycomb. These images show the surface morphology and structure of the polymer. The molecular chains are closely arranged to form a physical stack. In addition, this functionalized structural modification makes BODIPY-based polymer material a promising metal ion detector.

3.2 Thermal stability analysis

3.2.1 TGA analysis

To test their thermal stability, thermogravimetric tests are performed on these polymers. The test result is shown in Figure S8. All tests are performed under N_2 atmosphere. The four TGA curves all show two weight loss stages, which represents that the four polymers have similar thermal decomposition behavior. The first stage is from 32 to 169°C , which is the loss of absorbed water. The second stage corresponded to the degradation of the polymer itself. PY1 starts to degrade at 183°C . At the same time, PY2 lost weight rapidly at 253°C and continue weight losing until 638°C . PY3 and PY4 begin to degrade at 192 and 249°C , respectively. Finally, a series of residues are obtained. PY3 corresponds to a mass loss of 61 %. These

Table 1 Molecular weight of the BODIPY-based polymers

Polymer	M_n (KDa)	M_w (KDa)	PDI	n
PY1	5.2	8.5	1.6	9
PY2	5.9	9.8	1.7	10
PY3	6.5	9.5	1.5	11
PY4	5.5	9.9	1.8	9

Fig. 2 SEM micrographs and partial enlarged photographs of BODIPY-based polymers **a** PY1, **b** PY2, **c** PY3, and **d** PY4

polymers are heated to 600 °C; much residual material (up to 39%) is left after degradation due to the BODIPY with a steady rigid structure. The results show that the introduction of different substituent leads to differences in the thermal stability of BODIPY-based polymers. The thermal stability of PY2 and PY4 is slightly higher than that of PY1 and PY3. This is because the longer chain structures of PY1 and PY3 are easier to collapse when heated. Overall, the initial and final decomposition temperatures of the four polymers are about 200 and 650 °C, respectively, indicating that they have excellent thermal stability and have certain research value.

3.2.2 DSC analysis

The differential scanning calorimeter (DSC) analysis of polymers is shown in Figure S9. The DSC curves of PY1 and PY3 show that the glass transition temperature (T_g) is 501 and 523 °C, respectively. After synthesizing the corresponding BODIPY-based polymer with 1,2-benzenedithiol as the raw material for substituted 1,3-propanedithiol, the T_g of PY2 and PY4 increased slightly, reaching 536 and 547 °C, respectively. Obviously, rigid substituents

with greater steric hindrance will hinder the movement of polymer segments, resulting in a slight increase in T_g [26]. T_g exhibits rigidity and flexibility, and the T_g of the four polymers are all greater than 500, reflecting the strong rigidity of their structure.

3.3 Detection of heavy metal ions

3.3.1 Ultraviolet visible (UV–Vis) spectra analysis

Firstly, the sensing ability of these four polymers to heavy metal ions is studied by UV–Vis spectroscopy. It has been found that they are only sensitive to Fe^{3+} . After 10 equivalents of Fe^{3+} (10 μM) interacted with each polymeric probe, the UV absorption spectrum changed significantly. Figure 3a shows that the maximum absorption peak of PY1 is at 501 nm. After adding Fe^{3+} , the maximum absorbance of PY1 decreases. When Fe^{3+} is added, the maximum absorption peak of PY2 (Fig. 3b) is red-shifted from 502 nm to 510 nm, and the absorbance is also greatly reduced.

Figure 3c and d also shows similar change trends. In order to eliminate the interference of the colored analyte species itself, UV tests of different concentrations of Fe^{3+}

Fig. 3 UV absorption spectra of polymers (1 μM) in the presence of 10 equivalents of metal ions (10 μM) in DMF buffer (pH = 7.0, rt) and pure Fe^{3+} solution (10 μM). **a** PY1, **b** PY2, **c** PY3, and **d** PY4

solutions were carried out, as shown in Figure S10. It is found that the absorbance of the 10 μM Fe^{3+} solution is negligible. In addition, it can be seen from the inset that when Fe^{3+} is added, the color of polymeric probes PY1, PY2, PY3, and PY4 changes from light pink to brownish yellow under natural light. However, they do not change color in other ionic solutions. Therefore, PY1, PY2, PY3, and PY4 can be used as probes for detecting Fe^{3+} by the naked eye.

