

AN ELECTROCHEMICALLY PREPARED SKY-BLUE LIGHT EMITTING ETHER FUNCTIONALIZED POLYFLUORENE AS CHEMOSENSOR FOR METAL IONS*

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Abstract Synthesis and electrochemical polymerization of 9,9-bis(2-(2-(2-methoxy ethoxy)ethoxy)ethyl)-fluorene (EO-F) into poly[9,9-bis(2-(2-(2-methoxy ethoxy)ethoxy)ethyl)-fluorene] (EO-PF) films are reported. The boron trifluoride diethyl etherate electrolyte enables facile preparation of EO-PF films at lower potential compared to LiClO₄/MeCN and the electrochemical polymerizations are discussed. The EO-PF shows good electrochemical behavior and can be dissolved in solvents such as DMSO and THF. The solubility of EO-PF in THF is 2 mg·mL⁻¹ and the number average molecular weight is 35300 with a polydispersity index of 1.65. The side chains on C₉ position of the monomer maintain unchanged after electrooxidation into corresponding polymer. The EO-PF dissolved in THF under 365 nm ultraviolet light is sky blue light emitting with the Commission Internationale de L'Eclairage-CIE coordinates of (0.19, 0.15). The electropolymerized EO-PF is used for the first time in chemosensing metal ions, demonstrating fluorescence quenching for Mn²⁺ and Fe³⁺ while fluorescence enhancement for Cr⁶⁺ ions.

Keywords: 9,9-Bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-fluorene; Boron trifluoride diethyl etherate; Chemosensory response; Electrochemical polymerization.

INTRODUCTION

Polyfluorenes (PFs) are an attractive class of conjugated polymers used in light emitting devices^[1, 2], field effect transistors^[3] and lasers^[4]. Efforts have been made on functionalization of C₉ position of fluorene that engender many derivatives with tunable physicochemical properties. Among them, the alkyl substitution at the C₉ position of PF provides this class of polymer good solubility toward optoelectronic and chemosensory application. Sun *et al.* have fabricated a white light emitting electrochemical cell (WLEC) based on a lithium salt doped PF with ethylene oxide side chains as a promising solid state lighting device^[5]. Pei *et al.* and Yu *et al.* pointed out that the poly(1,4-phenylene) as the conjugated backbone of ether functionalized PF facilitated transporting electrons and holes, while the two ethylene oxide moieties promoted ion transport^[1, 6]. These electrochemical characteristics of ether functionalized PF allow for its future application as a polyelectrolyte in LEC.

PF with C₉ position modified by different substitutes can serve as fluorescence chemosensor for detecting heavy metal ions in water body and living tissue. Theoretically, chemical signals can be produced due to the selectivity of recognition moieties for metal ions upon the binding interaction, the PF conjugated backbone as the transducer converts and amplifies the signals into changes in luminescent quenching or enhancement of fluorophore^[7]. For example, Chen *et al.* reported a poly(*p*-phenyleneethynylene) functionalized with triethylene

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glycol monomethyl ether as sensitive to Li^+ and Na^+ ions^[8]. More interestingly, Yu *et al.* investigated the electroluminescence of a crown ether functionalized PF and the revealed its specific selectivity of transition metals such as Fe^{3+} and Ru^{3+} ions, showing its candidacy for both optoelectronic material and chemosensory probe^[9].

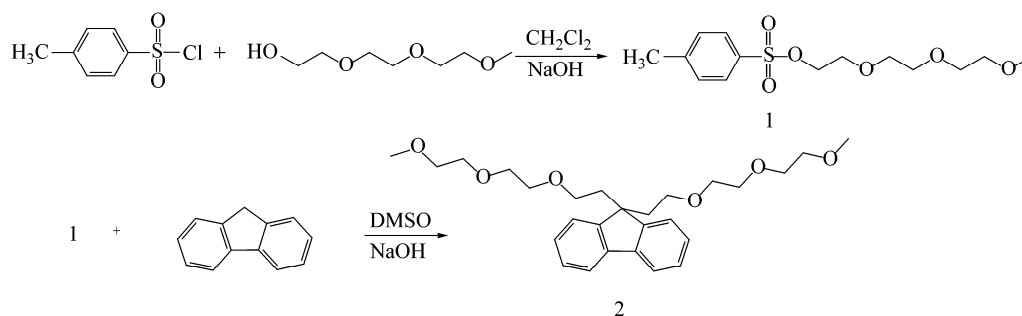
As soluble substituted PFs are generally synthesized *via* Suzuki, Yamamoto and Stille coupling reactions^[10], other routes for synthesis of conjugated polymers are in exploration toward functional extension. In particular, electrochemical polymerization of aromatic monomers in boron trifluoride diethyl etherate (BFEE) has been numerous reported and considered as a facile and alternative method for depositing luminescent layers in organic electronic devices^[11–13]. The BFEE system has been proved to be a catalytic medium in electrosynthesis of PF derivatives at a low potential due to the interactions between the middle strong Lewis acid (BFEE) and the aromatic rings^[14]. In this regard, BFEE serves as both the solvent and supporting electrolyte, and no other supporting electrolyte is needed^[15]. To date, electrochemical synthesis of organic soluble PF derivatives such as poly(fluorene-9-acetic acid) and poly(9,9-dichlorofluorene) with moderate molecular weight (around 3000) have been investigated by Nie *et al.*^[16, 17]. The polymers by one-step preparation from this electrolyte showed good redox behavior, optical properties and high fluorescence quantum yields^[14]. Moreover, doped and dedoped process of CP films can be observed as the redox states of conjugated polymers (CP) subject to potentiodynamic scanning.

