



Novel fluorene-based copolymer with pendant aza-crown ether: Highly sensitive and specific detection for CuSO₄ and concurrent effect of anions

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ABSTRACT

A novel fluorene-based copolymer with aza-15-crown-5 as pendant group was synthesized by Suzuki-coupling reaction, and characterized by ¹H NMR, ¹³C NMR, EA, and GPC. The polymer was brightly blue emissive in common organic solvents, such as CHCl₃, CH₂Cl₂, and THF. Fluorescent titration experiments carried out in THF–MeOH system indicate that the polymer has quite good selectivity and high sensitivity for CuSO₄, which is contrasting to the weak responses for other copper salts such as Cu(ClO₄)₂, CuCl₂, Cu(NO₃)₂, and Cu(OAc)₂. Molecular simulation result suggests that this unique phenomenon may come from the synergistic effect of the bivalent counterion SO₄²⁻. This new system utilizing the strong luminescent property of polyfluorene as reporter and concurrent effect of the counterion SO₄²⁻ may be developed as chemosensor for the special detection for CuSO₄.

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1. Introduction

Conjugated polymers have been widely applied in the fields of opto-electronic materials, such as OLEDs, OFET, solar cells, etc. [1]. The high light absorption ability and molecular wire effect also make them promising candidates as fluorescent sensors for detection events. Recently, polyfluorene (PF) as an efficient blue emission material has attracted increasing attention due to its application in sensory materials for metal ions [2], anions [3], and biomolecules [4], even some biological events [5]. For example, Bazan's and Wang's groups have succeeded in designing a series of functionalized cationic PFs for the detection of DNA, proteins, saccharides, and even chemical reaction [4,5,6]; Zhou et al. reported a polyfluorene derivative with grafted imidazole as chemosensory units for Cu²⁺ [2b]; Wang et al. reported two polyfluorene derivatives with pendant phosphonate groups as highly sensitive and selective sensory units for Fe³⁺ [2a]. Whereas as a whole, research work based on functionalized polyfluorene for the detection of metal ions is still rare.

Fluorescent chemosensors for Cu²⁺ have been widely examined. Cu²⁺ usually acts as a quencher, mainly because of its intrinsic quenching behavior as a heavy metal ion through complexation with the receptor. Most of Cu²⁺ detection systems were based on small molecules [7], and the commonly used salt is Cu(ClO₄)₂ due to its good solubility in organic solvents, as well as the relatively lower

binding ability of perchlorate ion in comparison with other anions (Cl⁻, SO₄²⁻, NO₃⁻, etc.). It is very rare for a system to have response to both Cu²⁺ and its counterion simultaneously. Bunz et al. once reported a poly(*para*-phenylene ethynylene) with sugar framework in the side chain as sensory materials for Hg²⁺ and Pb²⁺, and the conjugated polymer exhibited higher association constants for Hg(NO₃)₂ and Hg(tfa)₂ than HgCl₂ and Hg(OAc)₂ [8].

In this article, we report a new copolymer containing the polyfluorene backbone and aza-15-crown-5 pendant. Aza-15-crown-5 has been studied a lot as a common receptor for alkaline, alkali, and some transition metals ions [9]. The photophysical properties of the polymer and its fluorescence responses to metal ions will be discussed. The polymer exhibited high sensitivity and good selectivity for CuSO₄, which was contrasting to the weak responses for other copper salts such as Cu(ClO₄)₂, CuCl₂, Cu(NO₃)₂, and Cu(OAc)₂.

