

Electrosynthesis, Characterization and Optical Sensing Application of Amino Acid Functionalized Polyfluorene*

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Abstract An amino acid side chain functionalized polyfluorene derivative poly[*N*-(9-fluorenylmethoxycarbonyl)-glycine] (P9FG) was facilely electrosynthesized and characterized, and the structure, properties and optical sensing application of the obtained polymer were described and discussed. The electropolymerization occurred at C₂ and C₇ positions of fluorene units, and amino acid side chain groups were not cleaved from polyfluorene backbone in mixed electrolytes of boron trifluoride diethyl etherate and dichloromethane. Thermal analysis demonstrated good thermal stability of P9FG. Fluorescent spectra indicated that P9FG was a good blue light emitting material that could be employed as optical sensors. The soluble P9FG as a turn-off fluorescent sensor could realize the detection of Fe³⁺, Cu²⁺ and Cr₂O₇²⁻, respectively. In addition, P9FG as a turn-off ultraviolet sensor could realize the detection of Cu²⁺ while as turn-on ultraviolet sensors could also realize the determination of Fe³⁺ and Cr₂O₇²⁻, respectively. All results indicate that P9FG is a promising candidate for optical sensing.

Keywords: Conjugated polymers; Polyfluorene derivatives; Electropolymerization; Optical sensors; Metal ions.

INTRODUCTION

Conjugated polymers (CPs) with unique semiconducting and photoelectrical properties have attracted considerable attention and resulted in numerous technological innovations^[1, 2]. They have been explored for a wide range of novel applications such as organic light emitting diodes, thin film transistors, solar cells, and chemo/bio-sensors due to their superior electronic and optical properties. In particular, their implementation in sensing schemes and devices is widely investigated and produced a multitude of sensory systems and transduction mechanisms^[3, 4]. Until now, many fluorescent CPs have been employed as the fluorescent sensing platform for the development of highly sensitive chemo/bio-sensors because they exhibit sensory signal amplification along the whole polymer backbone through the molecular wire effect^[5–7]. More importantly, their structures can easily be tailored to adjust solubility, absorption wavelengths, emission wavelengths, and energy offsets for excited state electron transfer in the solution or solid state^[6, 8].

Polyfluorene (PF) derivatives are a kind of prospective emitting layer fabricated polymer blue light emitting devices among CPs in that they have a variety of extraordinary properties including high electroluminescence,

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efficient photoluminescence, good charge transport, and excellent thermal stability in the mixed ethanol/water system. In addition, fluorinated-based CPs are also a promising class of optical sensing materials, which have been widely investigated for applications of chemo/bio-sensors because of their high chemical stability, good photostability, exceptionally high solubility, and solid-state fluorescence quantum yields^[9–15]. However, several disadvantages of PFs limit their potential application in chemo/bio-sensors, such as the low electron affinity, poor solubility, and fluorescence quenching resulting from the keto formation of the C₉ position oxidation. Recently, PFs modified by different groups were used to improve as-above mentioned flaws without significantly increasing the steric interactions in the polymer backbone^[16–18]. Just as the functionalized carboxylic acid group on CPs plays an important role in the construction of sensors^[19–22]. Different substituents enable solubility in common organic solvents and processing of high-quality thin films, which will make PFs suitable as optical sensing material^[23]. For instance, Wang *et al.* synthesized a PF derivative and used as a fluorescent probe for the detection of lead ion and copper ion^[24–26]. Wang and coworkers also designed several different functionalized PF derivatives and used for the detection of Fe³⁺, Hg²⁺, and Ag⁺^[27–29]. In our previous work, a good fluorescent sensor was fabricated based on poly(9-aminofluorene), which were employed for highly sensitive detection of Fe³⁺, inorganic phosphates, and carboxylates^[30, 31].

Among PF derivatives family, 9-fluorenylmethoxycarbonyl group (Fmoc) is stable toward acid and catalytic hydrogenation, but readily cleaved under mildly basic and non-hydrolytic conditions^[32]. Rault-Berthelot *et al.* have reported the anodic oxidation of Fmoc-amino acids in acetonitrile system containing tetrabutylammonium tetrafluoroborate, and the chiral discrimination of these polymers towards pure enantiomers was also presented^[33]. This work opened a way for the use of poly(Fmoc-amino acids) in bioelectrochemistry or combinatorial chemistry. Subsequently, Pei group studied chiral poly(Fmoc-amino acids) films synthesized by direct anodic oxidation of the corresponding monomers in a medium strong Lewis acid, boron trifluoride diethyl etherate (BFEE)^[34, 35]. To the best of our knowledge, there was no reports on the optical application of poly(Fmoc-amino acids).

The commonly employed reactions for the preparation of PFs are chemical oxidative polymerization like Suzuki, Yamamoto, and Stille reactions^[16, 36]. And the Suzuki's coupling reaction could provide PFs with a maximum molecular weight of several 10000 and the Yamamoto reaction also can lead to a higher molecular weight up to 200000^[37]. Nevertheless, these experiments cost too much time (up to 72 h) to build polymers with modest molecular weight, while the use of carefully purified monomers and the application of optimized reaction conditions are the main prerequisite for reaching such high molecular weights^[38]. Electrochemical polymerization, a kind of method that has been widely employed for the generation of CPs onto a conducting surface, as one of fast, reliable and convenient synthetic methods to obtain the target material with good mechanical, electrical and optical properties^[39–41]. Electrochemical methods can produce the polymers by direct anodic oxidation of corresponding monomers with several distinct advantages as being catalyst-free, requirement for only small amounts of monomers, one-step formation of polymers, ease of controlling the thickness of films and convenience of characterization^[41]. Nowadays, a series of PFs synthesized by direct anodic oxidation have been reported^[42–44]. Likewise, our group also investigated the electrochemical synthesis and characterization of poly(9-aminofluorene)^[29, 45], poly(9-hydroxyfluorene), poly(9-fluorene-carboxylic acid), and poly(9-hydroxyfluorene-9-carboxylic acid)^[46]. But only a few of these PFs were used for the optical application^[30, 31].

In this work, poly[*N*-(9-fluorenylmethoxycarbonyl)-glycine] (P9FG) was electrochemically synthesized in a mixture system of boron trifluoride diethyl etherate electrolyte (BFEE) and dichloromethane (DCM). Following by a series of characterization, which were served to confirm the polymerization site, thermal stability, and optical properties of the as-prepared polymer. The most interesting point is that P9FG film was chosen as optical material for fabricating optical sensors, which were employed to quantitative analysis of Fe³⁺, Cu²⁺ and Cr²⁺O₇²⁻ via fluorescence and ultraviolet strategies.

