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Novel chemosensory materials based on polyfluorenes with 2-(2′-pyridyl)-benzimidazole and 5-methyl-3-(pyridin-2-yl)-1,2,4-triazole groups in the side chain

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Abstract

Polyfluorenes with 2-(2′-pyridyl)-benzimidazole (P1, P2 and P4) and 5-methyl-3-(pyridin-2-yl)-1,2,4-triazole (P3) groups in the side chain were synthesized by Suzuki polycondensation. The responsive properties of polymers on metal ions and H^+ were investigated by absorption and emission spectra. The fluorescences of polymers (P1−P4) were completely quenched upon the transition metal ions such as Co^{2+}, Ni^{2+}, Fe^{3+} and Ag^+ due to the enhanced electronic communication properties of conjugated polymers. The obvious differences to Ni^{2+} ion responsive sensitivity were observed between P1 and P4 polymers. The fluorescences of P1 and P4 were quenched to 50 (I_0/I) and to 22 (I_0/I) upon the addition of a Ni^{2+} solution of 3.2×10^{-6} M, as well as 5.0×10^{-6} M, respectively, owing to the different conjugated backbone. The fluorescences of P2 and P3 were completely and hardly quenched upon the addition of a Al^{3+} solution of 1.0×10^{-4} M, respectively, owing to the different receptors in the side chain. P2 showed good selectivity to Ni^{2+} ion in the range of quencher concentration as low as 5 ppm, owing to the different chelating abilities of receptor with ions. Cu^{2+} and Mn^{2+} ions hardly quenched the fluorescences of polymers (P1−P4), which were different from the oligopyridyl-functionalized conjugated polymers. The results further opened the opportunities to develop the tailored sensory materials through the appropriate alteration of receptors in the side chain and the conjugated backbone.

Keywords: Polyfluorene; Fluorescent chemosensor; Responsive property

1. Introduction

Conjugated polymers have attracted great attention due to their potential applications as light-emitting diodes [1], photovoltaic devices [2], field-effect transistors [3], and biological and chemical sensors [4]. Conjugated polymers with special receptors can be used in detecting a wide range of analytes from explosives to biomolecules. Sensitive detection methods employed for sensing metal ions involve the design of "turn-on" fluorescent chemosensors on the basis of the photoinduced electron transfer (PET) mechanism in conjugated polymers. Fan et al. reported that conjugated polymers with *N*,*N*,*N*-trimethylethylenediamino groups as receptors, on a poly[*p*-(phenyleneethylene)-*alt*-(thienylene-ethynylene)] (PPETE) fluorescent conjugated polymer backbone, showed fluorescence enhancement upon binding Hg^{2+}, protons and other divalent cations [5]. The vast majority of the detection methods involve a "turn-off" effect in the presence of analytes. The conjugated "molecular wire" polymer greatly amplified the fluorescence quenching due to facile energy migration along the polymer backbone upon the excitations and the concept was first established by Zhou and Swager [6].

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Aza crown and crown ethers were investigated only for alkali metal ions with the selectivity depending on the size matching between metal ions and the inner diameter of receptor [7]. For other metal ions, ligands such as quinoline, pyridine, 2,2′-bipyridine, terpyridine and 1,10-phenanthroline groups have been successfully introduced into the backbone of conjugated polymers and these polymers exhibited metal ion-dependent ionochromic effects in their absorption and emission spectra [8−13]. These conjugated polymers have been found to be highly sensitive to a wide variety of metal ions, and their fluorescence is completely quenched or red/blue-shifted depending on the addition of different metal ions. In these sensory systems, factors such as the conformational changes in the backbone, the electron density and the electronic structures of metal ions need to be considered.

Recently, great efforts have been focused on the design of tailored sensory materials to detect specific metal ions, owing to the important result by Wayne et al. that the conjugation of receptors to the polymer backbone is not required for the fluorescence response [13]. Polyfluorenes with imidazole [14] and phosphonate [15] groups in the side chain as chemosensors have been reported. These polymers with imidazole and phosphonate groups are highly sensitive and selective chemosensors for Cu^{2+} and Fe^{3+} ions, respectively. As a result, the development of tailored sensory materials for the sensitive and selective sense of metal ions could be realized through the appropriate alteration of receptors in the side chain and backbone structure of π-conjugated polymers.