The authors have been studying aromatic monomers synthesis and electrochemical polymerization into corresponding conjugated polymers for electrochemical applications^[18–21]. In this article, 9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-fluorene (EO-F) is electrochemically polymerized in BFEE electrolyte, the resulting polymer electrochemical properties, UV-Vis absorption properties and photoluminescent (PL) properties are described and the structure is also discussed. The chemosensing responses of the EO-PF THF solution to metal ions are discussed. To the best of our knowledge, this is the first report about electrochemical method prepared poly[9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-fluorene] (EO-PF).

EXPERIMENTAL

Materials

The monomer, 9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-fluorene (EO-F), was synthesized as described in literature^[22], and the synthetic route is shown in Scheme 1. Fluorene (commercial with purity over 99%), triethylene glycol monomethyl ether ($\text{C}_7\text{H}_{16}\text{O}_4$, Sigma-Aldrich), toluene-4-sulfonyl chloride, dichloromethane, ethyl acetate, dimethyl sulfoxide (DMSO), tetrahydrofuran (THF) and sodium hydroxide (NaOH) of analytical grade were purchased from Sinopharm Chemical Co. Ltd and used as received. Acetonitrile (ACN, Sinopharm Chemical Co. Ltd) and boron trifluoride diethyl etherate (BFEE, Aladdin Reagent) were distilled before use. Deuterated chloroform (CDCl_3 , Aladdin Reagent) were stored at 0 °C before use. Lithium perchlorate (LiClO_4 , Aladdin Reagent) dried at 80 °C for 12 h before use. The anhydrous sulphate salts of Mn^{2+} , Fe^{3+} , Na^+ , Cu^{2+} , Ni^{2+} , Mg^{2+} and Cr^{6+} are all purchased from Sinopharm Chemical Co. Ltd.



Scheme 1 Synthetic route of 9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-fluorene monomer

Synthesis of EO-F Monomer

Synthesis of 2-(2-(2-methoxyethoxy)ethoxy)ethyl-4-methyl benzenesulfonate (1)

To a well stirred solution of toluene-4-sulfonyl chloride (0.05 mol, 9.53 g) in CH_2Cl_2 (100 mL), triethylene glycol monomethyl ether (0.05 mol, 8.21 g) was added dropwise and the mixture was kept in ice-water bath. NaOH (1 mol, 40.12 g) was added in small amounts under vigorous stirring for 3 h at 0 °C, then CH_2Cl_2 and ice-water (1:1 in volume) was added. After stirring for 1 h, the NaOH was well dissolved, the organic phase was obtained and washed with water, dilute HCl solution and dried over MgSO_4 . The pure 2-(2-(2-methoxyethoxy)ethoxy)ethyl-4-methylbenzenesulfonate (96.3% yield) was obtained by concentration under reduced pressure.

Synthesis of 9,9-bis(2-(2-(2-ethoxyethoxy)ethoxy)ethyl)-fluorene (2)

The intermediate product (0.05 mol, 15.21 g) and fluorene (0.025 mol, 4.16 g) were dissolved in DMSO (50 mL) under stirring to a homogeneous solution and heated to 70 °C, then aqueous NaOH (50 wt%, 75 mL) was added dropwise over 30 min. The mixture was kept at 70 °C and under strong stirring for 8 h before cooled down to room temperature. The organic layer was extracted with CH_2Cl_2 (3×100 mL) and the combined fractions were washed with water, dilute HCl solution and dried over MgSO_4 . The crude product was purified by silica gel chromatography, with mixed CH_2Cl_2 and ethyl acetate (3:1 in volume) as eluent. The final product was concentrated by reduced pressure distillation to remove solvent (10.21% yield).

$^1\text{H-NMR}$ (650 MHz, CDCl_3), δ : 7.61(d, 2H; Ar H), 7.34(d, 2H; Ar H), 7.24(m, 4H; Ar H), 3.41(t, 4H; CH_2), 3.35(t, 4H; CH_2), 3.31(t, 4H; CH_2), 3.26(d, 6H; CH_3), 3.22(t, 4H; CH_2), 2.54(t, 4H; CH_2), 2.26(t, 4H; CH_2).

Methods

Electrochemical polymerization and examinations were performed with three-electrode configuration in a one-compartment cell controlled by computer. The working and counter electrodes were glass carbon electrode and platinum rod with diameters of 4 mm and 0.5 mm, respectively. The glass carbon electrode was carefully polished with diamond paste, ultrasonically washed by distilled water and acetone successively before each use. All potentials were referred to Ag/AgCl/3.5 mol/L KCl. All solutions were deaerated by a dry nitrogen stream and maintained a slight nitrogen overpressure during experiments. The as-prepared EO-PF films were washed by distilled water repeatedly to remove the electrolyte. Before spectral characterizations, the polymers were dedoped by soaking in 25% ammonia for 24 h then washed repeatedly with distilled water and they were dried at 60 °C for 12 h.