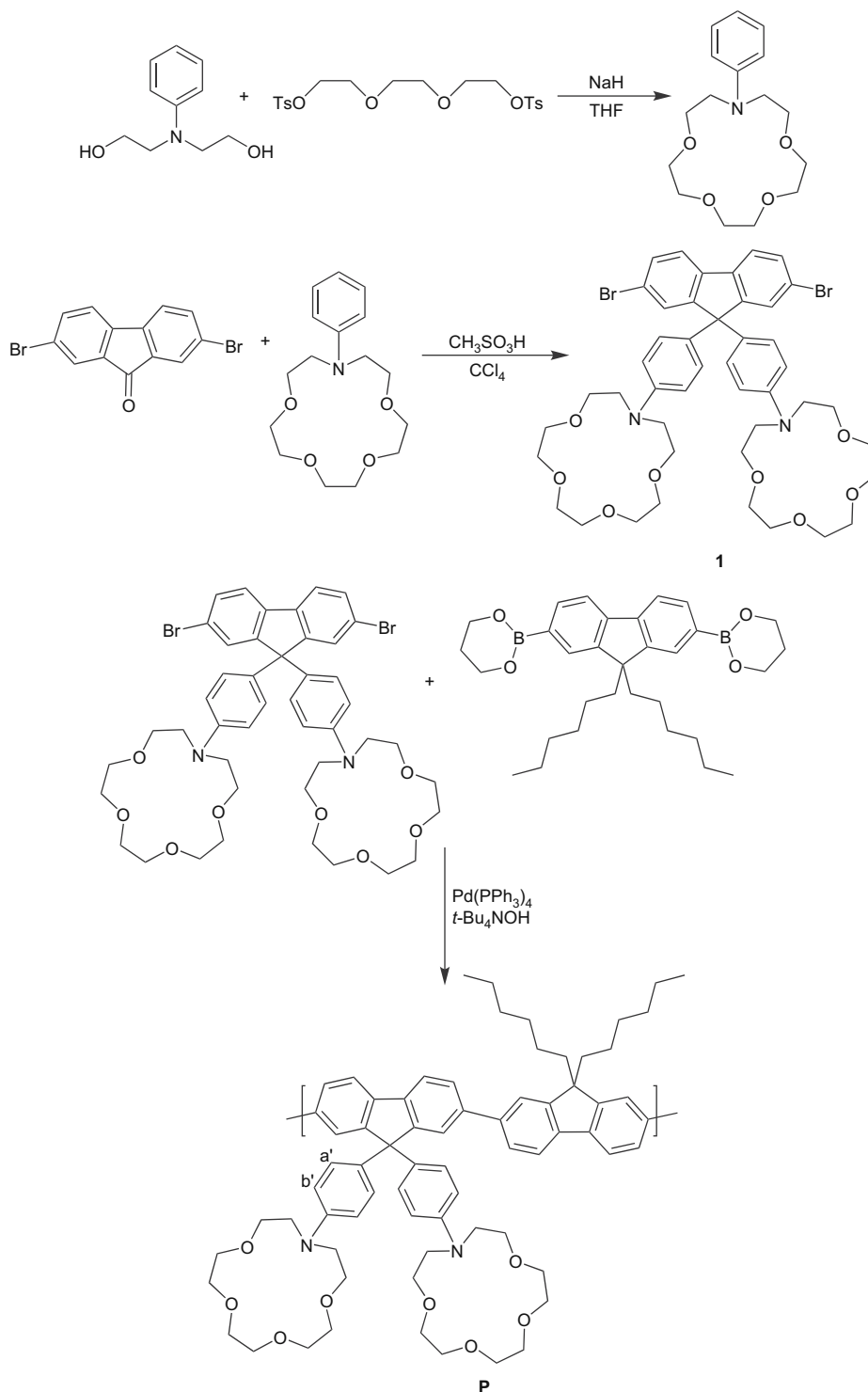
2. Experimental section

2.1. Materials

2,7-Dibromofluorenone [10], tri(ethylene glycol) di-*p*-tosylate [11], and *N*-phenylaza-15-crown-5 [12] were prepared according to the literature procedure. 2,2'-(Phenylazanediy)diethanol, tetrakis(triphenylphosphine)palladium and 2,2'-(9,9-dihexyl-9*H*-fluorene-2,7-diyl)-bis(1,3,2-dioxaborinane) were purchased from Acros. Other materials were used directly without further purification unless otherwise stated.

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Scheme 1. Synthesis of monomer **1** and the copolymer **P**.

2.2. General information

The ^1H NMR and ^{13}C NMR spectra were recorded on a MECUYRVX300 spectrometer in CDCl_3 and $\text{DMSO}-d_6$ using tetramethylsilane as an internal reference, respectively. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Carlorerba-1106 microanalyzer. The molecular weight of the polymer was determined by Agilent 1100 GPC using the column PLgel 5 μm MIXED-C and THF eluent. The number-average and weight-average molecular weights were estimated by using

a calibration curve of polystyrene standards. UV–vis absorption spectra were recorded on Shimadzu 160A recording spectrophotometer. PL spectra were recorded on Hitachi F-4500 fluorescence spectrophotometer. The PL quantum yields were measured from the dilute THF solution of the polymer (ca. 10^{-6} mol/L) by an absolute method using the Edinburgh Instruments (FLS920) integrating sphere excited with Xe lamp. The PL lifetimes were measured by a single photon counting spectrometer from Edinburgh Instruments (FLS920) with a hydrogen-filled pulse lamp as the excitation source. The data were analyzed by iterative