EXPERIMENTAL

Materials and Apparatus

9FG (98%, Alfa Aesar) was purchased from Aladdin Chemistry Co. Ltd. Boron trifluoride diethyl etherate (BFEE, Beijing Changyang Chemical Plant, China) was distilled and stored at $-20\text{ }^{\circ}\text{C}$ before use. Dichloromethane (DCM, analytical grade) was the product of Tianjin Bodi Chemicals Co. Ltd. and used after reflux distillation. Tetrabutylammonium tetrafluoroborate (Bu_4NBF_4 , 99%; Acros Organics; SIGMA-ALDRICH, Co.) was dried under vacuum at $60\text{ }^{\circ}\text{C}$ for 24 h before use. Anhydrous ethanol (HPLC, 99.5%) purchased from Xiya Reagent Co. Ltd (Shandong, China) was used without further purification. The mixed ethanol/water system (1:1, *V/V*) was used for studying the sensing of ions, the as-prepared P9FG was dissolved in anhydrous ethanol. All cations and anions were prepared in doubly distilled water, and all these ions are purchased from J&K Chemical Co. Ltd. Doubly distilled water was utilized for all experiments. Other reagents were all analytical grade and used as received without further treatment.

Electrochemical tests and polymerization were performed in a one-compartment cell using a potentiostat-galvanostat (model 263A, EG & G Princeton Applied Research) under computer control. Infrared spectra were determined with a Bruker Vertex 70 Fourier-transform infrared (FTIR) spectrometer with samples in KBr pellets. Absorption spectra were measured using an Agilent 8453 UV-Vis spectrophotometer. All fluorescence experiments were carried out using a Hitachi F-4500 spectrophotometer with excitation slit set at 5 nm and emission slit at 5 nm. The ^1H -NMR spectra were recorded on a Bruker AV 400 NMR spectrometer with d_6 -DMSO used as the solvent. The X-ray photoelectron spectroscopy (XPS) was recorded by a PHI 5000 Versaprobe spectrometer. Thermogravimetric analysis (TGA) was performed with a Pyris Diamond TG/DTA thermal analyzer (PerkinElmer). All thermal analysis were performed under a nitrogen stream in the temperature range of 300–1075 K with a heating rate of 10 K/min.

Electrochemical Preparation of P9FG Films

Electrochemical syntheses were performed in a one-compartment cell with the use of a Model 263 potentiostat-galvanostat (EG&G Princeton Applied Research) under computer control. The working and counter electrodes for linear sweep voltammetry (LSV) and cyclic voltammetry (CV) experiments were platinum wires with a diameter of 0.5 mm and placed 0.5 cm apart. An Ag/AgCl electrode directly immersed in the solution served as the reference electrode. Prior to each experiment, these electrodes mentioned above were carefully polished with abrasive paper (1500 mesh), cleaned successively with water and acetone, and then dried in air successively. To obtain a sufficient amount of polymer films for characterization, stainless steel sheets with a surface area of 10 and 12 cm^2 each were employed as the working and counter electrodes, respectively. After polymerization, P9FG films were washed repeatedly with anhydrous acetonitrile to remove the electrolyte, monomers, and oligomers. The molecular weight of polymers was measured by GPC ($M_n = 2585$, $M_w = 2707$).

RESULTS AND DISCUSSION

Electrosynthesis of P9FG Film

Figure 1 shows anodic polarization curves of 9FG in DCM containing BFEE with different percentages. The onset oxidation potential of 9FG was approximately 1.48 V in pure DCM containing Bu_4NBF_4 . With the addition of BFEE to DCM, the onset oxidation potential of 9FG decreased initially from 1.483 V to 1.117 V, then increased from 1.117 V to 1.193 V. Obviously, the oxidation potential value of 9FG in DCM/BFEE system was much lower than that in pure DCM solution (1.48 V). The large descent in the onset oxidation potential can be attributed to the interaction between the middle strong Lewis acid BFEE and the aromatic monomers, decreasing the aromaticity of fused rings^[47–49]. In general, high oxidation potential easily causes the monomers over oxidation at the polymerization potential, resulting in destruction of the conjugated structure of the polymers and degradation of their properties. The decrease in the onset oxidation potentials can prevent side reactions effectively and lead to high-quality polymer films. The lower the oxidation potentials, the less the probability of side reactions as well as the occurrence of coupling defects. Thus, DCM containing 30% BFEE was more appropriate for the electrochemical polymerization of 9FG.

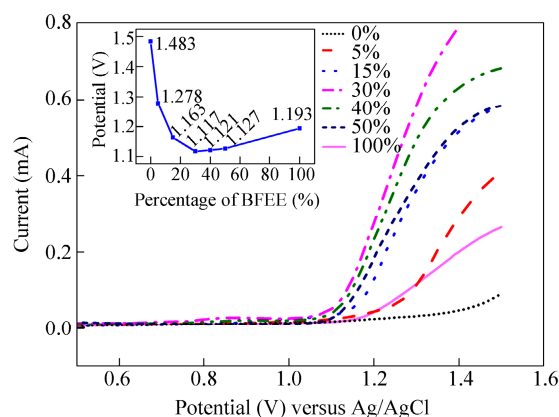


Fig. 1 Anodic polarization curves of 9FG in mixed electrolytes of both BFEE and DCM with different volume ratios containing $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ Bu}_4\text{NBF}_4$ and $0.02 \text{ mol} \cdot \text{L}^{-1}$ monomer

The successive cyclic voltammograms (CVs) of 9FG were performed in BFEE, DCM, and the mixed electrolytes of BFEE and DCM with different volume ratios (in Fig. 2). In DCM, CVs of 9FG monomer were not satisfactory because no apparent redox waves were observed and the anodic current densities decreased quickly with an increase in the scan numbers. Visual inspection during CV experiments revealed that there was no polymer film formed on the working electrode surfaces. However, 9FG was easily electropolymerized in the mixed electrolyte of BFEE and DCM in comparison with pure DCM. All CVs showed similar characteristics that the redox current densities increased with increasing cycle number of potential in the mixed electrolytes, suggesting that the amount of conducting polymers electrodeposited on the surface of bare Pt increased with each cycle. Visual inspection revealed that large amounts of brown P9FG films were obtained on the surface of electrode. Broad features of the observed redox waves resulted from the complexity of the doping process which involved the formation of polarons, bipolarons and their mutual interconversion^[50]. Some contribution to this broadening originating from the polydispersity cannot be excluded^[51, 52]. The obvious potential shift of the wave current maximum provided information about the increase in the electrical resistance in the polymer and the overpotential needed to overcome the resistance^[51].