Instrumentation and Characterization

The $^1\text{H-NMR}$ spectrum was conducted at room temperature on a Bruker Avance III NMR spectrometer operating at a 1 H frequency of 600 MHz, CDCl_3 and d_6 -DMSO were used to dissolve EO-F and the resulting EO-PF respectively. The cyclic voltammetry (CV) tests were performed on the electrochemical workstation (Lanlike LK9805Z). FTIR spectra were recorded by using a Bruker Tensor 27 spectrometer with reagent grade KBr pellets. The molecular weights of polymer were determined by GPC (Waters) using polystyrene standards and THF as eluent. UV-Vis absorption and photoluminescent spectra for dedoped EO-PF films were performed with ultraviolet visible spectrophotometer (UV-Vis, Hitachi-3010) and Fluorolog-3 spectrofluorometer (Jobin-Yvon) respectively. Solutions for PL quenching are THF/ H_2O (9/1 in volume) containing different concentrations of sulfate salts.

RESULTS AND DISCUSSION

Synthesis and Electrochemical Polymerization

The general synthetic route toward monomer (9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-fluorene) is outlined in Scheme 1. $^1\text{H-NMR}$ spectrum of the monomer is shown in Fig. 1, chemical shifts from *ca.* $\delta = 3.5$ to 2.1 are assigned to the polar 2-(2-(2-methoxyethoxy)ethoxy)ethyl side group. The chemical shifts at 7.19, 7.22, 7.34 and 7.61 can be ascribed to C_2 (C_7), C_3 (C_6), C_1 (C_8), C_4 (C_5) protons in fluorene^[16]. And $^1\text{H-NMR}$ of the resulting polymer is reflected in Fig. 2, chemical shifts from *ca.* $\delta = 4.1$ to 2.6 are assigned to the polar 2-(2-(2-

methoxyethoxy)ethoxy)ethyl side group, and chemical shifts at 7.34, 7.58, 7.81 can be assigned to protons of C₃ (C₆), C₁ (C₈), C₄(C₅) protons in PF. As shown, some peaks became broader after electropolymerization and most of the peaks moved to lower field, probably due to the increased conjugation length in the EO-PF main chain^[14]. The peak at 7.19 is attributed to the terminal proton of the polymer as little shift in field compared to the relative peak of the monomer. In this case, the EO-PF is mainly of C₂, C₇ linkage. Moreover, the chemical shifts at $\delta = 3.4$ are possibly ascribed to residual BFEE electrolyte. The dedoped EO-PF can be peeled off from the electrode and soluble in solvents such as THF and DMSO. The solubility of EO-PF in THF was *ca.* 2 mg/mL, and the number average molecular weight determined by GPC was 35300 with polydispersity index of 1.65.