The 3-(pyridin-2-yl)-1*H*-1,2,4-triazole and 2-(2′-pyridyl)-benzimidazole derivatives are important ligands, and the obtained metal complexes were often shown attractive chemical and physical properties [16,17]. Peter G. Pickup group successfully introduced 2-(2′-pyridyl)-benzimidazole into conjugated polymer backbone to form novel hybrid conjugated Ru and Os metallopolymers. 2-(2′-Pyridyl)-benzimidazole derivatives were also shown to be useful metal ion binding ligands in the self-assembly of supramolecular polymers and were widely used in the preparation of the Ru^{2+}, Zn^{2+}, and Fe^{2+} metallo-supramolecular conjugated polymers. Triazole derivatives were shown to have more efficient electron-transport and hole-blocking characteristics than oxadiazole moiety in polymer light-emitting diodes [18].

In this paper, we report the novel polyfluorenes with 5-methyl-3-(pyridin-2-yl)-1,2,4-triazole and 2-(2′-pyridyl)-benzimidazole groups in the side chain and the sensing properties of some metal ions. To the best of our knowledge, it is the first report that 5-methyl-3-(pyridin-2-yl)-1,2,4-triazole and 2-(2′-pyridyl)-benzimidazole groups attached in the side chain of π-conjugated polymers are used as special receptors to detect metal ions.

2. Experimental section

2.1. Measurement and characterization

^1H and ^{13}C NMR spectra were recorded on a Bruker DRX 300 spectrometer in deuterated chloroform solution. GC−MS was recorded on a Trace 2000 Series (Finn igan Co.) with a quartz capillarity column (J&W DB-5MS: 30 m × 0.25 mm × 0.25 μm).The number-average (M_n) and weight-average (M_w) molecular weights of polymers were determined by a Waters GPC 2410 in tetrahydrofuran (THF) by using a calibration curve of polystyrene standards. Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.). Cyclic voltammetry was carried out on a potentiostat/galvanostat model 283 (Princeton Applied Research) with platinum electrode at a scan rate of 50 mV/s against a saturated calomel electrode (SCE) with nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile (CH_3CN).

2.2. Fluorescence titration procedure

The ion responsive properties of polymers were studied by using absorption and fluorescence emission spectroscopy in THF solution at a polymer concentration of 5.0×10^{-6} M. Many kinds of metal ions, such as alkali, alkali earth, and transition metal ions were used in our experiment. Fluorescence spectra were obtained on Fluorometer (JY-FL-3). UV−vis absorption spectra were recorded on a HP 8453 spectrophotometer. Polymers' (P1−P4) concentration of 5×10^{-6} M was based on the repeated units in the THF solution. Fluorescence titration was carried out by sequentially adding the cation aqueous solution of 0.2 M (0.02 M) to the polymer solution (10 ml) and stirred for 5 min prior to measuring fluorescence spectra.

2.3. Materials

All manipulations involving air-sensitive reagents were performed under an atmosphere of dry argon. All reagents, unless otherwise specified, were obtained from Aldrich and Beida Syn Chem Co, and were used as received.

2.4. Monomers synthesis (Scheme 1)

2.4.1. 3,6-Dibromo-9-(6′-bromohexyl)-carbazole (**1**)

To a solution of sodium hydride (2.47 g, 61.6 mmol, 60%) in dry THF (50 ml), 3,6-dibromocarbazole (10 g, 30.8 mmol) in dry THF (50 ml) was added dropwise. The mixture was refluxed for 1.5 h under N_2 atmosphere, and the resulted mixture was further added dropwise to 1,6-dibromohexane (90 mmol) in THF (10 ml). The reaction mixture was refluxed for another 24 h and then cooled to room temperature. It was extracted with dichloromethane followed by washing with water. The oil phase was separated and dried overnight with $MgSO_4$. The solvent was removed by evaporation, and the crude product was purified by silica column chromatography to give 9.1 g of white solid (yield: 60%). ^1H NMR ($CDCl_3$, 300 MHz, δ, ppm): 8.14 (d, 2H, $J = 1.8$ Hz, Cz−H), 7.52 (m, 2H), 7.20 (t, 2H, $J_1 = 6.1$ Hz, $J_2 = 2.5$ Hz, Cz−H), 4.23−4.21 (t, 2H, $J_1 = 6.9$ Hz, $J_2 = 7.2$ Hz, CzN−CH_2). 3.33−3.30 (m, 2H, Br−CH_2), 1.85−1.81 (m, 8H, CH_2) (aliphatic). ^{13}C NMR ($CDCl_3$, 75 MHz, δ, ppm): 139.3, 129.0, 123.5, 123.3, 112.0, 110.3 (carbazole ring), 43.1 (N−CH_2), 33.6, 32.5, 28.7, 27.8, 26.4. Anal. Calcd for $C_{18}H_{18}NBr_3$: C, 44.26; H, 3.70; N, 2.86. Found: C, 44.75; H, 3.83; N, 2.85. GC–MS (488, M^+).