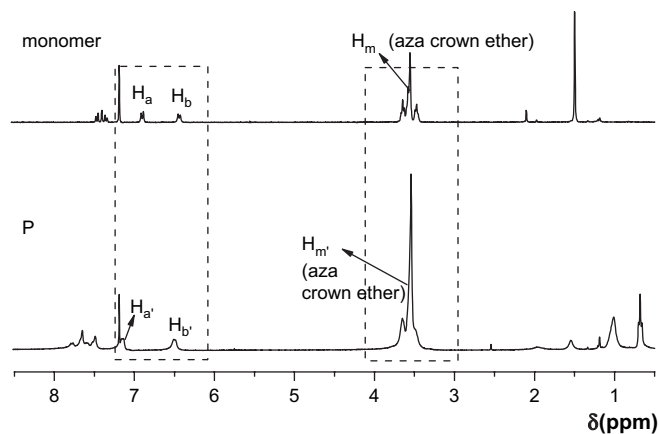


Fig. 1. ^1H NMR spectra of monomer **1** and the copolymer **P**.

convolution of the luminescence decay profile with the instrument response function using the software package provided by Edinburgh Instruments.

The optical properties were studied in dilute solutions. The concentration of the polymer was 5×10^{-6} M in THF (based on the moles of the repeat units), and the metal ions were in MeOH solution with the concentration of 5×10^{-3} M. UV-vis and fluorescence titrations were carried out by sequentially adding different quantities of each metal ion into the polymer solution. After stirring, the spectra were recorded. The excitation wavelength was chosen at 400 nm, according to the maximum absorption wavelength.

2.3. Synthesis of monomer **1**

A mixture of 2,7-dibromofluorone (550 mg, 1.62 mmol), *N*-phenylaza-15-crown-5 (8.23 g, 27.9 mmol) and $\text{CH}_3\text{SO}_3\text{H}$ (156 mg, 1.63 mmol) in 5 mL of CCl_4 was heated at 80°C for 40 h. Then the reactant was extracted with CHCl_3 , and the monomer **1** was gained as white solid after column chromatography using EA/PE (1:2, v/v) as eluent (637 mg, 43%).

^1H NMR (300 MHz, CDCl_3 , δ ppm): 7.74 (d, $J = 6$ Hz, 2H), 7.67 (s, 2H), 7.62 (d, $J = 6$ Hz, 2H), 7.17 (d, $J = 9$ Hz, 4H), 6.71 (d, $J = 9$ Hz, 4H), 3.91 (t, $J = 6$ Hz, 8H), 3.85–3.82 (m, 24H), 3.76–3.74 (m, 8H). ^{13}C NMR (300 MHz, CDCl_3 , δ ppm): 154.8, 146.6, 138.1, 131.5, 130.6, 129.6, 129.2, 121.9, 121.6, 111.3, 71.5, 70.4, 70.3, 68.8, 64.3, 52.8. Anal. Calcd. for $\text{C}_{45}\text{H}_{54}\text{Br}_2\text{N}_2\text{O}_8$ (%): C, 59.35; H, 5.98; N, 3.08; found: C, 59.72; H, 6.37; N, 3.08. ESI mass $M^+ m/z$ 909.0 (M^+).

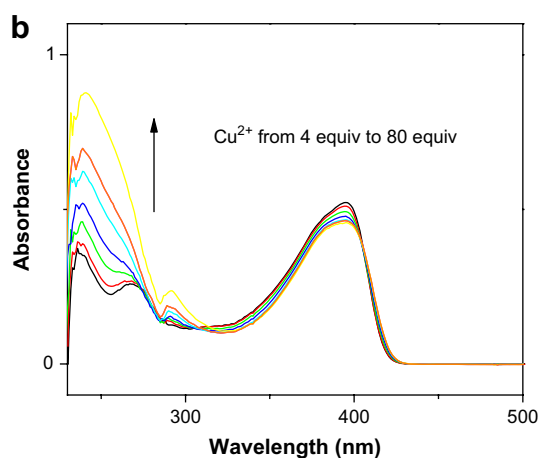
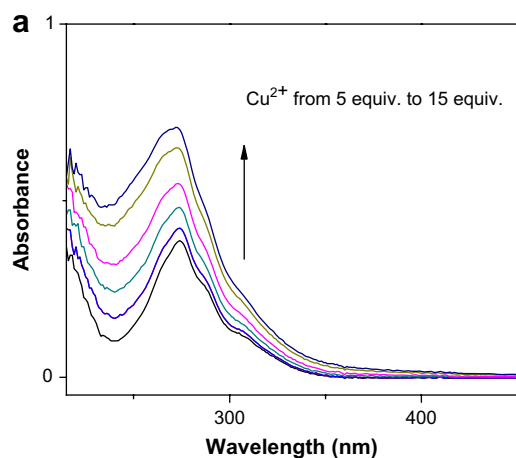