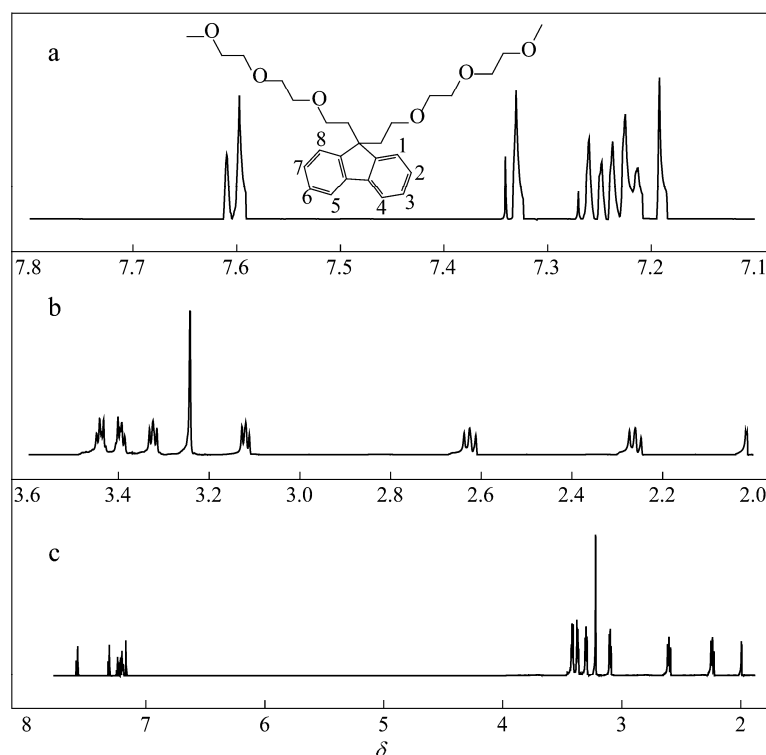


Fig. 1 ¹H-NMR spectra of EO-F monomer

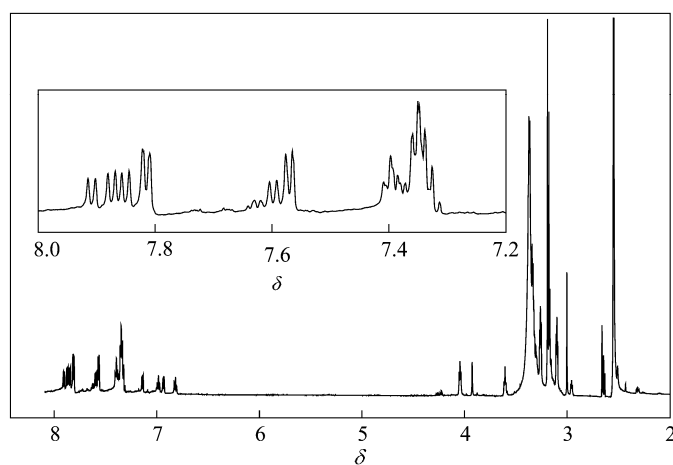


Fig. 2 ¹H-NMR spectra of electrochemically prepared EO-PF

Typical CVs of 50 mmol/L EO-F monomer oxidation in pure BFEE and 0.1 mol/L LiClO₄/ACN for comparison are shown in Fig. 3. It is noted that the employed electrolytes were electrochemically silent in the whole potential range. Initially, the pure BFEE turned from colorless to green as the EO-F monomer dissolved in it, while the color of LiClO₄/ACN electrolyte with the monomer stayed unchanged. As shown in Fig. 3(b), the monomer oxidation peak in BFEE can clearly be seen at 1.21 V versus Ag/AgCl lower than that in 0.1 mol/L LiClO₄/ACN (1.87 V versus Ag/AgCl). And the increase in the redox wave currents per cycle indicated that the amount of polymer deposited on the glass carbon electrode was increasing^[12, 15]. However, in neutral ACN electrolyte (Fig. 3a), the anodic current wave decreased with the increase of CV scan numbers that indicated no polymer was formed^[13]. Pei *et al.* speculated that steric interaction between ethylene oxide side groups twisted the conjugated fluorene unit from planar configuration^[1]. For this reason, the oxidation of the monomer in ACN is presumably inhibited by the side group steric hindrance.

Shi *et al.* investigated that BFEE existed in diethyl ether as a polar molecule [(C₂H₅)₃O]⁺BF₄⁻^[23]. Therefore, the polarized [(C₂H₅)₃O]⁺ ion may complex with $-(CH_2CH_2O)-$ groups that facilitated the formation of π -complexes between the monomer and the Lewis acid. The resonance of the aromatic ring can be reduced and the stability of radical cations synchronously can be enhanced^[12–14]. Based on this discussion, the oxidation potential was lowered down in BFEE compared with LiClO₄/ACN. Bazzoui *et al.* pointed out that the decreased oxidation potential may facilitate the formation of high quality conducting polymer^[24]. Therefore in this case, BFEE electrolyte is a good medium for the electrosynthesis of EO-PF films.

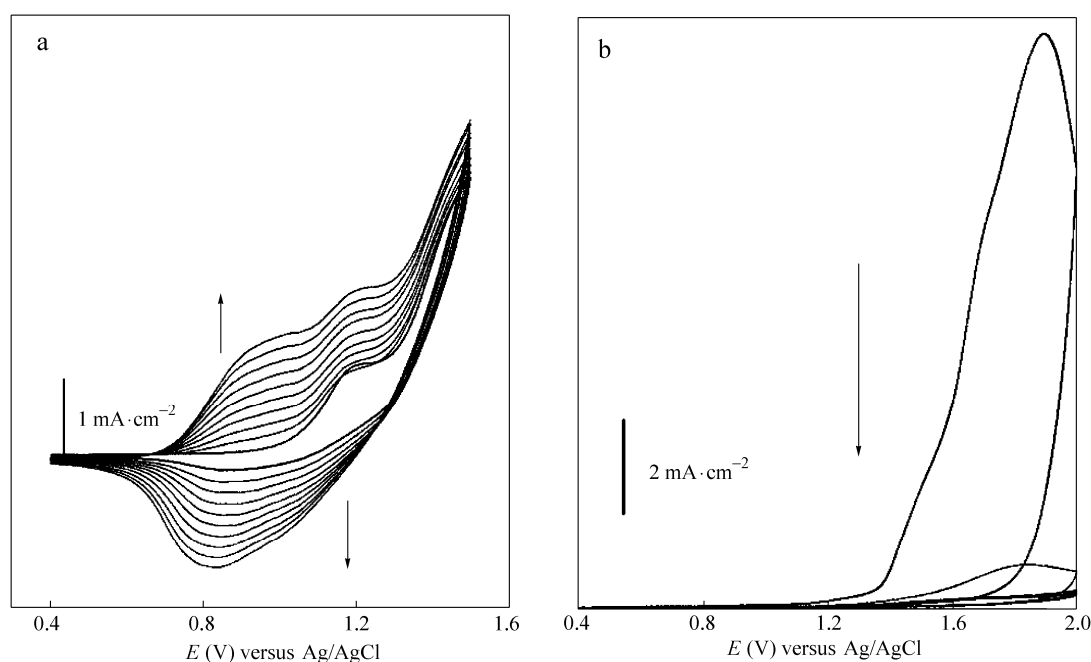


Fig. 3 Cyclic voltammograms of 50 mmol/L EO-F monomer anodic oxidation polymerization in (a) 1 mol/L LiClO₄/ACN, and (b) BFEE electrolytes, at the scanning rate of 20 mV·s⁻¹

As the CV scan of EO-F monomer in BFEE continued (Fig. 3b), the color of electrolyte grew into dark green that indicated the oligomers were dissolved in this medium^[13, 25]. At the same time, a green film, EO-PF, was formed on the glass carbon electrode. Furthermore, the polymer in BFEE can be reduced and oxidized between 0.78 and 0.91 V versus Ag/AgCl. And the broad redox waves were ascribed to a wide distribution of conjugated chain length^[26]. The prepared EO-PF film appeared yellow color after dedoping.