2.4.2. *1,4-Dibromo-2-methoxy-5-[(6′-bromo)hexyloxy]-benzene (**2**)*

A solution of bromine (0.64 g, 4.1 mmol) in chloroform (50 ml) was slowly added to a solution of 1-(6′-bromo)hexyloxy-4-methoxy-benzene (7.3 g, 2 mmol) in chloroform (100 ml) at 0 °C. The mixture was stirred at room temperature for 24 h and was then neutralized by iced aqueous KOH. After washing with water, diluted hydrochloric acid solution and brine, the organic layer was dried overnight with $MgSO_4$. Removal of the solvent followed by recrystallization from ethanol afforded a white solid (yield: 75%). ^1H NMR ($CDCl_3$, 300 MHz, δ, ppm): 7.11 (s, 2H, Ar–H), 4.01–3.96 (t, 2H, $J = 6.4$ Hz, OCH_2), 3.87 (s, 3H, OCH_3), 3.47–3.43 (t, 2H, $J = 7.1$ Hz, Br–CH_2), 1.93–1.54 (m, 8H, CH_2) (aliphatic). ^{13}C NMR ($CDCl_3$, 75 MHz, δ, ppm): 150.6, 150.1, 118.7, 117.0, 111.3, 110.4, 70.1, 57.0, 33.8, 32.7, 28.9, 27.8, 25.2. Anal. Calcd for $C_{13}H_{17}O_2Br_3$: C, 35.10; H, 3.82. Found: C, 35.13; H, 4.06. GC–MS (442, M^+).

2.4.3. *2-(2′-Pyridyl)-benzimidazole (**3**) [16e]*

O-Phenylene diamine (40.0 mmol, 4.32 g) and picolinic acid (40.0 mmol, 4.92 g) were added to 100 ml of 85% polyphosphoric acid, and the mixture was then heated to 190 °C. After 8 h, the solution was cooled and added to 1000 ml of ice water. The solution was made alkaline (pH = 10, NaOH) and allowed to stir overnight. A purple/lavender precipitate was filtered and collected. Further purification to remove excess *o*-phenylene diamine was achieved by reprecipitation. The lavender precipitate was dissolved in 200 ml of sodium carbonate solution (10%) and stirred to dissolve all the material. The pH of the solution was brought from 11 to 7.8, resulting in the reprecipitation of the lavender product. The precipitate was collected by filtration and dried. The product was further purified by column chromatography and recrystallization to give a white solid (yield: 25%). M.p. 219 °C. ^1H NMR ($CDCl_3$, 300 MHz, δ, ppm): 8.54 (d, 1H, $J = 4.8$ Hz, Py–H), 8.49 (t, 1H, $J = 7.9$ Hz, Py–H), 7.92–7.87 (m, 2H, Py–H), 7.39–7.26 (m, 4H, Ar–H). GC–MS (195, M^+).

2.4.4. *6,7-Dimethyl-2-(2′-pyridyl)-benzimidazole (**4**)*

It was prepared according to the procedure of synthesizing 2-(2′-pyridyl)-benzimidazole (yield: 21%). ^1H NMR ($CDCl_3$, 300 MHz, δ, ppm): 8.59 (d, 1H, $J = 4.8$ Hz, Py–H), 8.47 (d, 1H, $J = 8.0$ Hz, Py–H), 7.88–7.83 (m, 2H, Py–H), 7.28–7.36 (m, 2H, Ar–H), 2.35 (s, 6H, Ar–CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, δ, ppm): 150.1, 148.8, 137.3, 132.7, 132.0, 124.2, 121.7, 112.0, 119.8, 20.4 (Ar–CH_3).