Characterization of P9FG

Structure of P9FG

Figure 3(a) shows the FTIR spectra of 9FG monomer and dedoped P9FG polymer. The bands at 734 , 773 and 816 cm^{-1} were assigned to the C—H out-of-plane vibration of the phenyl and the band at 1024 cm^{-1} was due to the C—H in-plane vibration of the phenyl. These bands were similar to those of 1,2,4-trisubstituted benzene rings with respect to the wave number and the patterns of absorption bands^[39, 53, 54]. The C=O vibration frequency for the ester group appeared as a large peak at 1724 cm^{-1} in both 9FG monomer and dedoped P9FG, while the —OCONH— also has a strong intensity band in the range from 1746 cm^{-1} to 1690 cm^{-1} . Additionally, the presence of the strong —COOH elongation and deformation vibration peaks at 1400 , and 1245 cm^{-1} in the spectrum of the dedoped P9FG demonstrated that the —COOH group was not destroyed^[31, 39, 40].

In addition, the newly-emerged moderate intensity peak at 1084 cm^{-1} corresponded to the characteristic vibration band of the doping anions (B—F bonds). Compared with the monomer, the peaks in the spectrum of dedoped P9FG were not obviously broadened, which is quite different from those of other conducting polymers, and may be attributable to the relatively short chain length of the as-formed P9FG^[54, 55]. The strong intensity peak at 3435 cm^{-1} might be was O—H ($3600\text{--}3200 \text{ cm}^{-1}$), —NH— ($3500\text{--}3300 \text{ cm}^{-1}$), and crystal water ($3600\text{--}3100 \text{ cm}^{-1}$). All the information above indicated that the side chain stayed stable before/after the electrochemical polymerization.

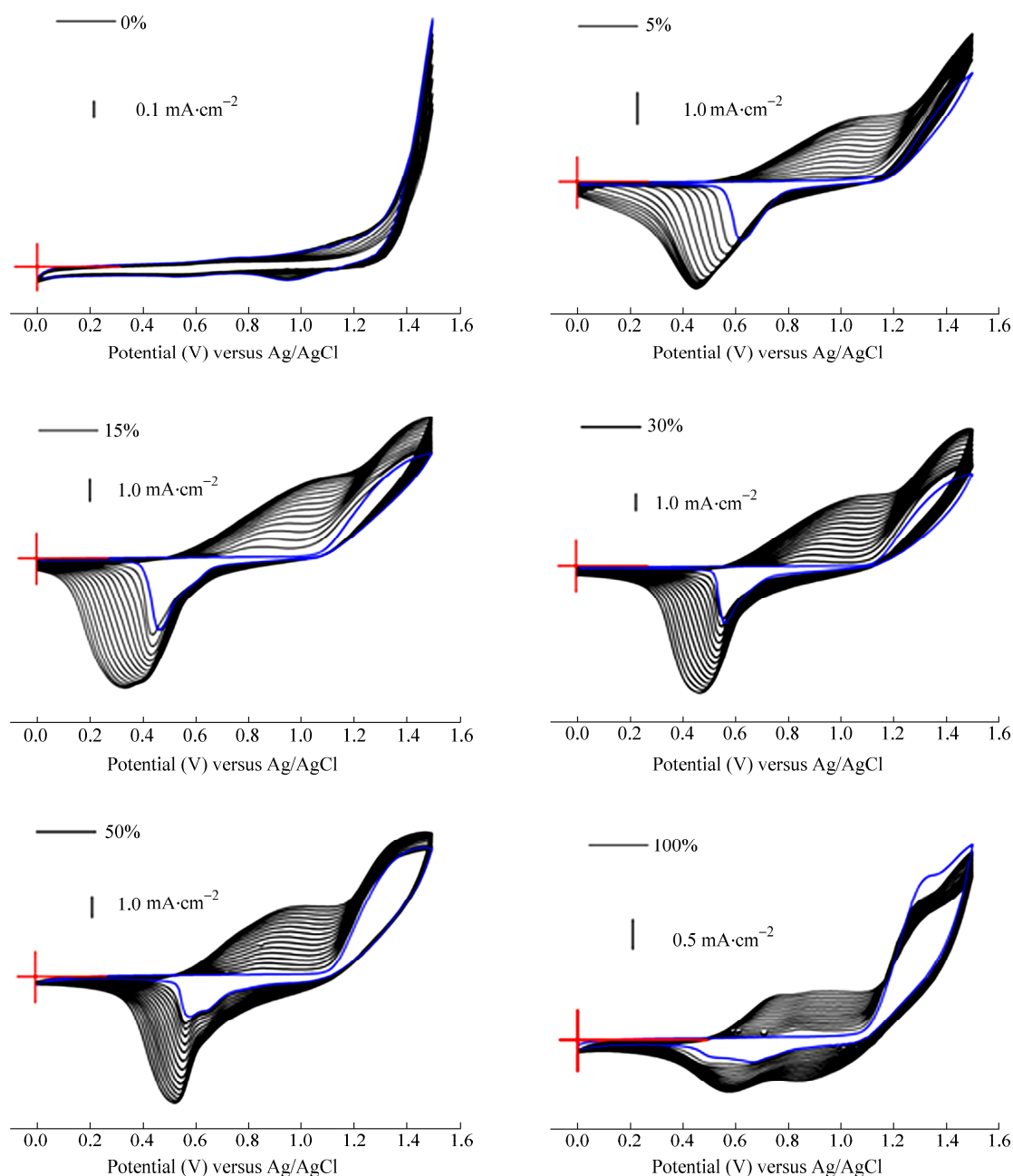


Fig. 2 CVs of 9FG in the mixed electrolytes of BFEE and DCM with different volume ratios containing $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ Bu}_4\text{NBF}_4$ and $0.02 \text{ mol}\cdot\text{L}^{-1}$ monomer

In Fig. 3(b), the ^1H -NMR spectra of 9FG and the dedoped P9FG prepared from DCM containing 30% BFEE were recorded. Some new peaks appeared after polymerization between δ of 7.3 and 8.2, and most of the peaks moved to lower fields as the length of main chain conjugation was longer in P9FG than in 9FG^[39, 52, 55]. The proton chemical shift of 12.99 in the spectrum of the monomer can be ascribed to the proton of $-\text{COOH}$ group, and this signal was still present in the spectrum of P9FG. Hence, it is obviously that the side chain has not changed. In Fig. 3(b), the protons at the C_1 and C_8 could be found at δ of 7.85, but the proton signals of C_4 and C_5 positions shifted to δ of 8.03 from δ of 7.92. The protons at the C_3 and C_6 also could be found at δ of 7.42

almost had no change from 7.41. The chemical shifts at 7.37 could be ascribed to the protons at C₂ and C₇ positions, which disappeared in the spectrum of P9FG^[50, 52]. This indicates that a new C—C bond formed mainly *via* the coupling at C₂ and C₇ positions of 9FG, which is in well accordance with FTIR results.