Electrochemistry

The electrochemical behavior of the EO-PF film deposited potentiodynamically from BFEE was examined in

pure BFEE (Fig. 4) for deeper insight into the redox process and stability of the polymer film.

As shown in Fig. 4(a), broad anodic and cathodic peaks can be observed in the steady state cyclic voltammograms. Besides, two couples of electrochemical redox peaks (O_1 , R_1) and (O_2 , R_2) are well separated. Obviously, the variation of peak current densities as a function of the scan rates is linear and the correlation coefficients are given, representing the surface bound redox process and non-diffusion controlled behavior of the polymer^[27]. Alkan *et al.* speculated that $[\text{BF}_3\text{OH}]\text{H}^+$ species were in BFEE and the BF_3OH^- ion behaved as the dopant^[28]. The first redox reaction with (E_a-E_c) of 0.28 V can be related to π electron exchange in PF backbone. And the second redox process at the higher potential, a wider (E_a-E_c) of 0.39 V was needed to exchange doping ion and electron between the polymer and the electrolyte^[29, 30].

The stability of conducting polymer is one of the primary parameters for the application in polymeric and organic optoelectronics^[31]. The stability and redox activity of EO-PF film was also investigated in pure BFEE, as shown in Fig. 4(b). The polymer modified glass carbon electrode was cycled between 0 V and 1.5 V for 100 times at a scan rate of 20 $\text{mV}\cdot\text{s}^{-1}$. The EO-PF films could be cycled repeatedly between the conducting (oxidized) and insulating (neutral) states. No significant decrease in currents was observed till the 50th cycle while the first redox couple started to disappear. It is probably because the degradation of the polymer film deriving from conjugated structural transformation after long term cycling and switching on/off between redox states.

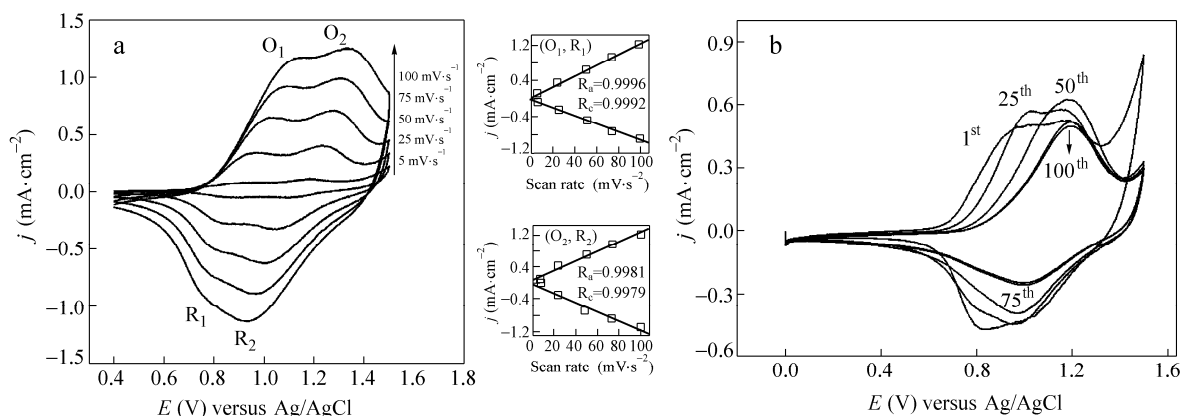


Fig. 4 (a) The electrochemical investigation of EO-PF film on GC electrode in pure BFEE at various scanning rates and the linear relationship of redox peaks current densities (O_1 , R_1) and (O_2 , R_2) of EO-PF in BFEE against scanning rates, and (b) the electrochemical cyclability of EO-PF film scanned 100 cycles in BFEE at potential scan rate of 25 $\text{mV}\cdot\text{s}^{-1}$

FTIR Analysis

Vibrational spectra have been widely used to interpret the structural transformation of aromatic monomers into corresponding conjugated polymers^[12–17]. Therefore, the FTIR spectra of dedoped EO-PF and EO-F are shown in Fig. 5(a) and 5(b), respectively. The absorption peaks at 740 cm^{-1} and 769 cm^{-1} in Fig. 5(b) belong to the characteristic in-plane C—H bending modes of 1,2-disubstituted benzene ring of fluorene. And the new peak at about 850 cm^{-1} is attributed to out-of-plane C—H bending modes of 1,2,4-trisubstituted benzene ring^[13, 16, 17]. In Fig. 5(b), the sharp peaks at 1109 cm^{-1} can be attributed to C—O—C asymmetric stretching mode^[32]. And the intensive band at 1450 cm^{-1} is assigned to the $-\text{CH}_2-$ deformation vibration of side chains^[33]. These bands shifted to high wave numbers for dedoped polymer were probably due to the polar side chains as electron donating moieties and the increased conjugated length. Furthermore, the two couples of sharp peaks at 2857 cm^{-1} and 2927 cm^{-1} (Fig. 5a), 2873 cm^{-1} and 2925 cm^{-1} (Fig. 5b) can be ascribed to the aliphatic C—H stretching vibration of the alkyl ether moieties^[25]. These characteristic bands of alkyl ether indicate that the side chains maintained unchanged during the polymerization. Also, two wide bands at 3478 cm^{-1} and 3483 cm^{-1} are attributed to the existence of H_2O as the alkyl ether moieties are highly hygroscopic^[1, 34].

