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Synthesis, characterization and photophysical properties of novel fluorene-based copolymer with pendent urea group: Fluorescent response for anions through H-bonding interaction

Linna Zhu, Chuluo Yang*, Wenjun Zhang, Jingui Qin

Department of Chemistry, Hubei Key Lab on Organic and Polymeric Optoelectronic Materials, Wuhan University, Wuhan 430072, PR China

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Abstract

A novel fluorene-based copolymer $\mathbf{P_1}$ with diphenyl urea as pendent group, as well as its analogous copolymer $\mathbf{P_2}$ without urea group for comparison, were synthesized by Suzuki-coupling reaction, and characterized by ^{1}H NMR, EA, IR and GPC. The polymers were brightly blue emissive in THF, DMF, or DMSO solution. Anion titration experiments carried out in THF indicate that the polymer $\mathbf{P_1}$ has good selectivity for fluoride ion, acetate ion, and dihydrogen phosphate ion, and the sensitivity and selectivity of $\mathbf{P_1}$ toward these anions come from the strong hydrogen-bond interaction between the anions and the urea group of the copolymer. This new system utilizing the strong luminescence property of the polyfluorene as reporter and the hydrogen-bond-forming ability of urea group may act as novel effective anions receptor and chemosensor.

Keywords: Polyfluorene; Urea; Fluorescent chemosensor

1. Introduction

Fluorescent sensors have been exploited a lot these years, due to their fast response, facility, intuitive and easy to handle properties. Recently, fluorescent sensors based on conjugated polymers (CPs) are attracting increasing attention because CPs have many advantages over small molecules, such as high light absorption ability, molecular wire effect, and good film forming property [1]. These good qualities make them potential materials in practical use. For example, Swager's group had accomplished excellent achievements in chemosensor by using side chain functionalized poly(phenylene ethynylene)s (PPEs) for detecting vapors of electron-accepting analytes, such as explosive TNT and DNT, as well as some electron-donating aromatic compounds [2]; Sun et al. had reported amplified fluorescence quenching of a conjugated poly(phenylene ethynylene) polymer compared to its model compound for detection of F^-, with 34-fold enhancement [3]. Leclerc's group had developed several functionalized polythiophenes system in both chemical and biological sensing [4]. Among the conjugated polymers, polyfluorene is an effective blue emission material, with high photoluminescence efficiency and favorable thermal stabilities [5]. However, so far they are mostly employed as luminescent host materials in polymeric light emitting diodes (PLEDs) [6]. Only in recent years, some work has been made in sensing materials in chemistry and biology [7,9,10]. With specifically designed detection groups, the polyfluorene derivatives may provide significant fluorescence change upon addition of certain analyzer. Bazan's and Wang's groups had made a great success in designing a series of biosensors based on cationic polyfluorenes, to detect nucleic acids, glucose, and some important biomolecules in life processes [8]. Pei et al. reported a polyfluorene derivative grafted imidazole as a chemosensor material for Cu^{2+} [9]; Wang et al. reported two polyfluorene derivatives with pendent phosphonate groups, and their emission were highly quenched by Fe^{3+} [10]. Whereas as a whole, research works based on functionalized polyfluorene as chemosensors is still rare, especially for detection of anions [11].

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* Corresponding author.
E-mail address: clyang@whu.edu.cn (C. Yang).

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As we know, except for metal ions, some anions play a very important role in many biological and chemical processes, thus the detection of them has been focal point of many research work [12]. As to the proper detection part, urea subunit and its analog thiourea are well-known functional groups for the designing of anion receptors [13], since they are ready to act as efficient hydrogen-bonding donors. Many anion-sensing systems with these functional groups have been explored. Nevertheless, most of them are based on small molecules, and the association constants are usually not high in nonpolar solvents [13]. In this paper, we designed and synthesized a novel fluorene-based copolymer with diphenyl urea as pendent group, as well as its analogous copolymer without the urea group for comparison. We hope that the interaction between the hydrogen donor urea group in the side chain and the hydrogen acceptor anions would change the electron structure of the polymer chain, and consequently affect the polymer fluorescence. The photophysical properties of the two copolymers and their fluorescent response toward anions will be discussed.

2. Experimental section

2.1. Materials

The 2,7-dibromofluorenone and 4,4′-(2,7-dibromo-9*H*-fluorene-9,9-diyl)dianiline were prepared according to the literature procedure [14,15]. 1,4-Phenyldiboronic acid and tetrakis-(triphenylphosphine)palladium were purchased from Acros. Aniline was distilled before use. Other materials were used directly without further purification unless otherwise stated.