3.3.2 Fluorescence spectra analysis

It can be seen from Fig. 4a that the maximum emission peak of PY1 at $\lambda_{\text{ex}} = 380$ nm is 532 nm. The fluorescence intensity of PY1 is significantly reduced after adding Fe^{3+} , which is manifested as fluorescence quenching. As shown in Fig. 4b, the emission peak is 528 nm at the $\lambda_{\text{ex}} = 375$ nm. And PY2 exhibits a significant fluorescence quenching response to Fe^{3+} , while other metal ions do not cause significant fluorescence changes.

Analogously, it can be seen from Fig. 4c and d that PY3 and PY4 only show obvious fluorescence quenching response to Fe^{3+} , and the quenching rate of PY4 is as high as 90%. The obvious fluorescence quenching can be attributed to the two factors of Fe^{3+} electron transfer and

paramagnetic properties. Fe^{3+} is paramagnetic ion with an empty d-shell and exhibits strong fluorescence quenching effect, quenching the fluorophore via electron or energy transfer [27]. On the other hand, when the lone pairs of electrons on $-\text{O}-$ and $-\text{S}-$ interact with Fe^{3+} in empty orbitals (hydrogen ions or electron-lacking neutral molecules), fluorescence quenching is caused by Fe^{3+} due to electron transfer. As a result, an electron-deficient area is formed and acts as an acceptor [28, 29]. Under excitation with light, the $-\text{O}-$ and $-\text{S}-$ in the ligand become electron donors. The polymer probe transfers its lone pair of electrons to Fe^{3+} through electron transfer from $-\text{O}-$ and $-\text{S}-$ to the acceptor and produce fluorescence quenching. Moreover, Fe^{3+} as paramagnetic species are bound by a fluorescent dye; there is static quenching through the paramagnetic nature of the metal ion.

In order to clear out the interference, experiments were carried out, and the results are shown in Figure S11. After 200 μM Cu^{2+} is added to the polymer solution; this concentration of Cu^{2+} reduces the absorbance of the solution due to its own color, while the fluorescence intensity is hardly affected. Therefore, this quenching is due to actual quenching, not changes in the absorbance. The inset shows that a significant change in fluorescence quenching

Fig. 4 Fluorescence spectra of **a** PY1 (1 μM , λ_{ex} =380 nm), **b** PY2 (1 μM , λ_{ex} =375 nm), **c** PY3 (1 μM , λ_{ex} =375 nm), and **d** PY4 (1 μM , λ_{ex} =385 nm) in the presence of 10 equivalents of metal ions (10 μM) in DMF buffer (pH=7.0, rt)

can be clearly seen with the naked eye. Figure S12 and Figure S13 show the changes in the fluorescence intensity of PY1, PY2, PY3, and PY4 upon ultraviolet light ($\lambda = 254$ nm) after interacting with metal ions. Therefore, these polymers can realize dual-channel detection of Fe^{3+} by fluorescence and colorimetry. See SI for related research on small molecules.

In order to further understand the recognition effect of the polymer probes on Fe^{3+} , the fluorescence titration experiment is carried out. The results are shown in Fig. 5, where the inset is a linear relationship curve between the maximum fluorescence intensity and the Fe^{3+} concentration. It can be seen from Fig. 5a and c that the fluorescence intensity of PY1 and PY3 decreases as the concentration of Fe^{3+} solution increases. When the concentration of Fe^{3+} solution is reduced to only 1.0 μM , it can still weaken the fluorescence intensity of PY1. Figure 5b shows that the fluorescence intensity of probes PY2 gradually decreases with the increase of Fe^{3+} concentration until the quenching is basically complete. Meanwhile, when the concentration of Fe^{3+} is 0.5 μM , the fluorescence intensity of PY4 (Fig. 5d) begins to decrease. Then, a 12.0 μM Fe^{3+} solution is added, the fluorescence peak disappears completely.

In addition, the standard slope of the linear relationship curve of each probe can be obtained from the inset in

Fig. 5. And the limit of detection (LOD) is calculated using the equation $\text{LOD} = 3\sigma/K$ (σ is the standard deviation of the blank probe; K is the slope of the standard curve) [30].