Fig. 2. UV-vis spectra of (a) monomer **1** and (b) copolymer **P** in THF solution upon addition of Cu^{2+} (in MeOH). The concentration of both monomer **1** and **P** is 5×10^{-6} M in THF, and CuSO_4 is 5×10^{-3} M in MeOH.

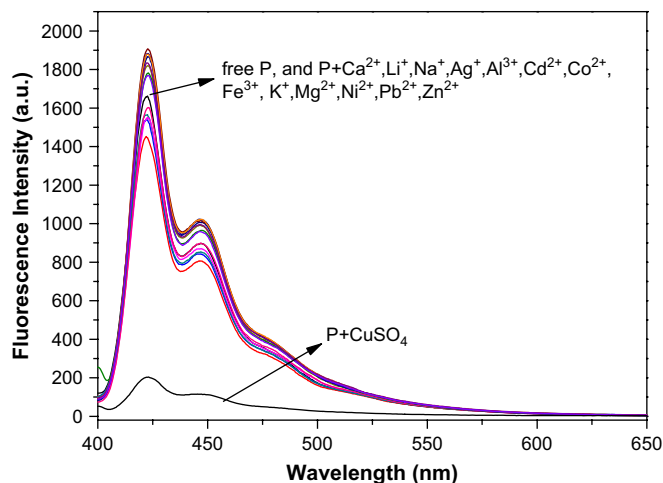


Fig. 3. Fluorescence response of **P** toward different metal ions. Each metal ion is of 20 equiv to the polymer. **P** is 5×10^{-6} M in THF, while all the metal ions are 5×10^{-3} M in MeOH.

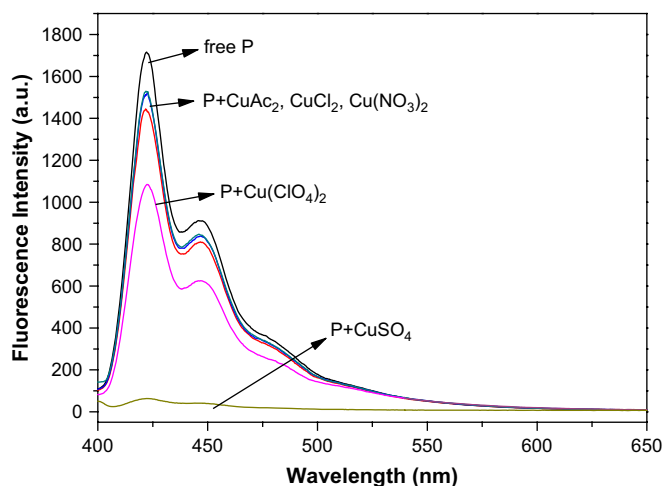


Fig. 4. Fluorescence response of **P** (in THF) toward $\text{Cu}(\text{ClO}_4)_2$, CuCl_2 , $\text{Cu}(\text{NO}_3)_2$, $\text{Cu}(\text{OAc})_2$ and CuSO_4 (in MeOH). Metal salts are of 20 equiv to the polymer.