2.2. General methods

The ^{1}H NMR and ^{1}C NMR spectra were recorded on a MECUYRVX300 spectrometer in $CDCl_3$ and 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 in THF. The number-average and weight-average molecular weights were estimated by using a calibration curve of polystyrene standards. FTIR experiments were carried out on Perkin Elmer spectrometer with KBr pellets. 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 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 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 (based on the moles of the repeated unit) in THF solution, and the anions were also in THF solution with the concentration of 10^{-3} M. UV and fluorescence titration were carried out by sequentially adding different quantities of each anion into the polymer solution. After stirring for 1 min, the spectra were recorded. The excitation wavelength was chosen at 360 nm, according to the maximum absorption wavelength.

*2.3. Synthesis of monomer **1***

A solution of 4,4′-(2,7-dibromo-9*H*-fluorene-9,9-diyl)dianiline (200 mg, 0.4 mmol) and phenylisocyanate (0.10 mL, 0.88 mmol) in dichloromethane was reacted at room temperature. During the reaction, an off-white solid came out. After 4 h, the resulting precipitate was filtered and washed with dichloromethane, and dried under vacuum. Yield: 195 mg, 66%.

^{1}H NMR (300 MHz, DMSO-d_6). δ (ppm): 8.71 (s, 2H), 8.65 (s, 2H), 7.93 (d, $J = 9.0$ Hz, 2H), 7.62 (t, $J = 7.5$ Hz, 4H), 7.42 (d, $J = 6.0$ Hz, 4H), 7.22 (t, $J = 7.8$ Hz, 4H), 7.37 (d, $J = 6.0$ Hz, 4H), 7.02 (d, $J = 6.0$ Hz, 4H), 6.94 (t, $J = 7.2$ Hz, 2H). ^{1}C NMR (300 MHz, DMSO-d_6). δ (ppm): 153.95, 153.13, 140.34, 139.40, 138.35, 138.05, 131.57, 129.34, 128.72, 123.58, 122.50, 121.95, 119.10, 118.79, 64.97. IR (KBr, cm^{-1}): 3328, 3053 (N–H stretching); 1663 (C=O stretching); 1600, 1544, 1496 (aromatic). Anal. Calcd. for $C_{39}H_{28}Br_2N_4O_2$: C, 62.92; H, 3.79; N, 7.53. Found: C, 63.50; H, 3.90; N: 7.08. ESI-MS: *m/z* 745.9 (M$^+$).