The LOD is listed in Table 2 and Table S1 and compared with literature data (Table S2). By comparison, it is found that the polymer probes synthesized in this paper have good selectivity to Fe^{3+} . However, small molecule probes have no obvious effect on Fe^{3+} and specifically recognize Hg^{2+} or Ag^+ . Because the terminal olefinic or acetylenic bond in the small molecular structure is more likely to undergo hydroxy-mercury reaction in the presence of Hg^{2+} . Hg^{2+} quenches the fluorescence intensity of O-BODIPY and A-BODIPY through the heavy atom effect. Also, it can be found from the results that polymeric probes are more sensitive to metal ions than small molecule probes. This may be due to the "molecular wire" mechanism [31].

Through fluorescence spectra analysis, it can be determined that the type of fluorescence quenching is static quenching in this paper. The polymer probe and the quencher Fe^{3+} form a metal complex through a weak bond, and the complex completely quenches the fluorescence. Indeed, a linear relationship diagram is drawn according to the Benesi-Hildebrand equation to find the complex constant between Fe^{3+} and the polymer probe:

Fig. 5 BODIPY-based polymers response to Fe^{3+} concentration. **a** PY1, **b** PY2, **c** PY3, and **d** PY4

Table 2 LOD, T_g and K_a for polymeric probes before and after the probe was combined with Fe^{3+}

Polymer probe	LOD (μM)	K_a (M^{-1})	T_g
PY1	0.98	4.0×10^4	501
PY2	0.89	3.75×10^4	536
PY3	0.41	6.0×10^4	523
PY4	0.14	14.0×10^4	547

$$1/(F - F_0) = 1/\{K_a(F_\infty - F_0)[M]^n\} + 1/(F_\infty - F_0) \quad (1)$$

F_0 and F are the fluorescence intensity in the absence and presence of Fe^{3+} , respectively. $[Q]$ represents the concentration of Fe^{3+} . F_∞ is the minimum fluorescence intensity of the solution in the presence of Fe^{3+} . Linear regression [32] is performed for $1/(F - F_0)$ and $1/[M]^n$. And the complex constant (K_a) is the ratio of the intercept to the slope. The complex linear graphs of all fluorescence probes are shown in Figure S14, and K_a between each probe molecule and metal ion is also shown in Table 2 and Table S1. In summary, the data show that each metal complex material has good stability.

The Job's plot (Figure S15) of the coordination of PY1, PY2, PY3 and PY4 to Fe^{3+} is analyzed in order to calculate the stoichiometric ratio of the fluorescent probe to the metal ion, keep the total concentration of the metal ion and the probe concentration at 10 μM , and continuously change the concentration of the metal ion solution and the probe solution. Take the percentage of metal ions in the mixed solution as abscissa, and the difference ($I_0 - I$) between the theoretical fluorescence intensity (I_0) and the actual fluorescence intensity (I) as ordinate to plot the job curve [33]. The inflection point of the curve is the stoichiometric ratio of the probe to the metal ion. It can be seen that these polymer probes have only one binding site, that is, the coordination ratio is 1:1 (metal ion/probe). Therefore, the four polymer molecular structures all contain one coordination site for Fe^{3+} . Scheme 2 shows the coordination of Fe^{3+} by PY1, PY2, PY3 and PY4.

As shown in Figure S16, the stoichiometric ratio between the small molecule probe O-BODIPY and Hg^{2+} is 2:1 (metal ion/probe). This is due to the fact that O-BODIPY has two terminal olefinic bonds. Similarly, the stoichiometric ratio between A-BODIPY and $\text{Hg}^{2+}/\text{Ag}^+$ is 2:1. This is because there are two terminal acetylenic bonds in the A-BODIPY structure. This is consistent with the results of

Scheme 2 Structural representation of the binding sites of **a** PY1+ Fe^{3+} , **b** PY2+ Fe^{3+} , **c** PY3+ Fe^{3+} , and **d** PY4+ Fe^{3+}

the mechanism verification experiment and supports the coordination diagram in Scheme S1.