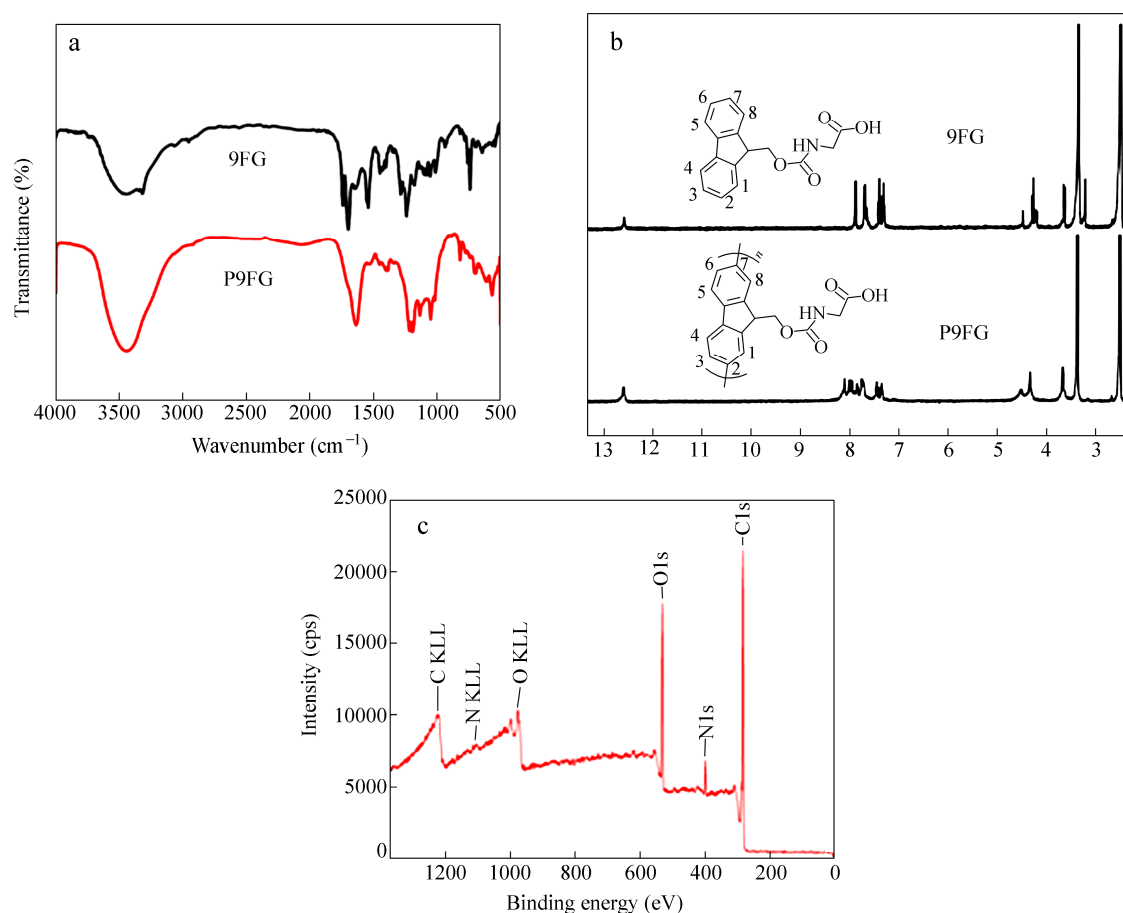


Fig. 3 (a) FTIR spectra of 9FG and P9FG, (b) ¹H-NMR spectra of 9FG and P9FG in d₆-DMSO, and (c) XPS spectrum of P9FG

For further investigating the structure of the polymer, the XPS of P9FG film was recorded. In Fig. 3(c), three elements (C, N, and O) were collected in the polymer, beyond H. Hence, it proves that the polymer contains N element. In addition, their relative contents were also calculated as shown in Table 1. The percentage (ω) of N and O elements in P9FG were smaller than that in 9FG, and the percentage of C element was bigger than that in 9FG. There was a small deviation between 9FG and P9FG, and the relative deviation (RD) within 2% which was in a reasonable range.

Table 1. The percentage of N and O elements of 9FG monomer and P9FG film.

Elements	ω_{9FG} (%)	ω_{P9FG} (%)	RD (%)
C	72.34	74.27	+ 1.93
N	4.96	4.25	-0.71
O	22.70	21.48	-1.22

From what has been discussed above, a conclusion can be given as follows that the polymerization of 9FG mainly occurred at C₂ and C₇ positions of 9FG (Figs. 3a and 3b) and the side chain groups were not changed, which was in accordance with results in previous reports^[33–35]. It can also confirm that the Fmoc group as a

protective group is eminently successful. In addition, the application in optical sensing for different analytes of other Fmoc-amino acids also confirmed that the side chain groups were not changed.

Properties of P9FG

The TG analysis of monomer 9FG indicated that the weight losses of monomer were about 85% between 440 K and 620 K (Fig. 4) and there was an evident degradation process for the monomer at 510 K. As shown in Fig. 4, there was a slight weight loss at 375 K, which closely related to the evaporation of water and other moisture trapped in the polymer. The following prominent degradation between 435 K and 620 K, up to 31.03%, and a corresponding maximal decomposition existed at 535 K. These might be caused by the breakdown of side-chain and the polymer decomposition. With the gradual increase of the temperature, there was another prominent decomposition from 620 K to 880 K and the weight loss of the polymer was about 16.14%. It could be attributed to the overflow of structural fragments decomposed from P9FG. After then, the weight loss was only 4.3% from 880 K to 1100 K, which indicated the residue was constant in weight. These also displayed the good thermal stability of the P9FG film.