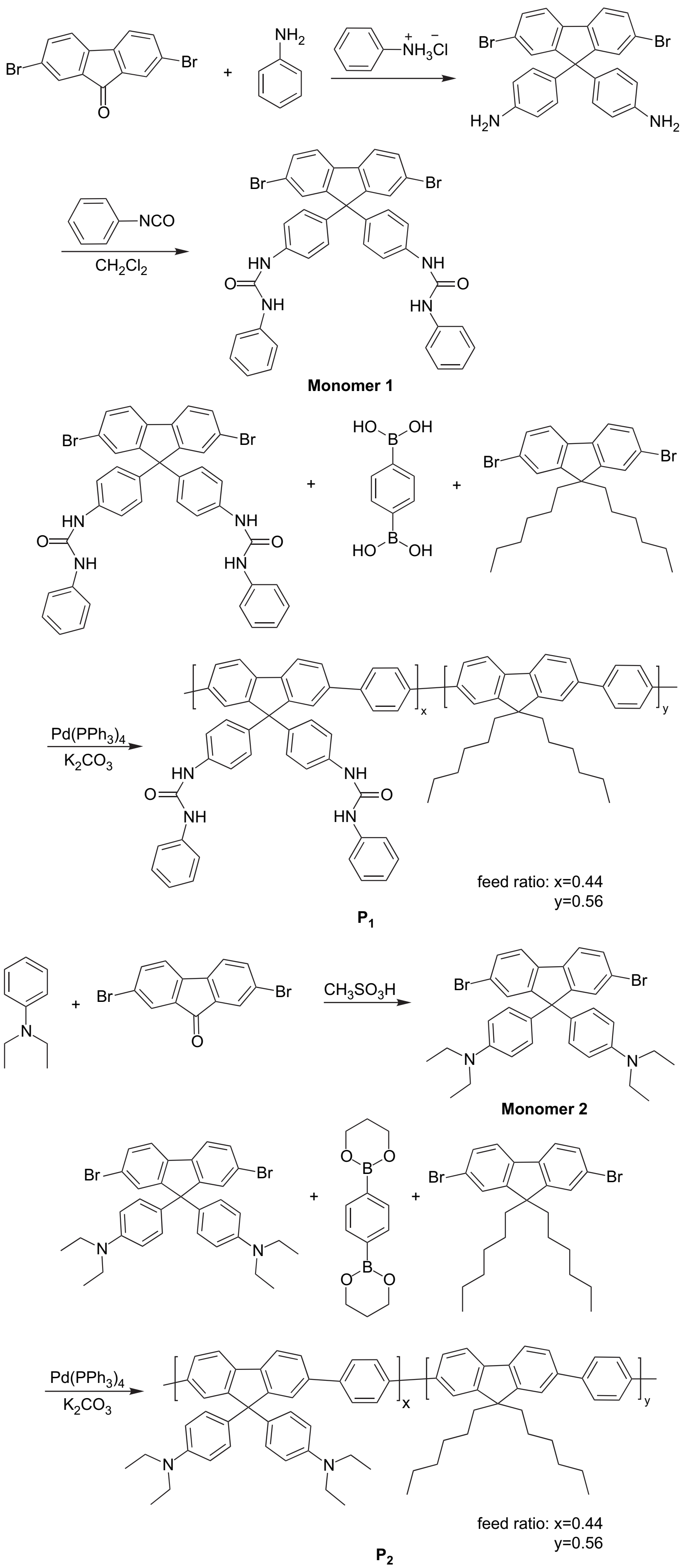
*2.4. Synthesis of monomer **2***

A mixture of *N,N*-diethylaniline (8.9 g, 60 mmol), 2,7-dibromofluorenone (1 g, 3 mmol), and methanesulfonic acid (0.3 g, 3.2 mmol) was stirring at 150 °C for 10 h. After cooling to room temperature, the reaction mixture was poured into saturated Na_2CO_3 solution, and extracted with $CHCl_3$. Then the organic layer was collected and washed with water, brine, and dried over anhydrous Na_2SO_4. After removing solvent, the product was finally purified by column chromatography using EA/PE (1:10, V/V) as eluent. The final product was gained as white solid. Yield: 1.5 g, 83%.

^{1}H NMR (300 MHz, $CDCl_3$). δ (ppm): 7.57 (s, 2H), 7.53 (d, $J = 6.0$ Hz, 2H), 7.44 (d, $J = 6.0$ Hz, 2H), 7.01 (d, $J = 9.0$ Hz, 4H), 6.55 (d, $J = 9.0$ Hz, 4H), 3.32 (q, $J = 12$ Hz, 8H), 1.15 (t, $J = 6.0$ Hz, 12H). ^{1}C NMR (300 MHz, $CDCl_3$). δ (ppm): 154.95, 146.89, 138.07, 131.08, 130.48, 129.62, 129.23, 121.84, 121.54, 111.56, 64.35, 44.44, 12.92. Anal. Calcd. for $C_{33}H_{34}Br_2N_2$: C, 64.09; H, 5.54; N, 4.53. Found: C, 64.09; H, 5.72; N: 4.32. ESI-MS: *m/z* 618.3 (M$^+$).

2.5. Synthesis of polymer P_1

To a solution of monomer **1** (100 mg, 0.134 mmol), 2,7-dibromo-9,9-dihexylfluorene (106 mg, 0.166 mmol), and 1, 4-phenylenediboronic acid (50 mg, 0.3 mmol), $Pd(PPh_3)_4$ (10 mg) in 6 mL of THF and 2 mL of aqueous potassium



feed ratio: x=0.44
y=0.56

feed ratio: x=0.44
y=0.56

Scheme 1. Synthesis of monomers **1** and **2**, and copolymers $\mathbf{P_1}$ and $\mathbf{P_2}$.

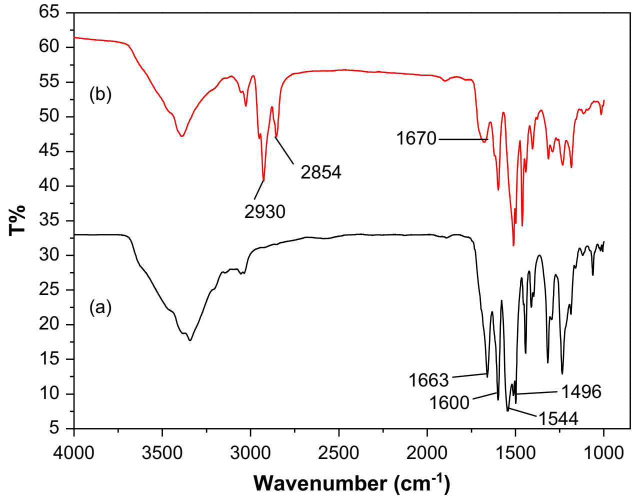


Fig. 1. FTIR spectra of monomer **1** (a) and **P$_1$** (b).

carbonate (2.0 M) were added. The above mixture was degassed for several minutes, and then stirred at 85 °C for 24 h. After cooling to room temperature, the resulting polymer was purified by reprecipitated in methanol for three times to afford **P$_1$** as a grayish green solid. Yield: 131 mg, 90%.