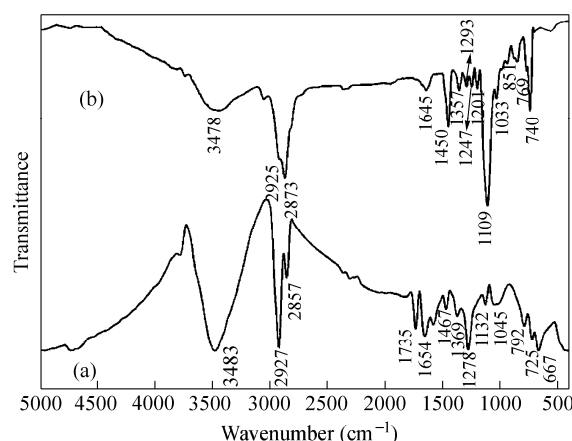


Fig. 5 FTIR spectra of (a) dedoped EO-PF film prepared from BFEE and (b) EO-F monomer

UV-Visible Absorption and PL Properties

The UV-Vis spectra of EO-PF as well as EO-F monomer were examined in THF, as shown in Fig. 6(a) and 6(b). The monomer (Fig. 6a) shows several absorptions mainly at 232 nm, 265 nm and 301 nm that are probably due to the π - π^* transition for the presence of fluorene unit^[13, 16, 17]. In comparison, a broad and red shifted absorption band in the spectrum of EO-PF means higher conjugated length than EO-F monomer. On the other hand, the EO-PF UV-Vis spectrum peaked at 338 nm with an onset wavelength of 397 nm, the band gap can be roughly estimated as 3.12 eV. And an intense blue light emitting can be observed for EO-PF in THF compared to the monomer in THF under 365 nm ultraviolet light (Fig. 6a and 6b insert).

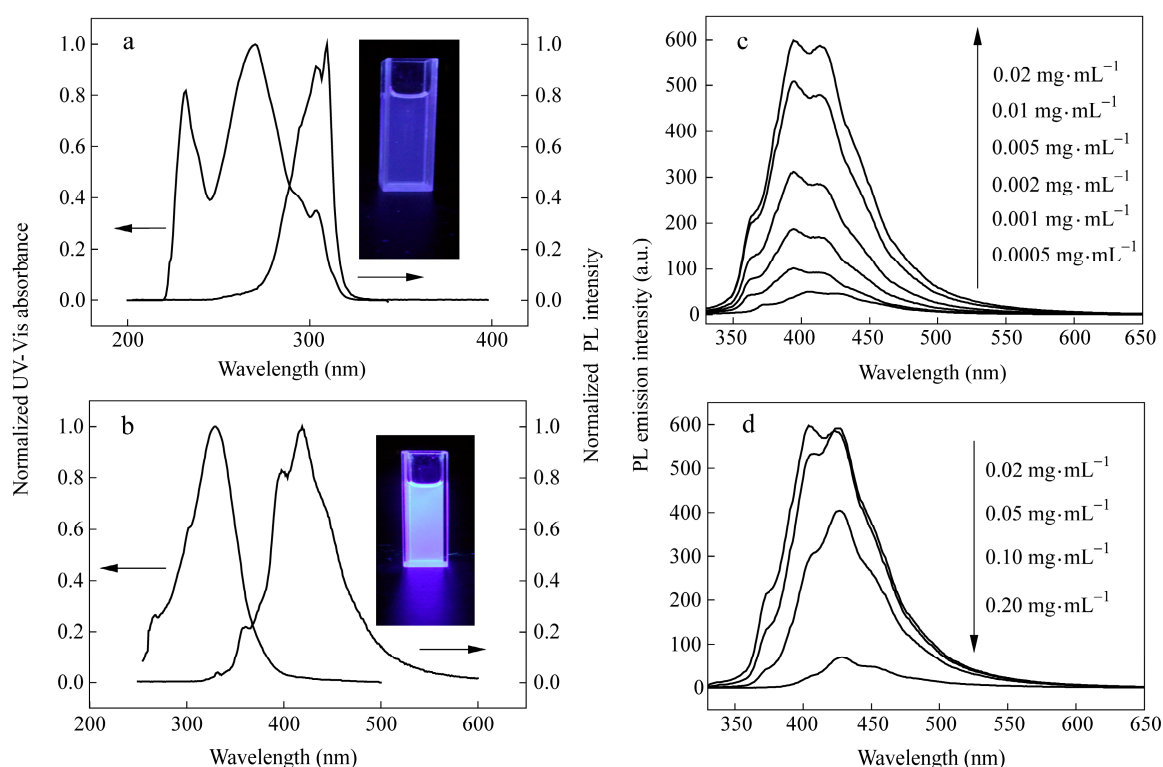


Fig. 6 UV-Vis absorption and PL spectra for (a) EO-F and (b) EO-PF dissolved in THF; And dependency of fluorescent emission intensity on the concentration of EO-PF in THF (c) and (d)

The PL spectra in Fig. 6(a) and 6(b) show the dedoped EO-PF and EO-F examined in THF under the excitation of 325 nm. In Fig. 6 (a), the main peak of absorption is at 265 nm while 302 nm for PL spectrum even both two curves tailed off to 310 nm, the bathochromic shift of PL spectrum can be found. As for Fig. 6(b), obvious peaks of emission spectra mainly locate at 397 nm and 424 nm, and peak width of half height is 69 nm for EO-PF. The CIE coordinates of EO-PF are (0.19, 0.15), indicating a sky blue color from the excited EO-PF within the blue light gamut. Besides, the red shifted emission peak can be ascribed to higher conjugated length of EO-PF, in well accordance with UV-Visible spectra^[12, 14]. This sky-blue color is promising for achieving a wide color gamut in displays and improving the quality of white light emitting devices^[35].