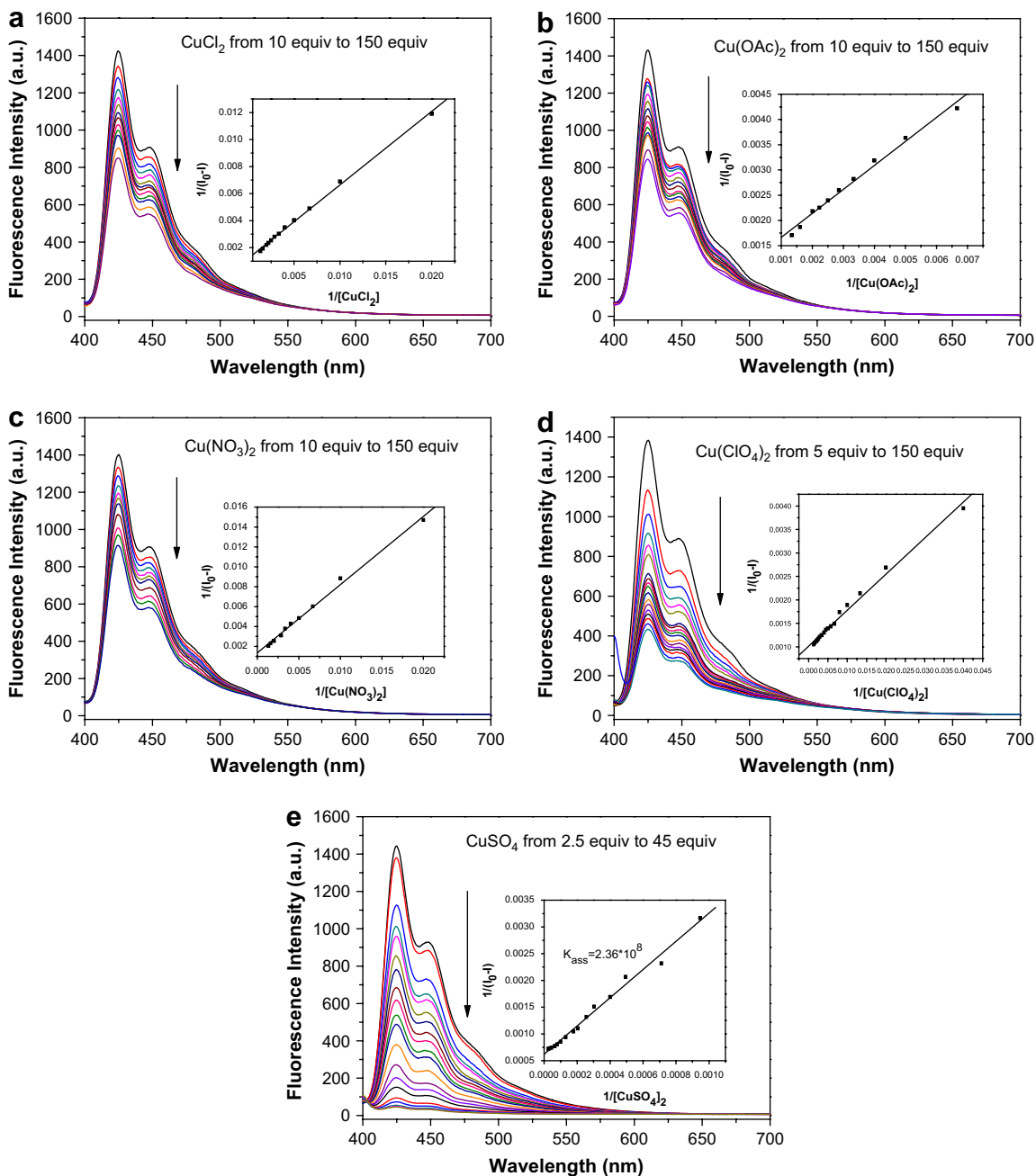


Fig. 5. Fluorescence titration of (a) CuCl_2 , (b) $\text{Cu}(\text{OAc})_2$, (c) $\text{Cu}(\text{NO}_3)_2$, (d) $\text{Cu}(\text{ClO}_4)_2$, and (e) CuSO_4 , respectively. (Inset: Benesi–Hildebrand equation linear fitting plots. I_0 is the original emission intensity of the polymer; I is the emission intensity after addition of metal salts.)

2.4. Synthesis of polymer **P**

To a mixture of monomer **1** (300 mg, 0.33 mmol), 2,2'-(9,9-dihexyl-9H-fluorene-2,7-diyl)bis(1,3,2-dioxaborinane) (165.7 mg, 0.33 mmol), *t*-BuNOH (2.5 mL) and $\text{Pd}(\text{PPh}_3)_4$ (10 mg), 8 mL of THF were added. The mixture was degassed several minutes, and then stirred at 100 °C for 3 d. After cooling to room temperature, the resulting polymer was purified by reprecipitating in methanol for three times to afford a greenish solid. Yield: 223 mg, 61.9%.