^{1}H NMR (300 MHz, DMSO-d_6). δ (ppm): 8.8–8.5 (br), 8.2–7.5 (br), 7.5–7.3 (br), 7.3–7.0 (br), 7.0–6.6 (br), 6.6–6.2 (br), 1.8–1.6 (br), 1.4–0.3 (br). IR (KBr, cm^{-1}): 3387, 3026 (N–H stretching); 2934, 2850 (C–H stretching); 1680 (C═O stretching); 1596, 1537, 1504 (aromatic). Anal. Calcd. for $C_{76}H_{68}N_4O_2$: C, 85.36; H, 6.41; N, 5.24. Found: C, 84.34; H, 5.79; N, 4.00.

2.6. Synthesis of polymer *P$_2$*

To a solution of monomer **2** (82.9 mg, 0.134 mmol), 2,7-dibromo-9,9-dihexylfluorene (81.7 mg, 0.166 mmol), and benzen-1,4-bis(boronic acid)-propane-1,3-diol diester (73.8 mg, 0.3 mmol), Pd(PPh$_3$)$_4$ (10 mg) in 6 mL of THF and 2 mL of aqueous potassium carbonate (2.0 M) were added. The above mixture was degassed for several minutes, and then stirred at 85 °C for 24 h. After cooling to room temperature, the resulting polymer was purified by reprecipitating in methanol for three times to afford **P$_2$** as a yellowish slice. Yield: 80 mg, 62%.

^{1}H NMR (300 MHz, CDCl$_3$). δ (ppm): 7.81–7.65 (br), 7.18 (br, 4H), 6.56 (br, 4H), 3.29 (br, 8H), 2.07 (br), 1.58 (br), 1.25 (br), 1.11 (br), 0.77 (br). Anal. Calcd. for $C_{72}H_{80}N_2$: C, 88.93; H, 8.10; N, 2.96. Found: C, 85.92; H, 8.07; N, 2.17.

3. Results and discussion

3.1. Synthesis and characterization

As depicted in Scheme 1, monomer **1** was facilely synthesized by the reaction of 4,4′-(2,7-dibromo-9*H*-fluorene-9,9-diyl)dianiline with phenylisocyanate, and monomer **2** was synthesized by the reaction of *N*,*N*′-diethyl aniline with 2,7-dibromofluorone. The Suzuki polycondensation of monomer