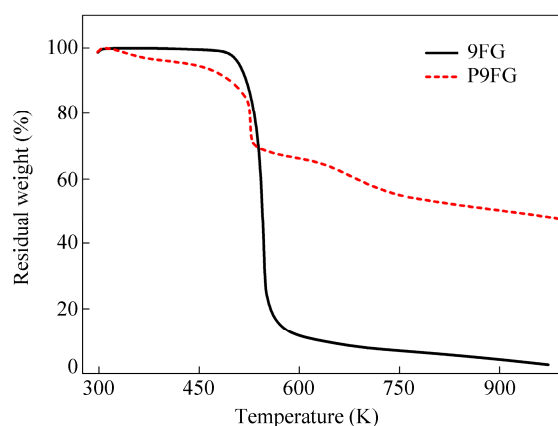


Fig. 4 TG curves of 9FG and P9FG

9FG monomer shows a maximum absorption at 302 nm (a single electron π - π^* transition) in Fig. 5(a). As a result of the increasing conjugated chain length and the wide molar mass distribution, the absorption of P9FG film was broader with an obvious peak centered at around 340 nm, and the overall absorption tailed off to about 410 nm. These spectral results confirmed the occurrence of electrochemical polymerization and the formation of a conjugated polymer. On the other hand, the optical band gap of P9FG calculated from the onset of the absorption spectrum (about 385 nm) was roughly 3.22 eV ($E_g = 1241/\lambda_{\text{onset}}$).

Figure 5(b) shows the emission spectra of the 9FG and P9FG, which were tested in the mixed ethanol/water system (1:1, *V/V*). The emission peak of the 9FG emerged at 327 nm, while the emission peak appeared at 412 nm of P9FG. Compared with the monomer, the peak of polymer has an 85 nm bathochromic shift because of the elongation of the polymer's delocalized π -electron chain sequence. The wide emission of P9FG is reasonable because polymers have different chain lengths, namely, polymerization degrees of every 9FG chain are different.

The irreversible destruction of the excited fluorophore (photobleaching) often becomes the factor limiting fluorescence detectability after a long time of UV irradiation. In order to quantitatively investigate the photostability of P9FG, the sealable cell that contained P9FG was exposed to UV-light. As shown in Fig. 6, the fluorescence intensity of P9FG almost has no change during 22 scans (the cuvette was exposed to UV-light for 30 s before each scan) with a total irradiation time of about 660 s. The relative standard deviation and relative mean deviation was 0.95% and 0.79%, respectively. These results suggested the superior photostability of P9FG.

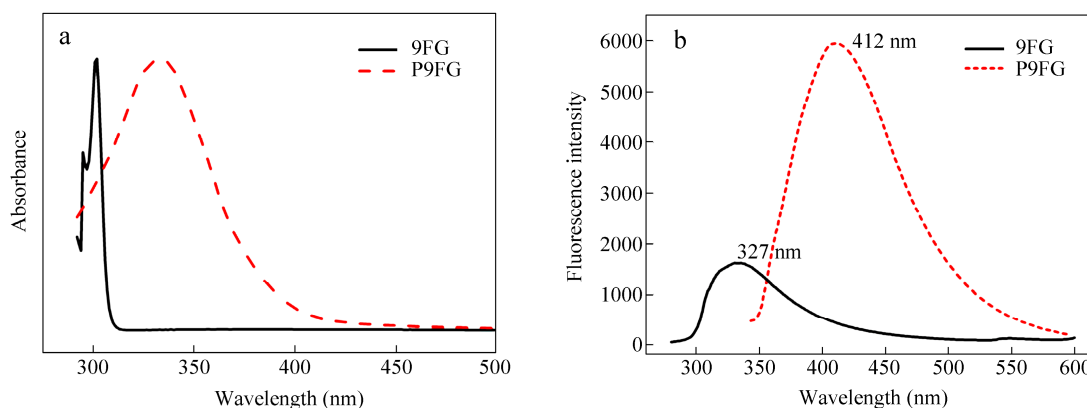


Fig. 5 UV-Vis spectra (a) and fluorescence spectra (b) of 9FG and P9FG in the mixed ethanol/water system (1:1, V/V)

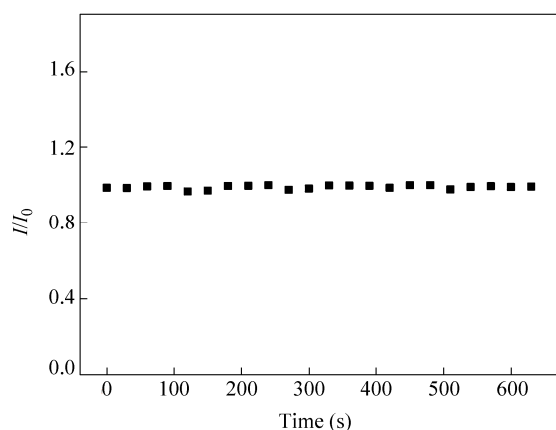


Fig. 6 The photostability of P9FG in the mixed ethanol/water system (1:1, V/V)

Optical Sensing Application of P9FG

Fluorescent sensing of P9FG

In Fig. 7(a), the fluorescence intensity of P9FG in the mixed system of ethanol and water with volume ratio of 1:1 (V/V) is higher than that of the others. From a to g, the fluorescence intensity of P9FG has almost no change (Fig 7b) when 20 μL of the deionized water was added into the mixed ethanol/water system (1:1, V/V) before each measurement. Hence, the mixed ethanol/water system (1:1, V/V) was chosen as the optical system.

Initially, the effect of various metal ions like K^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Al^{3+} , Zn^{2+} , Hg^{2+} , Co^{2+} , Sr^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Sn^{2+} , Cd^{2+} , Cr^{2+} , and Cu^{2+} on fluorescence intensities of P9FG was investigated in ethanol/water (1:1, V/V) system. As can be seen from Fig. 8(a), the addition of Cu^{2+} or Fe^{3+} could cause significantly fluorescence quenching, inducing a color change from blue to colorless under UV light. Similarly, when $\text{Cr}_2\text{O}_7^{2-}$ was added, the fluorescence of P9FG dramatically quenched. Nevertheless, the addition of the other various anions such as F^- , Cl^- , Br^- , I^- , NO_2^- , NO_3^- , HSO_4^- , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, SCN^- , CO_3^{2-} , HCO_3^- , CH_3COO^- , and PO_4^{3-} produced negligible changes in fluorescence intensities of P9FG under identical conditions (Fig. 8b). Furthermore, the complexation ability of P9FG with Fe^{3+} , Cu^{2+} and $\text{Cr}_2\text{O}_7^{2-}$ was investigated by a photoluminescent technique in Fig. 8(e).