The anti-interference ability of the polymer probes to identify Fe^{3+} is studied, and the results are shown in Fig. 6. It shows that the presence of other heavy metal ions and serum proteins has no significant effect on the recognition

of Fe^{3+} by the polymers. However, the recognition effect of PY4 on Fe^{3+} is disturbed when the concentration of Mg^{2+} reaches 200 μM . It results in decreasing fluorescence quenching rate, with fluorescence recovering by 20.5 % (Figure S17). When the K^{+} concentration reaches 200 μM , the fluorescence recovery is 8.2%. The interference degree

Fig. 6 Fluorescence response of polymeric probes (1 μM) to other metal ions (10 μM) and bovine serum albumin (0.1 mg/mL) in the presence of Fe^{3+} . **a** PY1, **b** PY2, **c** PY3, and **d** PY4

of K^+ or Mg^{2+} increases with the increase in concentration, but PY4 still maintains recognition ability for Fe^{3+} . Similarly, high concentrations of K^+ and Mg^{2+} have varying degrees of influence on the recognition effect of PY1, PY2 and PY3 on Fe^{3+} . It results in a change in the fluorescence quenching rate, but the fluorescence intensity remains quenched all the time. Consequently, these probes can be used to detect Fe^{3+} under most conditions.

The fluorescence quantum yield (Φ) is determined by the comparison method [34]. The calculation equation is as follows:

$$\Phi_1 = \Phi_2 (S_1/S_2) (A_2/A_1) (n_1/n_2)^2 \quad (2)$$

S_1 and S_2 are the integrated area under the fluorescence emission curve of the analyte and standard, respectively. A_1 and A_2 are the absorbance at the excitation wavelength of the analyte and standard, respectively. n refers to the refractive index of the solvent (because the concentration used in this experiment is extremely low, the influence of the solute can be ignored, and it is regarded as consistent, both are 1.33). RhB ($\Phi_2 = 0.89$) is used as the standard [35].

Table 3 Fluorescence quantum yield (Φ) before and after the polymeric probes were combined with Fe^{3+}

Sample	S (average)	A (average)	n	$\Phi/\%$ (average)
RhB	8922.36	0.0386	1.33	0.89
PY1	37785.1	0.331	1.33	0.44
PY1 + Fe^{3+}	21467.85	0.195	1.33	0.42
PY2	42680.45	0.3202	1.33	0.51
PY2 + Fe^{3+}	17293.37	0.1368	1.33	0.49
PY3	41218.82	0.3338	1.33	0.48
PY3 + Fe^{3+}	15092.6	0.1291	1.33	0.45
PY4	31269.03	0.2166	1.33	0.56
PY4 + Fe^{3+}	19900.52	0.1625	1.33	0.47

All experiments are performed in triplicate, and the average value is calculated to get Φ .

It can be seen from Table 3 that Φ of the polymer probe has changed after combining with Fe^{3+} . Then, it is found that Φ of polymers are reduced by comparing with the small molecules (Table S1). This may be due to the fluorescence quenching caused by the steric effect of the polymer and the heavy atom effect of the S atom. In addition, we found that Φ of PY2 and PY4 is larger than those of PY1 and PY3. This is because the introduction of the more rigid benzenedithiol in the structure of PY2 and PY4 restricts the spatial rotation of the polymer chain, so that the polymer achieves a better coplanarity. And it is in full agreement with the above-mentioned DSC conclusion.

In order to further explore whether the sensing response is reversible, we conducted cyclic response tests. As shown in Figure S18, a cyclic titration experiment was performed with Fe^{3+} and Na_2EDTA aqueous solutions, and the fluorescence intensity and absorbance of each step were recorded. After adding EDTA as a stronger chelating agent, a large part of the quenched fluorescence was recovered. The absorbance of the solution has also changed and can be directly observed with the naked eye. Therefore, PY1, PY2, PY3, and PY4 are used as reversible chemical probes to detect Fe^{3+} .

3.3.3 Detection mechanism

FTIR analysis studied the binding mechanism of probes with Fe^{3+} . Considering that these probes have similar structure, the spectrum of PY4 is selected to analyze the changes before and after the combining with Fe^{3+} . The results show that in Fig. 7a, the characteristic peak of PY4 is C-S-C at 1143 cm^{-1} . However, this characteristic peak disappears, and a new peak appears after combining Fe^{3+} . It proves that S atoms are helpful for PY4 to bind Fe^{3+} .