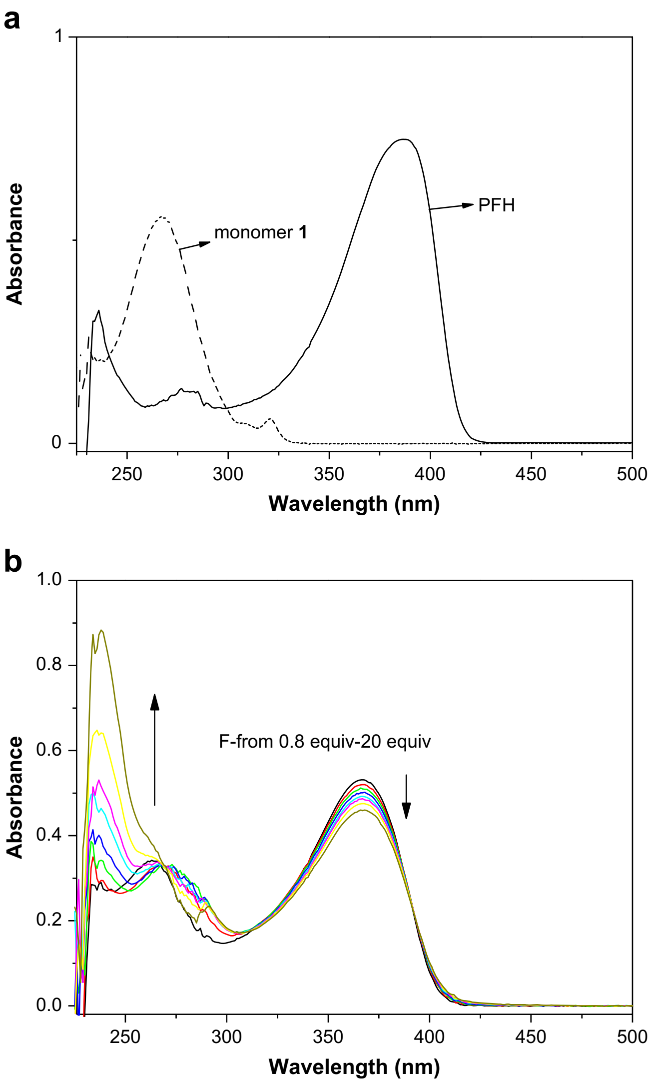


Fig. 2. Absorbance spectrum of monomer **1** and PFH (poly-9,9-dihexyl fluorene) in THF solution (a); absorption changes of **P$_1$** in THF solution upon addition of F$^-$ (b).

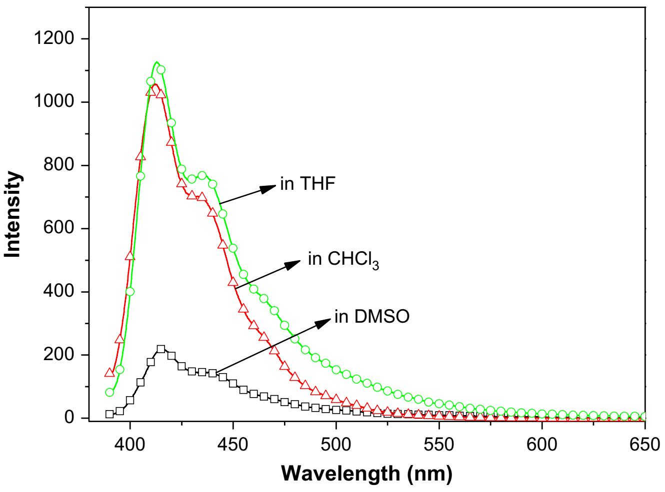


Fig. 3. Fluorescence of copolymer **P$_1$** in different solvents.