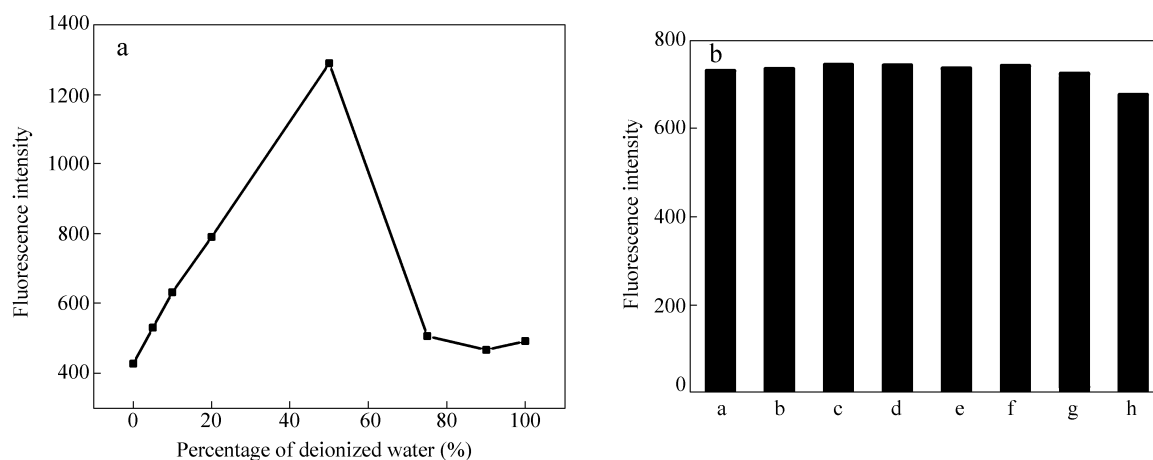
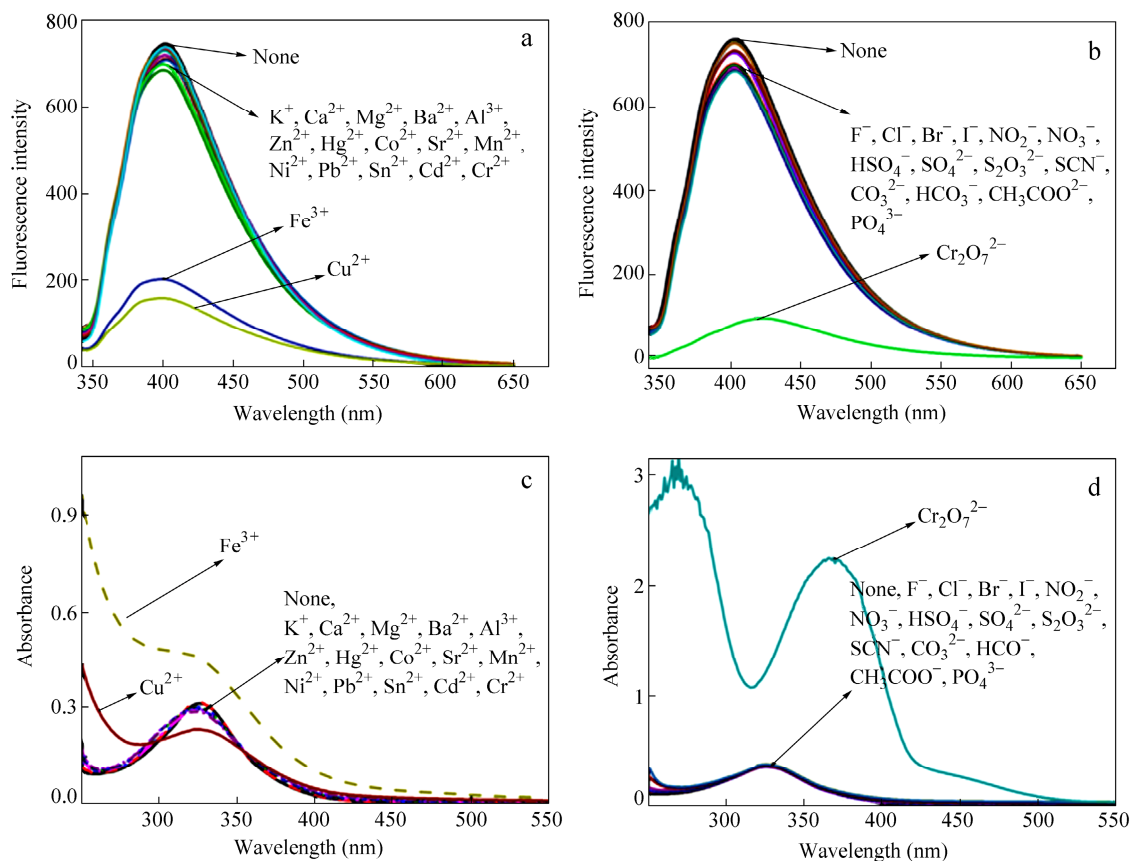


Fig. 7 (a) Effect of the mixed system of ethanol and water with different volume ratios on fluorescence intensity of P9FG, (b) effect of deionized water with different volumes on fluorescence intensity of P9FG in the mixed ethanol/water system (1:1, V/V) in (a) (a–h: the volume of water from 20 μ L to 160 μ L)