2.4.5. *5-Methyl-3-(pyridin-2-yl)-1H-1,2,4-triazole (**5**) [17b]*

Equimolar amounts of 2-cyanopyridine and hydrazine monohydrate were mixed and a small amount of ethanol was added to obtain a clear solution. After standing overnight at room temperature, the almost colorless crystals of 2-pyridinecarboxamidrazone could be filtered off. The product was washed with diethyl ether and dried in the air. The solid obtained was added to a mixture of acetic acid and acetic anhydride at 0 °C and the solution was stirred at room temperature for 2 h. The solution was then concentrated under vacuum and the resulting oil heated at 130 °C for 1 h. The solid obtained was purified by repeated crystallization from diisopropyl ether (yield: 50%). M.p. 163–165 °C. ^1H NMR ($CDCl_3$, 300 MHz, δ, ppm): 14.2 (s, N–H), 8.69 (d, 1H, $J = 4.3$ Hz, Py–H), 8.15 (d, 1H, $J = 7.9$ Hz, Py–H), 7.80 (t, 1H, $J_1 = 6.8$ Hz, $J_2 = 7.5$ Hz, Py–H), 7.32 (t, 1H, $J_1 = 5.2$ Hz, $J_2 = 7.0$ Hz, Py–H), 2.49 (s, 3H, Me).^{13}C NMR ($CDCl_3$, 75 MHz, δ, ppm): 158.5, 156.5, 149.4, 147.4, 137.5, 124.5, 121.7, 13.3 (Me).

2.4.6. *2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (monomer **1**) [20]*

It was prepared following the published procedure and the obtained boronic ester was recrystallized from methanol to give a white solid product (yield: 50%). ^1H NMR ($CDCl_3$, 300 MHz, δ, ppm): 7.81 (m, 2H), 7.76 (s, 2H), 7.72 (m, 2H) (fluorene ring), 1.97 (m, 4H), 1.37 (s, 24H, CH_3), 1.22–0.98 (m, 20H), 0.81 (t, $J = 6.7$ Hz, 6H), 0.54 (m, 4H) (aliphatic). ^{13}C NMR ($CDCl_3$, 75 MHz, δ, ppm): 150.9, 144.3, 134.1, 129.3, 121.7, 119.8 (fluorene ring), 84.1, 55.6 (C_9-fluorene ring), 40.5, 32.2, 30.3, 29.6, 25.3, 24.0, 23.0, 14.5 (aliphatic). Anal. Calcd for $C_{41}H_{64}O_4B_2$: C, 76.74; H, 10.04. Found: C, 76.43; H, 9.95.

2.4.7. *3,6-Dibromo-9-(N-(2-(2′-pyridyl)-benzimidazole)-hexyl)-carbazole (monomer **2**)*

A mixture of 3,6-dibromo-9-(6′-bromohexyl)-carbazole (4.88 g, 10 mmol), 2-(2′-pyridyl)-benzimidazole (1.95 g, 10 mmol), sodium hydroxide (0.44 g, 11 mmol), and dimethyl sulphoxide (30 ml) were stirred and heated at 130 °C for 24 h under argon atmosphere. It was subsequently poured into ice water (100 ml). It was extracted with dichloromethane followed by washing with water. The oil phase was separated and dried overnight with $MgSO_4$. The solvent was evaporated and the obtained product was purified by silica gel column chromatography (petroleum ether:ethyl acetate = 2:1 as eluent) to give a white solid (yield: 43%). ^1H NMR ($CDCl_3$, 300 MHz, δ, ppm): 8.54–8.52 (d, 1H, $J = 4.8$ Hz, Py–H), 8.43–8.40 (d, 1H, $J = 7.9$ Hz, Py–H), 8.15–8.14 (d, 2H, $J = 1.8$ Hz, Cz–H), 7.87–7.81 (m, 2H, Py–H), 7.54–7.51 (dd, 2H, $J = 1.9$ Hz, Cz–H), 7.39–7.28 (m, 4H, Ar–H), 7.22–7.19 (m, 2H, Cz–H), 4.80 (t, 2H, $J = 7.3$ Hz, BmN–CH_2), 4.20 (t, 2H, $J = 7.0$ Hz, CzN–CH_2), 1.88–1.33 (m, 8H, CH_2) (aliphatic). ^{13}C NMR ($CDCl_3$, 75 MHz, δ, ppm): 150.6, 149.7, 148.5, 142.6, 139.2, 136.8, 136.5, 129.1, 124.7, 123.7, 123.7, 123.5, 122.6, 120.1, 112.0, 110.3, 110.1, 45.2 (BmN–CH_2), 43.1 (CzN–CH_2), 29.8, 28.7, 26.8, 26.5 (aliphatic). Anal. Calcd for $C_{30}H_{26}N_4Br_2$: C, 59.80; H, 4.32; N, 9.30. Found: C, 59.89; H, 4.50; N, 9.30.