A dependency of fluorescent emission intensity on the concentration of EO-PF in THF is revealed in Fig. 6(c) and 6(d). As fluorophore concentrations increased from 0.0005 mg·mL⁻¹ to 0.02 mg·mL⁻¹ PL intensity increased, further increased EO-PF concentrations from 0.02 to 0.20 mg·mL⁻¹ led to a self-quenching effect and consequently weakening the fluorescent emission. Therefore, the PL intensity of EO-PF culminated in the concentration of 0.02 mg·mL⁻¹ in THF. The self-quenching is presumably on the fact that as the concentrations keep increasing, the decreased distance between fluorene fluorophores allows for interactions such as ground-state molecular association^[36], charge-electric energy transfer^[37], fluorescence resonance energy transfer (FRET)^[38] that result in decreased fluorescent intensity.

Chemosensory Properties

The electropolymerized EO-PF is a combination of ether groups as recognition moieties with conjugated backbone as excited states transducer. It renders amplified PL intensity variations in the presence of different metal ions^[7]. Therefore, the chemosensing responses of EO-PF (0.02 mg·mL⁻¹) in THF to metal ions are recorded by PL spectra as shown in Fig. 7. Obviously, the added water in EO-PF/THF solution slightly influences the PL intensity. Among these cations, Mn²⁺ and Fe³⁺ ions lead to the strongest PL quenching while Cr⁶⁺ results in the greatest fluorescence enhancement. And PL intensity variations against concentrations of Mn²⁺, Fe³⁺ and Cr⁶⁺ ions are given in Figs. 8(a), 8(b) and 8(c) respectively. The significant PL quenching in the presence of Mn²⁺ and Fe³⁺ suggests the high selectivity of EO-PF to the two ions^[8, 9]. The proximity between ether-bound metal ions and conjugated backbone engenders the photoexcited energy of conjugated backbone to transfer^[9, 37, 39]. In addition, the enhanced PL intensity is probably due to the inhibited internal charge-transfer process upon the binding of ether moieties and Cr⁶⁺ ions^[40], and this “turning on” fluorescence can be used to detect the hazardous Cr⁶⁺ ions.

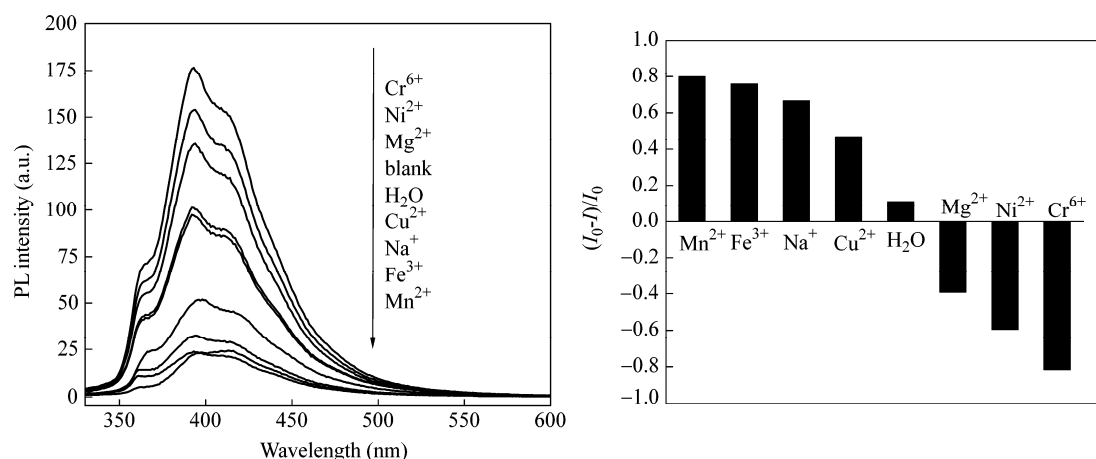


Fig. 7 PL response excited at 325 nm from EO-PF (0.02 mg·mL⁻¹) in THF/H₂O (9/1 in volume) solutions containing various metal ions at the concentration of 0.1 mmol/L (left); The PL response profile by adding different metal ions (right)