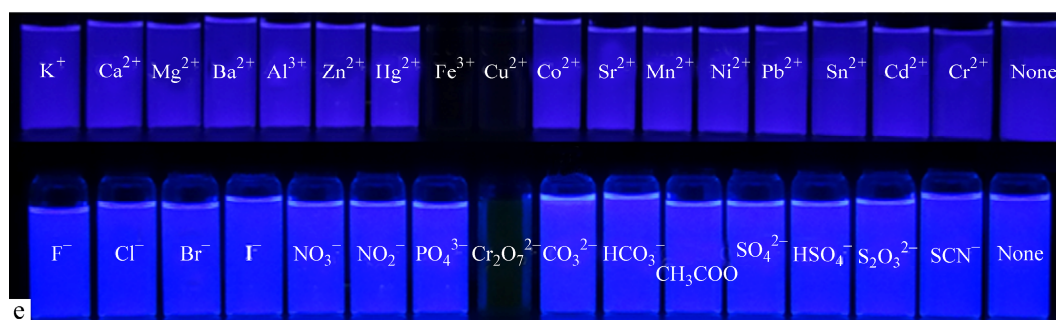


Fig. 8 Fluorescence quenching efficiencies of P9FG (2.0×10^{-7} mol·L $^{-1}$ in repeat units) in the presence of various metal cations (a), anions (b), UV-Vis spectra of P9FG with metal ions (c) and anions (d) (each 1.0×10^{-3} mol·L $^{-1}$), and the color changes under 365 nm UV light (e) in the mixed ethanol/water system (1:1, V/V)

As shown in Fig. 9(A1), the addition of Fe^{3+} immediately leads to a significant fluorescence quenching of the P9FG emission. In addition, the relationship between fluorescence intensity (I) and the Fe^{3+} concentration of the fabricated sensor is shown in Fig. 9(A2). Obviously, I gradually decreased with increasing Fe^{3+} , revealing that this method was suitable for detecting the unknown content of Fe^{3+} . $\lg I$ versus $\lg[\text{Fe}^{3+}]$ depicts the relationship between the common logarithm of I ($\lg I$) and the common logarithm of Fe^{3+} . The $\lg I$ versus $\lg[\text{Fe}^{3+}]$ graph in Fig. 9(A2) revealed that there was a good linearity from 4.0×10^{-11} mol·L $^{-1}$ to 1.6×10^{-7} mol·L $^{-1}$ ($y_1 = 2.8924 - 0.0128x_1$ ($R_1^2 = 0.9755$)) and from 1.6×10^{-7} mol·L $^{-1}$ to 1.6×10^{-3} mol·L $^{-1}$, ($y_2 = 4.5377 - 0.266x_2$ ($R_2^2 = 0.9883$)).

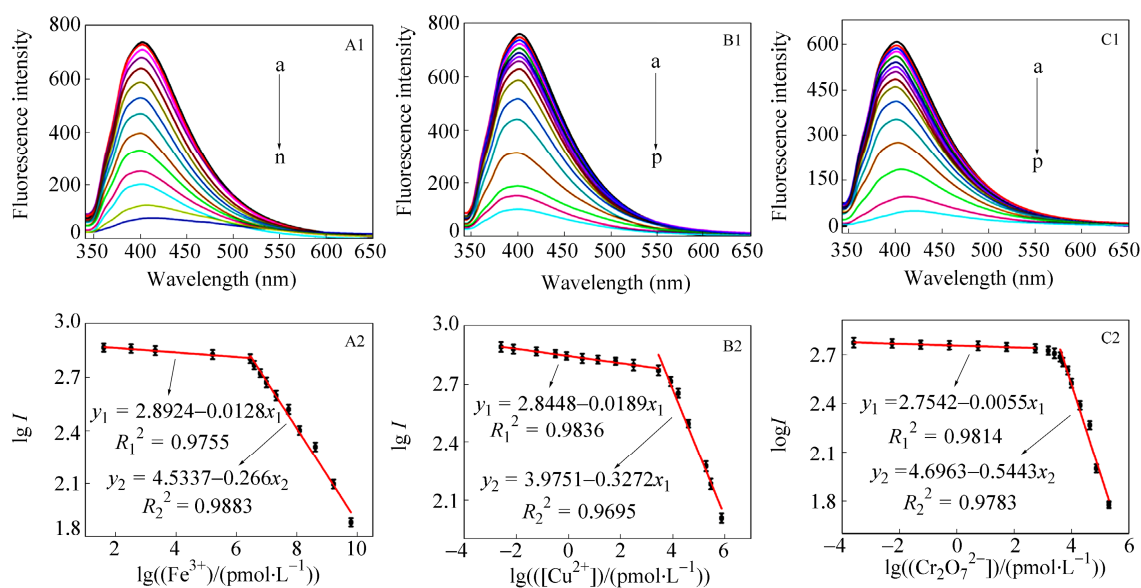


Fig. 9 (A1) Fluorescence emission spectra of P9FG (2.0×10^{-7} mol·L $^{-1}$ in repeat units) with successive addition of Fe^{3+} (a: blank, b–n: 4.0×10^{-11} – 1.6×10^{-3} mol·L $^{-1}$), and (A2) the $\lg I$ of P9FG versus the concentrations of $\lg(\text{Fe}^{3+})$; (B1) Fluorescence emission spectra of P9FG (2.0×10^{-7} mol·L $^{-1}$ in repeat units) in the presence of different concentrations of Cu^{2+} (a: blank, b–p: 2.0×10^{-12} – 3.2×10^{-4} mol·L $^{-1}$), and (B2) the linear range of $\lg I$ versus the $\lg(\text{Cu}^{2+})$; (C1) fluorescence emission spectra of P9FG (1.7×10^{-7} mol·L $^{-1}$ in repeat units) in the presence of different concentrations of $\text{Cr}_2\text{O}_7^{2-}$ (a: blank, b–p: 2.0×10^{-13} – 1.65×10^{-4} mol·L $^{-1}$) and (C2) plots of the $\lg I$ as a function of $\text{Cr}_2\text{O}_7^{2-}$ concentrations (All of them were carried in the mixed ethanol/water system (1:1, V/V)).

The limit of detection (LOD) was calculated using the following equations^[54]:

$$\text{LOD} = 3 s/m$$

where s is the standard deviation of the lowest concentration of the linearity range and m is the slope of linear equation in Fig. 9(A2). The detection limit was found to be $1.3 \times 10^{-11} \text{ mol}\cdot\text{L}^{-1}$. Similarly, Cu^{2+} and $\text{Cr}_2\text{O}_7^{2-}$ were also presented in Fig. 9(B1) and Fig. 9(C1), they displayed a good linear range from $2.0 \times 10^{-12} \text{ mol}\cdot\text{L}^{-1}$ to $2.3 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ and $2.3 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ to $3.2 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ with a detection limit of $0.6 \times 10^{-12} \text{ mol}\cdot\text{L}^{-1}$ ($S/N = 3$) for Cu^{2+} and from $2.0 \times 10^{-13} \text{ mol}\cdot\text{L}^{-1}$ to $1.2 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ and $1.2 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ to $1.65 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ with a detection limit of $0.6 \times 10^{-13} \text{ mol}\cdot\text{L}^{-1}$ for $\text{Cr}_2\text{O}_7^{2-}$. Obviously, these results indicated that P9FG possessed specific recognition ability towards Fe^{3+} , Cu^{2+} and $\text{Cr}_2\text{O}_7^{2-}$.