2.4.8. *3,6-Dibromo-9-(N-(6,7-dimethyl-2-(2′-pyridyl)-benzimidazole)-hexyl)-carbazole (monomer **3**)*

It was prepared according to the procedure of synthesizing monomer **2** (yield: 50%). ^1H NMR ($CDCl_3$, 300 MHz, δ, ppm): 8.51–8.50 (d, 1H, $J = 4.8$ Hz, Py–H), 8.52–8.34 (m, 1H, Py–H), 8.14–8.13 (d, 2H, $J = 1.8$ Hz, Cz–H), 7.85–7.6 (m, 2H, Py–H), 7.52–7.48 (dd, 2H, $J = 1.8$ Hz, Cz–H), 7.35–7.28 (m, 2H, Ar–H), 7.22–7.19 (m, 2H, Cz–H), 4.79–4.75 (t, 2H, $J = 7.2$ Hz, BmN–CH$_2$), 4.25–4.17 (t, 2H, $J = 7.1$ Hz, CzN–CH$_2$), 2.41 (m, 6H, Ar–CH$_3$), 1.85–1.24 (m, 8H, CH$_2$) (aliphatic). ^{13}C NMR (CDCl$_3$, 75 MHz, δ, ppm): 151.0, 149.0, 148.4, 139.2, 136.7, 135.2, 132.6, 131.6, 129.0, 124.5, 123.4, 123.4, 123.3, 120.1, 112.0, 110.3, 110.2, 45.2 (BmN–CH$_2$), 43.1 (CzN–CH$_2$), 29.9, 28.7, 26.8, 26.5 (aliphatic), 20.8, 20.4 (Ar–CH$_3$). Anal. Calcd for C$_{32}$H$_{30}$N$_4$Br$_2$: C, 60.90; H, 4.76; N, 8.88. Found: C, 61.10; H, 4.86; N, 8.83.

*2.4.9. 3,6-Dibromo-9-(N-(5-methyl-3-(pyridin-2-yl)-1,2,4-triazole)-hexyl)-carbazole (monomer **4**)*

It was prepared according to the procedure of synthesizing monomer **2** (yield: 54%). ^{1}H NMR: (CDCl$_3$, 300 MHz, δ, ppm): 8.49–8.46 (d, 1H, $J = 4.8$ Hz, Py–H), 8.16–8.13 (m, 3H), 7.82–7.77 (m, 1H), 7.54–7.51 (m, 2H), 7.31–7.20 (m, 3H), 4.73–4.69 (t, 2H, $J = 7.5$ Hz, TazN–CH$_2$), 4.23–4.21 (t, 2H, $J = 7.1$ Hz, CzN–CH$_2$), 2.41 (s, 3H, Taz–CH$_3$), 1.85–1.23 (m, 8H, CH$_2$) (aliphatic). ^{13}C NMR (CDCl$_3$, 75 MHz, δ, ppm): 159.3, 151.6, 148.8, 148.0, 139.3, 136.9, 129.0, 124.0, 123.3, 123.7, 123.5, 112.0, 110.3, 50.3 (TazN–CH$_2$), 43.2 (CzN–CH$_2$), 29.9, 28.7, 26.7, 26.2 (aliphatic), 13.9 (Taz–Me). Anal. Calcd for C$_{26}$H$_{25}$N$_5$Br$_2$: C, 55.03; H, 4.40; N, 12.35. Found: C, 55.08; H, 4.41; N, 12.44.