^1H NMR (300 MHz, CDCl_3 , δ ppm): 7.87–7.84 (br), 7.73–7.68 (br), 7.56 (br), 7.21 (br), 6.56 (br), 3.73 (br), 3.62 (br), 1.62 (br), 1.09 (br), 0.78–0.73 (br). Anal. Calcd. for $\text{C}_{70}\text{H}_{86}\text{N}_2\text{O}_8$ (%): C, 77.60; H, 8.00; N, 2.59; found: C, 77.82; H, 7.96; N, 2.38.

3. Results and discussion

3.1. Synthesis and characterization

As depicted in Scheme 1, the monomer **1** was synthesized by the reaction of *N*-phenylaza-15-crown-5 with 2,7-dibromofluorene. The Suzuki polycondensation of monomer **1** and 2,2'-(9,9-dihexyl-9H-fluorene-2,7-diyl)bis(1,3,2-dioxaborinane) with the feed ratio of 50:50 mol%, were carried out in a mixed solvent of THF/ H_2O (v/v: 3/1), with *t*-Bu $_4\text{NOH}$ aqueous solution (50%) as base and 1 mol% $\text{Pd}(\text{PPh}_3)_4$ as catalyst. The actual ratio of the two components was estimated to be 52:48 mol% from the ^1H NMR data. The copolymer **P** exhibited good solubility in common organic solvents, such as CHCl_3 , CH_2Cl_2 , THF, DMF, and DMSO. The number-

Table 1

Association constants of the copper salts with different counterions calculated from Benesi–Hildebrand equation

	Cu(NO ₃) ₂	Cu(OAc) ₂	Cu(ClO ₄) ₂	CuCl ₂	CuSO ₄
K _a (M ⁻¹)	2.0 × 10 ³	2.6 × 10 ³	1.3 × 10 ⁴	2.0 × 10 ³	2.4 × 10 ⁸
R	0.997	0.995	0.995	0.999	0.995

K_a is the association constant, R is the correlation coefficient.

average molecular weight of the polymer was 90 000 g/mol by using a calibration curve of polystyrene standards, with PDI (M_w/M_n) of 3.1.

The ¹H NMR spectra of monomer **1** and the copolymer **P** are shown in Fig. 1. For monomer **1**, chemical shifts of H_a, H_b were ascribed to the protons of the phenyl rings at C9 position of fluorene; while H_m was assigned to the protons of the aza-crown ether. These peaks also clearly appeared in the ¹H NMR spectrum of the polymer **P**, indicating the existence of the monomer **1** in the copolymer. In addition, the chemical shifts of the copolymer in the high fields (1.62–0.73 ppm) implicated the presence of the other component 9,9'-dihexyl-9H-fluorene.

3.2. UV–vis response

The UV–vis spectrum of the polymer in THF solution is shown in Fig. 2. The absorption maximum at 395 nm was assigned to the π–π* transition state of the polyfluorene conjugated backbone. The absorption bands at 237 nm and 268 nm may come from the side chain. Upon addition of the metal ions (Co²⁺, Ag⁺, Mg²⁺, Cd²⁺, Fe³⁺, Al³⁺, Ni²⁺, Pb²⁺, Zn²⁺, Li⁺, Na⁺, K⁺, Ca²⁺, and Cu²⁺), only Cu²⁺ caused significant spectral changes. As shown in Fig. 2, upon adding Cu²⁺ into the THF solution of the polymer, the backbone absorbance at 395 nm had little changes because the pendant units were bonded to the conjugated backbone through a sp³ hybridized C atom. In contrast, the absorbances of pendant group at 237 nm and 268 nm increased along with the increase of Cu²⁺ concentration. This deduction was further verified by the change of absorbance of monomer **1** upon addition of Cu²⁺ (Fig. 2a), in which the peak at 273 nm also showed a gradual enhancement with the increase of Cu²⁺ concentration. Further more, two isosbestic points could be observed at 305 nm and 405 nm, respectively. This phenomenon suggests that there are new species formed due to the complexation of Cu²⁺ with the aza-15-crown-5 units.