Ultraviolet sensing of P9FG

The UV spectroscopy of P9FG with different ions was monitored for studying the selectivity and interaction. Three different absorption bands of Fe^{3+} , Cu^{2+} (Fig. 8C) and $\text{Cr}_2\text{O}_7^{2-}$ (Fig. 8D) with different intensities in the mixed ethanol/water system (1:1, V/V) were presented. The absorption maximum of P9FG was exhibited at 328 nm, and the absorbance reduced after the addition of Cu^{2+} (Fig. 8C). The absorbance of P9FG decreased linearly with increasing Cu^{2+} (Fig. 10B1) concentrations in the range from $3.3 \times 10^{-7} \text{ mol}\cdot\text{L}^{-1}$ to $1.8 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ (Fig. 10B2), indicating that P9FG could use as a turn-off ultraviolet sensor for the detection of Cu^{2+} . However, the absorbance of P9FG increased upon adding Fe^{3+} (Fig. 8C) or $\text{Cr}_2\text{O}_7^{2-}$ (Fig. 8D) and displayed a linear relationship from $3.0 \times 10^{-7} \text{ mol}\cdot\text{L}^{-1}$ to $8.2 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ (Fig. 10B1 and Fig. 10B2) for Fe^{3+} and from $3.0 \times 10^{-7} \text{ mol}\cdot\text{L}^{-1}$ to $2.3 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ (Fig. 10C1 and Fig. 10C2) for $\text{Cr}_2\text{O}_7^{2-}$, respectively. These results revealed P9FG as a turn-on ultraviolet sensor for the detection of Fe^{3+} or $\text{Cr}_2\text{O}_7^{2-}$. Moreover, the aforementioned three ions could be easily distinguished from UV spectroscopy.

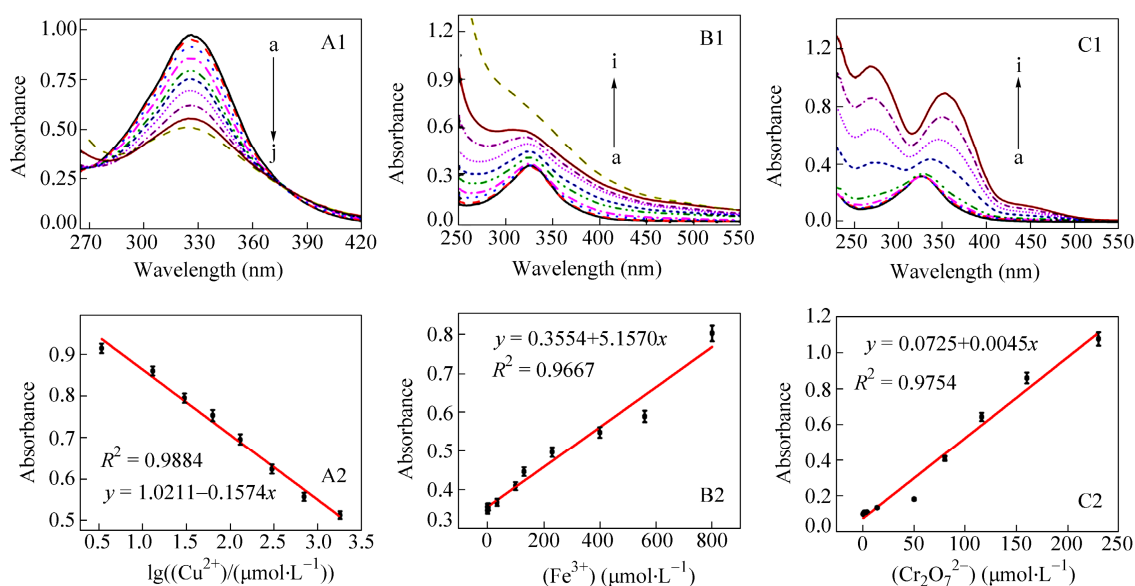


Fig. 10 (A1) UV-Vis experiments of P9FG ($6.0 \times 10^{-7} \text{ mol}\cdot\text{L}^{-1}$ in repeat units) with Cu^{2+} (a: blank, b–j: 3.3×10^{-7} – $1.8 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$) and (A2) the absorbance of P9FG versus the concentration of Cu^{2+} ; (B1) UV-Vis experiments of P9FG ($2.0 \times 10^{-7} \text{ mol}\cdot\text{L}^{-1}$ in repeat units) with Fe^{3+} (a: blank, b–j: 3.0×10^{-7} – $8.2 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$), and (B2) the absorbance of P9FG versus the concentration of Fe^{3+} ; (C1) UV-Vis experiments of P9FG ($2.0 \times 10^{-7} \text{ mol}\cdot\text{L}^{-1}$ in repeat units) with $\text{Cr}_2\text{O}_7^{2-}$ (a: blank, b–i: 3.0×10^{-8} – $2.3 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$), and (C2) the absorbance of P9FG versus the concentration of $\text{Cr}_2\text{O}_7^{2-}$ (All of them were carried in the mixed ethanol/water system (1:1, V/V), respectively.)

In addition, other amino acid functionalized polyfluorenes like poly(Fmoc-L-histidine), poly(Fmoc-L-serine) and poly(Fmoc-L-proline) presented fluorescent and ultraviolet responses of different ions, which indirectly indicated that amino acid side chain groups were not cleaved from polyfluorene backbone in mixed electrolytes of boron trifluoride diethyl etherate and dichloromethane.

CONCLUSIONS

In this work, P9FG was facilely synthesized by the direct electropolymerization of monomer 9FG in DCM/BFEE system. A series of characterizations such as ^1H -NMR spectra, FTIR spectra, and XPS spectra were carried out to confirm that the site for polymerization occurred at C_2 and C_7 positions of 9FG, and the side chain were not cleaved from polyfluorene backbone. P9FG displayed a good thermal stability and optical properties. Moreover, P9FG could easily realize fluorescent or ultraviolet detection of Fe^{3+} , Cu^{2+} and $\text{Cr}_2\text{O}_7^{2-}$ in combination with fluorescence and UV spectra responses. The resulting P9FG will provide a promising platform for optical sensing applications.

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