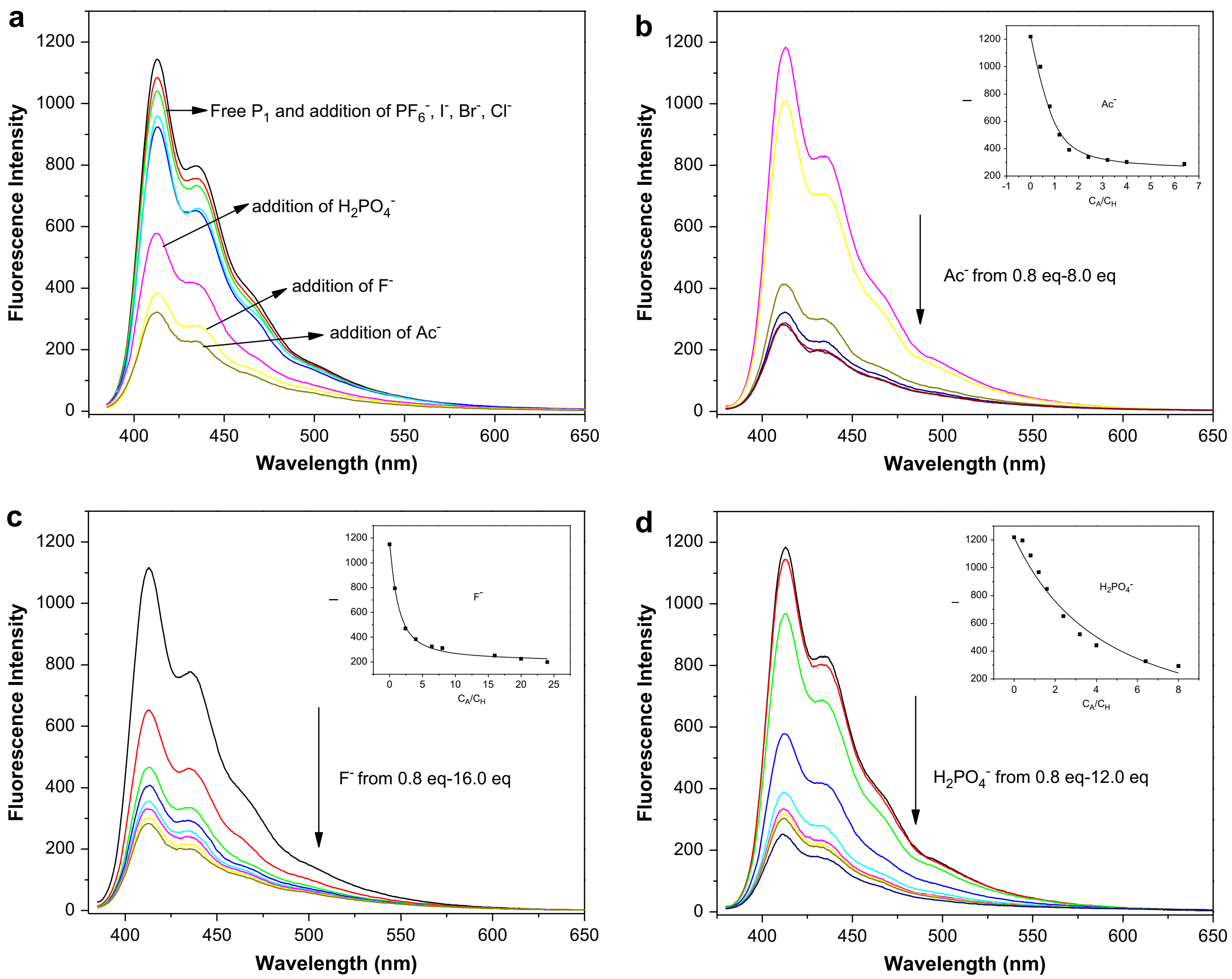


Fig. 4. Fluorescence response of the copolymer $\mathbf{P_1}$ toward different anions (a), fluorescence titration to CH_3COO^- (b), F^- (c) and $H_2PO_4^-$ (d) in THF. (Inset: nonlinear curve-fitting plots of the copolymer with addition of F^-, $H_2PO_4^-$, and CH_3COO^-. I: the emission intensity. C_A: the concentration of the anions, C_H: the concentration of the copolymer).

1, 2,7-dibromo-9,9-dihexylfluorene and 1,4-phenylenediboronic acid with the feed ratios of 22:28:50 mol%, or monomer **2**, 2,7-dibromo-9,9-dihexylfluorene and benzen-1,4-bis(boronic acid)-propane-1,3-diol diester with the feed ratios of 22:28:50 mol%, were carried out in a mixture of THF/H_2O (v/v: 3/1), with 2 M aqueous sodium carbonate solution as base and 1 mol% $Pd(PPh_3)_4$ as catalyst. The actual ratios of three components are estimated from the elemental analysis to be 19:31:50 mol% for $\mathbf{P_1}$ and 16:34:50 for $\mathbf{P_2}$. The copolymer $\mathbf{P_1}$ is soluble in THF, and slightly soluble in $CHCl_3$, CH_2Cl_2, DMF and DMSO, while $\mathbf{P_2}$ has good solubility in common organic solvent, such as $CHCl_3$, CH_2Cl_2, and THF, probably because of the ethyl chain. On the basis of GPC, the number-average molecular weights of the copolymers are 5000 g/mol for $\mathbf{P_1}$ and 16 390 g/mol for $\mathbf{P_2}$, respectively.

The FTIR spectra of monomer **1** and copolymer $\mathbf{P_1}$ were shown in Fig. 1. For monomer **1**, the absorption at 1663 cm^{-1} was assigned to carbonyl stretching of amide of the urea group, and those at 1600, 1544 and 1496 cm^{-1} were to the aromatic framework. These peaks can also be seen in the polymer, however, the intensity of carbonyl stretching (1663 cm^{-1}) significantly decreased in the polymer, because of the dilution of monomer **1** in the copolymer. For the polymer, the absorption peaks appeared at 2930, 2854 cm^{-1} come from C–H stretching of alkyl chains, indicating the existence of 9,9-dihexyl-9*H*-fluorene component.

For monomer **1**, the chemical shifts of N–H were found at 8.71 and 8.65 ppm, and they appeared at ca. 8.6 ppm as a broad band in the copolymer. Compared to monomer **1**, new peaks appeared at high field around 1–2 ppm were ascribed to the alkyl chains of the 9,9-dihexyl-9*H*-fluorene component.

3.2. Optical properties

In the UV–vis spectrum, the copolymer $\mathbf{P_1}$ in THF shows an absorption maximum at 367 nm, assigned to the π–π* transition state of the conjugated backbone. The absorption bands at 267 and 237 nm may come from the side chain diphenyl urea by comparison with the absorption spectrum of monomer **1** (Fig. 2a). Among the anions tested, F^-, Cl^-,

Br^-, I^-, PF_6^-, CH_3COO^-, $H_2PO_4^-$ as their tetrabutylammonium salts in THF, only F^- interacts with the copolymer (Fig. 2b). The absorption band at 237 nm has a distinct increase with the growth of the fluoride ion concentration, while the band around 267 nm gradually decreases, and an isobestic point can be observed at 269 nm. This phenomenon suggests that there is a new species formed, because of the fluoride ion complexation with urea group. We assume that the obvious absorption change of F^- compared to all the other anions may originate from the strong H-bond interaction in the ground state between the F^- and the urea group due to high negativity of fluorine.