3.3. Fluorescent response

The copolymer **P** emitted strong blue fluorescence in common solvents such as CH₂Cl₂, CHCl₃, and THF. Fluorescent titration processes were carried out in THF, with all the metal ions in MeOH (Co²⁺, Ag⁺, Mg²⁺, Cd²⁺, Fe³⁺, Al³⁺, Ni²⁺ as their nitrate salts, and Pb²⁺, Zn²⁺, Li⁺, Na⁺, K⁺, Ca²⁺ as their perchlorate salts, Cu²⁺ was tested as its sulfate salt). Fig. 3 shows the fluorescence response of the copolymer **P** toward different metal ions in a concentration of 10⁻³ M. Among these metal ions, only Cu²⁺ exhibited a prominent quenching behavior, while other metal ions caused little changes of the polymer emission. Quantificationally, the fluorescent quantum yield of the polymer solution decreased from 48.6% to 10.1% with the addition of 50 equiv CuSO₄.

We note that when the other copper salts, for instance Cu(ClO₄)₂, CuCl₂, Cu(NO₃)₂, and Cu(OAc)₂ were tested under the same condition, the fluorescence quenching was rather weak compared to the case of CuSO₄. Fig. 4 shows the different fluorescence responses of **P** to copper salts with different counterions. And Fig. 5a–e represents the fluorescence titration of these salts to the polymer, respectively. As calculated from Benesi–Hildebrand equation [13], the association constants of these copper salts are listed in Table 1.

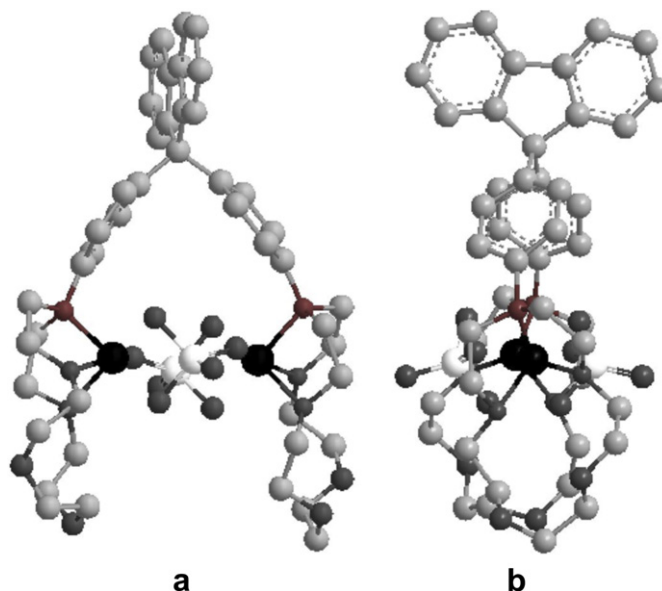


Fig. 6. Optimized molecular complexation model between the monomer **1** and CuSO₄ based on PM3 of MOPAC 2007 software. (a) Side view; (b) front view. (Representations: black, red, dark gray, gray and white balls denote the copper, nitrogen, oxygen, carbon and sulfur atoms, respectively; H atoms are omitted for clarity.) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Of these copper salts investigated, CuCl₂, Cu(OAc)₂ and Cu(NO₃)₂ can be grouped as low-dissociating salts in MeOH, while Cu(ClO₄)₂ has higher dissociation constant in MeOH. As shown in Fig. 4, the addition of Cu(ClO₄)₂ caused significantly higher fluorescence quenching among the above four copper salts. From this point of view, the fluorescence quenching behavior seemed to be correlative with the dissociation abilities of these salts [8]. Whereas inconsistent with this suspicion, CuSO₄ with low-dissociating constant exhibited much stronger quenching ability than Cu(ClO₄)₂. Herein the dissociation constant was inadequate to interpret the fluorescence quenching behavior. Then should the nature of the anions count for the fluorescence quenching? We note that only SO₄²⁻ is bivalent in these anions studied. However, when ZnSO₄ solution in MeOH was added into the THF solution of the polymer, no significant quenching was observed. Therefore it is reasonable to postulate that the anions may play an important role when Cu²⁺ coordinated with the aza-crown ether group.

To understand the specific fluorescence quenching of CuSO₄ for the polymer, we performed the geometry optimization for the interaction between the monomer **1** and CuSO₄ for simplification. As shown in Fig. 6, the two pendant phenyl rings are tilted away from each other, with torsion angle of 92.9°. A copper ion coordinates with the N atom, and the two O atoms adjacent to the N atom in the crown ether part, and two SO₄²⁻ as counterions situate into the quasi-cavity formed by two aza-crown ether units. The quasi-cavity may be apropos for two sulfate ions, while four nitrate ions or perchlorate ions are obviously too large to get into the cavity. The geometry optimization may be accessorial in understanding the synergistic effect of the sulfate anion.