*2.4.10. 1,4-Dibromo-2-methoxy-5-[N-(2-(2′-pyridyl)-benzimidazole)hexyloxy]benzene (monomer **5**)*

It was prepared according to the procedure of synthesizing monomer **2** (yield: 65%). ^{1}H NMR (CDCl$_3$, 300 MHz, δ, ppm): 8.71–8.69 (d, 1H, $J = 4.7$ Hz, Py–H), 8.44–8.41 (d, 1H, $J = 8.0$ Hz, Py–H), 7.84–7.81 (m, 2H, Py–H), 7.44–7.29 (m, 4H, $J = 6.8$ Hz, BmAr–H), 7.10–7.07 (d, 2H, $J = 5.8$ Hz, Ar–H), 4.89–4.84 (t, 2H, $J = 7.4$ Hz, BmN–CH$_2$), 3.90–3.87 (t, 2H, $J = 6.3$ Hz, OCH$_2$), 3.82 (s, 3H, OCH$_3$), 1.94–1.20 (m, 10H, CH$_2$). ^{13}C NMR (CDCl$_3$, 75 MHz, δ, ppm): 150.7, 150.6, 150.1, 149.9, 148.7, 142.6, 136.8, 136.6, 124.7, 123.7, 123.3, 122.5, 120.1, 118.7, 117.0, 111.3, 110.4, 110.2, 70.1, 57.0, 45.3, 29.9, 28.9, 26.5, 25.6. Anal. Calcd for C$_{25}$H$_{25}$N$_3$O$_2$Br$_2$: C, 53.67; H, 4.48; N, 7.51. Found: C, 53.64; H, 4.51; N, 7.35.

2.5. Polymer synthesis (general procedures of Suzuki polycondensation, taking P1 as an example)

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (monomer **1**) (632 mg, 1.0 mmol), 3,6-dibromo-9-(*N*-(2-(2′-pyridyl)-benzimidazole)-hexyl)-carbazole (monomer **2**) (602 mg, 1.0 mmol) and tetrakis(triphenylphosphine)-palladium (5 mg) were dissolved in the mixture of toluene/THF (10 ml) and stirred for 0.5 h, and then Et$_4$NOH aqueous solution (20%, 4 ml) was added. The mixture was heated to 100 °C and stirred for 2 days under argon atmosphere. Then the polymer was capped by adding 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (100 mg) and stirred for 12 h, and then capped by bromobenzene (1 ml) followed by heating for another 12 h. The mixture was poured into stirred methanol (250 ml) to generate plenty of light-white precipitates. The solid was collected by filtration and then dissolved in toluene and washed with water. The careful reprecipitation procedure in acetone/methanol was repeated for several times. The polymer was further purified by washing with refluxing acetone in Soxhlet for 2–3 days. The light-white solid was dried under vacuum at room temperature.

P1 (yield: 52%): ^{1}H NMR (CDCl$_3$, 300 MHz, δ, ppm): 8.56–8.53 (m, 3H), 8.43–8.40 (d, 1H, $J = 7.9$ Hz, Py–H), 7.87–7.74 (m, 10H), 7.51–7.41 (m, 6H) (fluorene ring, carbazole ring and 2-(2′-pyridyl)-benzimidazole ring), 4.84 (b, 2H, BemN–CH$_2$), 4.38 (b, 2H, CzN–CH$_2$), 1.92 (b, 4H), 1.69–1.13 (m, 20H), 1.14–0.78 (m, 18H) (aliphatic). ^{13}C NMR (CDCl$_3$, 75 MHz, δ, ppm): 151.7, 150.7, 149.8, 148.6, 142.7, 140.8, 140.3, 139.6, 136.7, 136.6, 133.1, 126.2, 125.6, 124.7, 123.7, 123.6, 123.3, 122.5, 121.6, 120.2, 119.9, 119.0, 110.1, 109.0 (fluorene, carbazole and 2-(2′-pyridyl)-benzimidazole ring), 68.0, 55.4 (C$_9$-fluorene ring), 45.3 (BemN–CH$_2$), 40.7 (CzN–CH$_2$), 31.8, 30.1, 29.9, 29.3, 29.0, 27.0, 26.7, 25.6, 24.0, 22.6, 14.1 (aliphatic). Anal. Calcd for C$_{59}$H$_{66}$N$_4$: C, 85.30; H, 7.95; N, 6.75. Found: C, 84.62; H, 8.14; N, 6.05.