Fig. 7 **a** FTIR spectrum of PY3 and PY4 with equimolar amount of Fe^{3+} , and **b** XPS spectrum of PY3 and PY4 with Fe^{3+}

The binding mechanism of the polymer and Fe^{3+} is further analyzed by XPS spectroscopy (Fig. 7b). Several strong peaks with binding energies (BEs) of 163.21, 192.32, 284.82, 399.1, 532.19, and 685.08 eV belong to S, B, C, N, O, and F elements, respectively, which exist in pristine polymer probe PY4. Upon binding Fe^{3+} , new shoulder peaks with BEs of about 710.91 eV and 725.41 eV appeared, confirming that Fe^{3+} was bound to PY4. The high-resolution XPS spectra of the core levels of C, N, O, B, F, S, and Fe are shown in Table S3. All element energy-level regions are analyzed by peak deconvolution. The C, N, B, and F elements in the XPS spectrum of Fe^{3+} -loaded PY4 do not clearly show significant changes of BEs in comparison with that of PY4, indicating that these four elements do not contribute to the combination of Fe^{3+} . However, in the O element XPS spectrum of Fe^{3+} -loaded PY4, the energy level peak of 399.10 eV shifted to lower BE by 0.50 eV, suggesting that O atoms took part in the binding of Fe^{3+} . The shift of BE is due to decrease in electron cloud density on the O atom after the Fe^{3+} -O coordination bonds is formed [36]. The component peak at 163.21 eV is attributed to heterocyclic sulfur (C-S). In contrast, it can be seen from the S element spectrum of Fe^{3+} -loaded PY4 that this peak has a positive shift, increasing BEs by 0.42 eV, which indicates that S atoms also contribute to the binding of Fe^{3+} ions.

The high-resolution XPS spectra of each element for Fe^{3+} -loaded PY3 are similar to those for Fe^{3+} -loaded PY4, meaning that the oxygen and sulfur atoms in the polymer chains are contributed to the combination of Fe^{3+} . In addition, the XPS spectra of Fe element show two peaks at 711.41 eV and 725.03 eV. The presence of peak at 711.41 eV indicates that Fe^{3+} forms a complex with -S- and -O- bonds. Combined with the previous fluorescence analysis, the change in fluorescence intensity upon polymer binding Fe^{3+} can be attributed to the photoelectron transfer (PET) mechanism [37].

Scheme 2 shows the recognition and coordination diagram of fluorescent polymeric probes and Fe^{3+} . By comparing the ability of polymers to recognize heavy metal ions, it is found that the small molecule probe O-BODIPY (Scheme S1) has the ability to specifically recognize Hg^{2+} . This is because the terminal olefinic group of the O-BODIPY structure hydroxy-mercury reacts [38] with Hg^{2+} , and it can be obtained by ^1H NMR and MS analysis (Figure S19). A-BODIPY has the ability to recognize Hg^{2+} and Ag^+ . It is presumed that the terminal alkynyl group can react with Ag^+ to generate heavy metal acetylide [39], and react with Hg^{2+} to undergo hydroxy-mercury reaction, which can be obtained by ^1H NMR and MS analysis (Figure S20). Undoubtedly, this reflects the controllability of the sensor recognition site.

4 Conclusions

In this work, four polymers with BODIPY fluorophore on the main chain have been successfully synthesized. First, the BODIPY-based small molecule is designed and two $\text{C}=\text{C}/\text{C}\equiv\text{C}$ groups are introduced to each molecule, making it one of the constructing modules of polymers. And then, the thiol compound is selected as another building module to successfully synthesize fluorescent polymers probes via thiol-ene click reaction. Thioether can be easily introduced through this reaction, so that these polymeric probes can sensitively identify heavy metal ions.

These polymeric probes show porous morphology on a microscopic level, and all have good thermal stability. Upon addition of Fe^{3+} , the fluorescence of these probes is significantly quenched, and the quenching rate is as high as 90 %. These probes can also be recycled. It is found that the polymers with rigid chain exhibited higher fluorescence quantum yield and better thermal stability than the flexible ones, and Φ of PY4 is as high as 0.56.

In addition, the sensing ability of polymeric probes is better than that of small molecules, and the method of synthesis and purification is simpler. Therefore, this work provides with practical application of click chemistry and easy synthesis of high-efficiency fluorescent probes.

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Declarations

Conflict of interest The authors declare that they have no competing interests.

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