The fluorescence quenching of the polymer could be partially restored upon addition of EDTA aqueous solution to the Cu²⁺–**P** system. As shown in Fig. 7, after adding 50 μL of 5 mM EDTA aqueous solution into the mixture, the fluorescence emission restored immediately, due to the stronger binding ability between Cu²⁺ and EDTA. Yet it could not be fully recovered, as the addition of water brought about fluorescence quenching of the polymer to

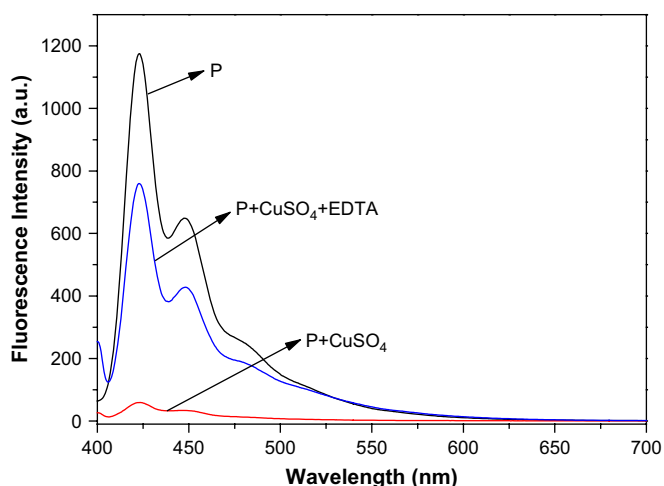


Fig. 7. Fluorescence response of **P** (5 μM , THF solution) upon the addition of CuSO_4 (50 μL , 5 mM, MeOH solution), followed by the addition of EDTA (5 mM in water).

Table 2

Fluorescence lifetimes of the copolymer **P** upon addition of CuSO_4

$[\text{CuSO}_4]/\mu\text{M}$	τ_1 (ns)	τ_2 (ns)	χ^2
0	2.63 (19.4%)	7.63 (80.6%)	1.046
25	2.26 (26.1%)	7.89 (73.9%)	1.036
50	1.64 (25.6%)	8.05 (74.4%)	1.048
75	1.03 (27.2%)	8.26 (72.9%)	1.026
100	0.82 (36.4%)	8.17 (63.6%)	1.015
125	0.78 (48.7%)	7.85 (51.3%)	1.004
150	0.76 (56.4%)	7.45 (43.6%)	1.032
175	0.80 (59.6%)	7.16 (40.4%)	1.012
200	0.85 (61.3%)	7.11 (38.7%)	1.062
250	0.87 (65.4%)	7.29 (34.6%)	1.006

some extent. This recovery experiment further confirmed that the Cu^{2+} ion interacts with the polymer through coordination with the pendant crown ether units.

In addition, we also measured the fluorescence lifetimes of the copolymer in THF solution before and after addition of CuSO_4 . The PL lifetimes (τ), their relative intensity contributions and goodness of fit (χ^2) are tabulated in Table 2. The decay of polymer was best described by bi-exponential fit, with $\tau_1 = 2.63$ ns and $\tau_2 = 7.63$ ns, which may correspond to two different states. Noticeably, the contribution of τ_1 gradually increased at the expense of that of τ_2 with the growing concentration of CuSO_4 , which implied a static quenching mode [14].

4. Conclusion

In summary, we have synthesized and characterized a novel fluorene-based copolymer with aza-crown ether as pendant group. This is the first report that the crown ether units are introduced into the side chain of conjugated polymer as special receptor to detect metal ions. Of all the metal ions screened, the polymer shows

selectivity for Cu^{2+} . The fluorescence titration experiments indicate that the polymer has quite good selectivity and high sensitivity for CuSO_4 , which is contrasting to the weak responses for other copper salts such as $\text{Cu}(\text{ClO}_4)_2$, CuCl_2 , $\text{Cu}(\text{NO}_3)_2$, and $\text{Cu}(\text{OAc})_2$. Through molecular simulation, it is postulated that the sensitivity and selectivity of the polymer for CuSO_4 may come from the synergistic effect of SO_4^{2-} . To the best of our knowledge, this is the first time to report the specific detection for CuSO_4 by the synergistic effect of counterion. This system may find use in the sensory of some pesticides containing CuSO_4 .

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