3.3. Fluorescent response

The fluorescence intensity of copolymer $\mathbf{P_1}$ is sensitive to the solvents as shown in Fig. 3. The fluorescence intensity was quite strong in those solvents without proton acceptor, such as THF and $CHCl_3$. In contrast, it weakened a lot in solvents with proton acceptor, such as DMSO, DMF and water. It is postulated that the urea groups on the polymer side chain tend to have quite strong hydrogen-bond interaction with the solvents with proton acceptor, and hence result in fluorescence quenching.

Considering the solvent effect, the titration process was carried out with all the anions as their tetrabutylammonium salts in THF. The quantum yield of the copolymer $\mathbf{P_1}$ in THF is found to be 46.3%, and its life time is about 7.5 ns in THF solution.

Fig. 4a shows the fluorescence response of copolymer $\mathbf{P_1}$ toward the F^-, Cl^-, Br^-, I^-, PF_6^-, CH_3COO^-, $H_2PO_4^-$ (as their tetrabutylammonium salts) anions with a concentration of 10^{-3} M in THF. Among the anions investigated, F^- and CH_3COO^- exhibit obvious quenching behavior to the polymer emission, while $H_2PO_4^-$ represents a medium quenching behavior to the polymer emission. The titration experiments of the three anions are shown in Fig. 4b–d. The association constants (K_a) calculated from nonlinear least-squares curve-fitting [16] (insets of Fig. 4b-d), are $2.70 \times 10^5\ M^{-1}$ for F^-, $1.01 \times 10^6\ M^{-1}$ for CH_3COO^- and $5.46 \times 10^4\ M^{-1}$ for $H_2PO_4^-$. It is noteworthy that the association constants for acetate ion and fluoride ion are among the highest value in the anion-sensing systems with similar receptors (urea subunits and analogs) [17]. For example, Diamond et al. reported a chloride selective sensor combining urea functional group, with a K_a of 10^4 magnitude in acetonitrile–chloroform (95:5 v/v) mixed solution [17a]; Lee et al. reported a fluoride selective sensor containing amidothiourea group, with a K_a of 10^4 magnitude in acetonitrile [17c]. The results indicate that the copolymer has a strong affinity for acetate ion and fluoride ion in THF. The relatively higher sensitivity toward acetate ion may be ascribed to the suitable size of the anion, which may rightly fit into the cavity formed by the N–H groups of the repeating units in the side chain, and hence efficiently interact with proton donors of the polymer through hydrogen-bond.

This remarkable quenching effect caused by the three anions may be ascribed to photoinduced electron transfer (PET) [18]. For example, upon complexation of F^- with urea protons via hydrogen-bond, the electron density of nitrogen in the polymer side chain increased, triggering considerable PET fluorescence quenching on copolymer backbone [19]. In addition, we measured the life time of $\mathbf{P_1}$ in THF solution upon addition of the three anions, as a result, the life time of $\mathbf{P_1}$ (7.5 ns) has no change with the existence of CH_3COO^- (7.3 ns), F^- (7.5 ns), or $H_2PO_4^-$ (7.4 ns) within experiment error, indicating that a statically quenched polymer-anion complexes dominates the fluorescence quenching mechanism in this system [3].

In respect that F^- usually coexists with other halide ions (Cl^-, Br^-, I^-), it is necessary to test the interference of other halide ions toward F^- detection. The fluorescence spectra were recorded by adding other halide ions into the polymer solution with fluoride ion (Fig. 5a), as well as by adding F^- into