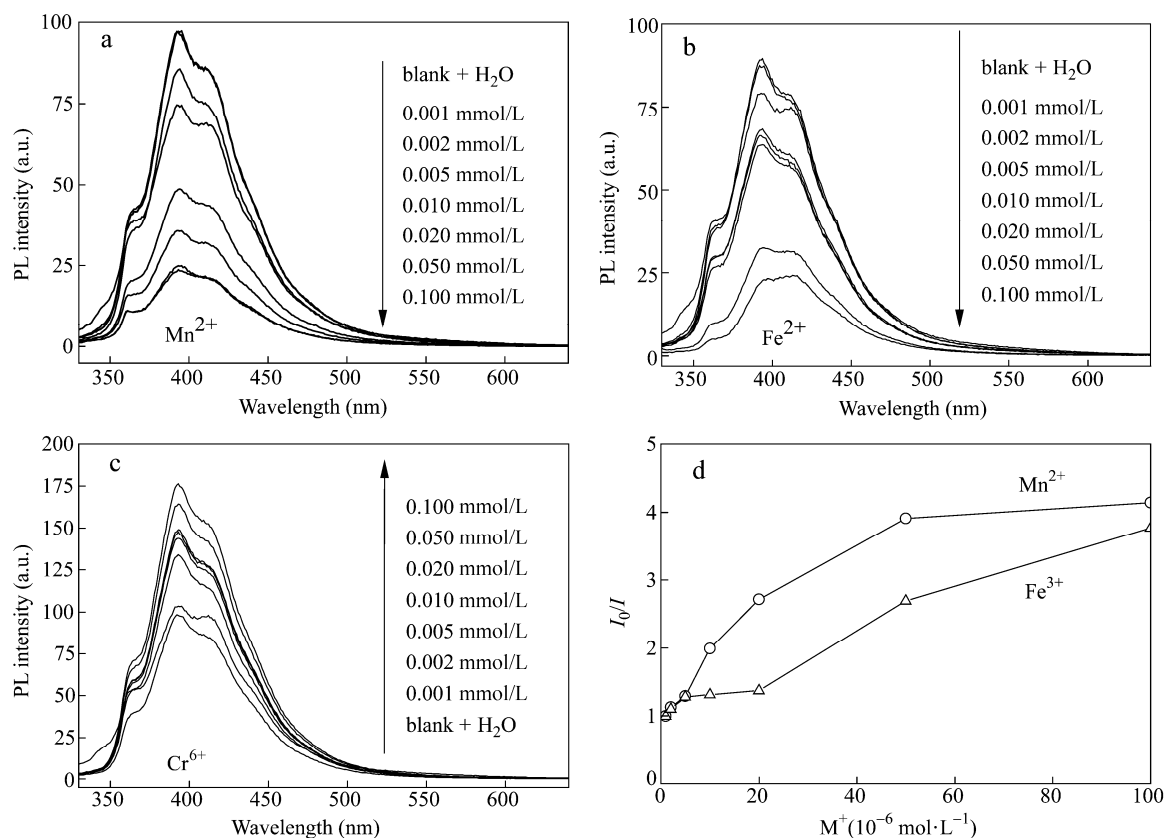


Fig. 8 PL responses excited at 325 nm from EO-PF ($0.02 \text{ mg} \cdot \text{mL}^{-1}$) in THF/ H_2O (9/1 in volume) solutions containing (a) Mn^{2+} , (b) Fe^{3+} and (b) Cr^{6+} ions at increased concentrations; And (d) Stern-Volmer plots for EO-PF PL quenching in the presence of Mn^{2+} and Fe^{3+} ions

The fluorescence quenching behaviors of EO-PF to Mn^{2+} , Fe^{3+} ions are described as Stern-Volmer plots in Fig. 8(d), a linear curved relationship can be observed, resembling a summation of two lines in different slopes. The quenching ratio increases steeply for Mn^{2+} ion in low concentrations but smooth in high concentrations, while the Fe^{3+} case appears conversely. Naga *et al.* proposed a plausible model for capturing metal ions by two ether moieties: interchain capturing for metal ions at low concentrations and intrachain capturing for metal ions at high concentrations^[41]. The modified Stern-Volmer equation is followed:

$$\frac{I_0}{I} = 1 + \{K_{\text{sv1}}(1-x) + K_{\text{sv2}}x\}[Q]$$

K_{sv1} , K_{sv2} are Stern-Volmer constants of the interchain capture, intrachain capture and x is ratio of the intrachain capture. The tangential slopes at $[Q] = 0$ and $100 \times 10^{-6} \text{ mol/L}$ of Mn^{2+} ion are set as K_{sv1} and K_{sv2} , respectively but converse case for Fe^{3+} ion. The K_{sv1} and K_{sv2} (M^{-1}) are calculated accordingly to be 9.2×10^4 , 4.6×10^3 for Mn^{2+} , and 3.3×10^4 , 2.9×10^4 for Fe^{3+} . The Stern-Volmer constants values of Mn^{2+} are larger than those of Fe^{3+} , indicating Mn^{2+} ion can be captured more efficiently by the ether moieties covalently linking on the C_9 position of PF.

CONCLUSIONS

9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-fluorene (EO-F) monomer was successfully synthesized and electrochemically polymerized into corresponding polymer (EO-PF) in BFEE. The obtained polymer exhibited electrochemical redox behavior and non-diffusion controlled process in pure BFEE. Decreased electrochemical

redox currents were observed on EO-PF subjected to potentiodynamic scanning. And the alkyl ether side chains maintained unchanged after electrochemical polymerization of EO-F monomer. The EO-PF was organic soluble and can be dissolved in solvents such as THF and DMSO. The solubility of EO-PF in THF was *ca.* 2 mg·mL⁻¹, the number average molecular weight was determined to be 35300 with the polydispersity index of 1.65. UV-Vis and PL spectra suggested that the soluble EO-PF was a sky blue light emitting material. The PL intensity dependence on EO-PF concentrations has been found and PL self-quenching happened when the concentration of EO-PF is over 0.02 mg·mL⁻¹ in THF. The fluorescence quenching for Mn²⁺ and Fe³⁺ was analyzed by a modified Stern-Volmer equation. The electrochemically prepared EO-PF can be used as luminescent probe in chemosensor for metal ions.

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