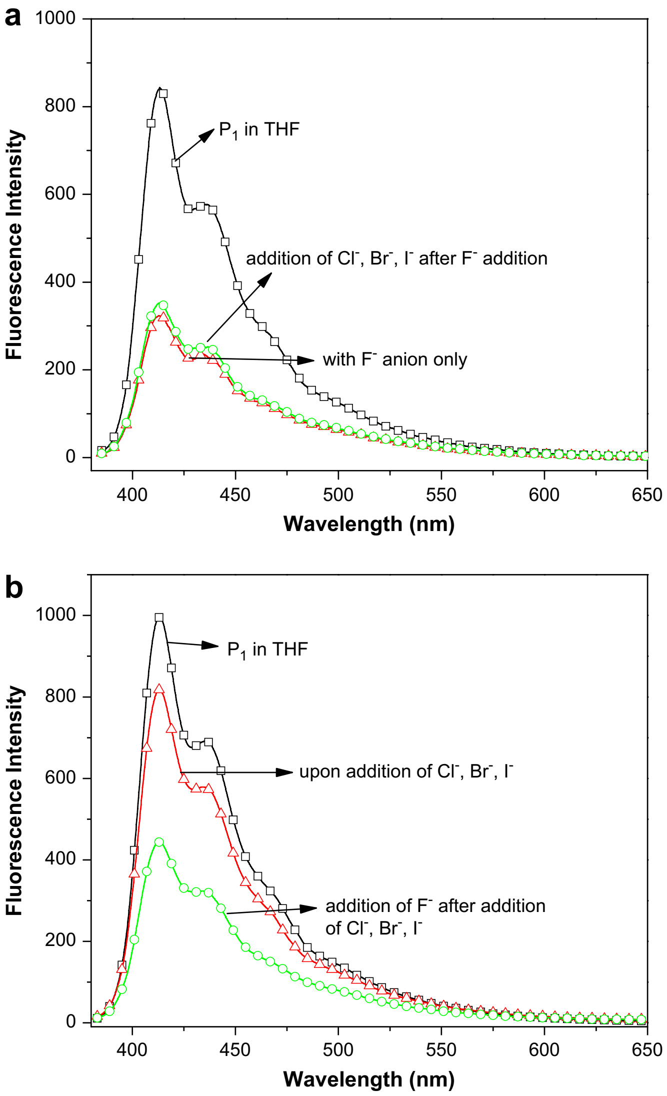


Fig. 5. The selectivity of copolymer $\mathbf{P_1}$ toward fluoride anion with the coexistence of other halides.

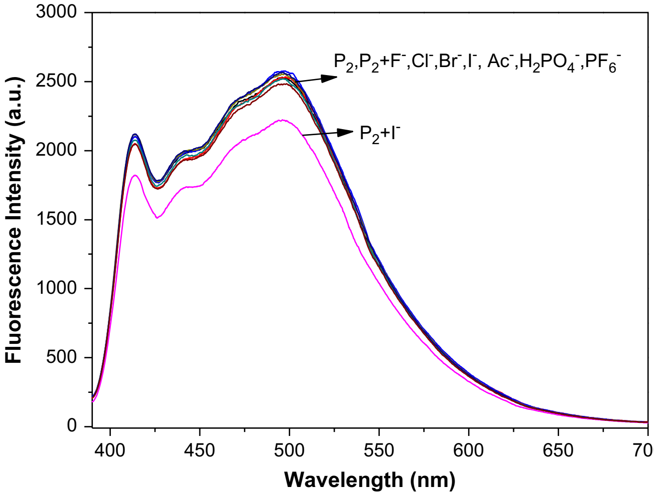


Fig. 6. Fluorescence response of copolymer $\mathbf{P_2}$ toward different anions.

the polymer solution with Cl^-, Br^-, and I^- (Fig. 5b). In Fig. 5a, almost no fluorescence change was observed as other halide ions were added into the polymer solution quenched by F^-. In Fig. 5b, only a slightly decrease of the polymer emission was observed as other halide ions added, however, a significant decrease was observed when fluoride ion was added to the above solution. The result indicates that this polymer is able to detect F^- with the coexistence of Cl^-, Br^-, and I^-.

For comparison, we also tested the fluorescence response of the analogous copolymer $\mathbf{P_2}$ for anions (Fig. 6). Upon addition of each anion (10 equiv) into the $\mathbf{P_2}$ solution in THF, the fluorescence intensity of the polymer is almost unchanged, except that I^- causes a little decrease of the emission, which may come from the heavy atom effect of I^-. The comparison experiments clearly demonstrate that the sensitivity and selectivity of $\mathbf{P_1}$ toward anions come from the strong hydrogen-bond interaction between the anions and the urea group of the copolymer.

4. Conclusion

In summary, we have synthesized and characterized a novel fluorene-based copolymer with diphenyl urea as pendent group. The copolymer $\mathbf{P_1}$ turned out to have high affinity toward Ac^-, F^- and $H_2PO_4^-$ through hydrogen-bonding interaction, especially with high association constants for acetate ion and fluoride ion. To the best of our knowledge, this is the first report that urea group is introduced to the side chain of conjugated polymer as special receptor to detect anions. This new system taking advantage of the strong luminescence property of the polyfluorene as reporter and the hydrogen-bond-forming ability of urea group may be developed as novel effective anions receptor and chemosensor.

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