P2 (yield: 56%): ^{1}H NMR (CDCl$_3$, 300 MHz, δ, ppm): 8.53–8.40 (m, 3H), 8.42–8.39 (d, 1H, $J = 8.0$ Hz, Py–H), 7.90–7.85 (m, 2H), 7.83–7.62 (m, 7H), 7.51–7.48 (d, 2H, $J = 8.5$ Hz), 7.28–7.20 (m, 3H) (fluorene ring, carbazole ring and 2-(2′-pyridyl)-benzimidazole ring), 4.82–4.81 (t, 2H, $J_1 = 6.8$ Hz, $J_2 = 7.4$ Hz, BmN–CH$_2$), 4.38–4.37 (m, 2H, CzN–CH$_2$), 2.44–2.42 (d, 6H, $J = 6.8$ Hz, BmAr–CH$_3$), 1.93–1.91 (m, 6H), 1.47–1.15 (m, 26H), 1.147–0.82 (m, 10H) (aliphatic). ^{13}C NMR (CDCl$_3$, 75 MHZ, δ, ppm): 150.7, 149.8, 142.7, 136.7, 136.6, 124.7, 123.7, 123.3, 122.5, 120.2, 110.2 (2-(2′-pyridyl)-benzimidazole ring), 151.7, 148.6, 140.8, 140.3, 139.6, 133.1, 126.2, 125.6, 123.6, 121.6, 119.9, 119.0, 109.0 (fluorene and carbazole ring), 68.0, 55.4 (C$_9$-fluorene ring), 45.2, 40.7, 31.8, 30.3, 30.1, 29.9, 29.7, 29.3, 29.1, 27.0, 23.9, 22.6, 20.8, 14.1 (aliphatic). Anal. Calcd for C$_{61}$H$_{70}$N$_4$: C, 85.32; H, 8.16; N, 6.52. Found: C, 84.81; H, 8.33; N, 5.87.

P3 (yield: 53%): ^{1}H NMR (CDCl$_3$, 300 MHz, δ, ppm): 8.53–8.15 (m, 4H), 7.89–7.75 (m, 9H), 7.54–7.26 (m, 2H) (fluorene ring, carbazole ring and pyridine ring), 4.79–4.74 (t, 2H, $J = 6.9$ Hz, TazN–CH$_2$), 4.41 (b, 2H, CzN–CH$_2$), 2.46 (s, 3H, TazN–CH$_3$), 2.17–1.93 (m, 4H), 1.48–1.13 (m, 25H), 0.85–0.79 (m, 13H) (aliphatic). ^{13}C NMR (CDCl$_3$, 75 MHz, δ, ppm): 159.4, 151.7, 151.6, 148.9, 148.0, 140.8, 140.4, 139.6, 136.9, 133.1, 126.2, 125.6, 123.9, 123.6, 121.6, 119.9, 119.0, 109.1, 68.0, 55.4 (C$_9$-fluorene ring), 40.7, 31.8, 30.1, 30.0, 29.3, 29.1, 26.9, 26.3, 25.6, 23.9, 22.6, 14.1 (aliphatic), 13.9 (Taz–Me). Anal. Calcd for C$_{55}$H$_{65}$N$_5$: C, 83.01; H, 8.17; N, 8.81. Found: C, 82.60; H, 8.30; N, 8.19.

P4 (yield: 60%): ^{1}H NMR (CDCl$_3$, 300 MHz, δ, ppm): 8.65–8.63 (d, 1H, $J = 4.7$ Hz, Py–H), 8.44–8.41 (d, 1H, $J = 8.0$ Hz, Py–H), 7.87–7.82 (m, 2H, Py–H), 7.79–7.42 (m, 5H, Ar–H), 7.42–7.14 (m, 8H, Ar–H), 4.84–4.81 (t, 2H, $J_1 = 7.3$ Hz, $J_2 = 7.1$ Hz, N–CH$_2$), 4.0–3.89 (m, 2H,

OCH_2), 3.80 (s, 3H, OCH_3), 1.91–1.76 (m, 6H), 1.44–1.29 (m, 6H), 1.16–0.91 (m, 21H), 0.83–0.61 (m, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ, ppm): 151.2, 150.8, 150.5, 149.8, 148.6, 142.7, 139.9, 137.1, 136.7, 136.6, 131.7, 128.0, 124.7, 123.7, 123.3, 122.5, 120.1, 119.4, 117.0, 115.5, 110.2, 69.8, 56.8, 55.0 (C_9-fluorene ring), 45.3, 40.6, 32.2, 31.8, 30.3, 30.0, 29.4, 28.9, 26.5, 25.7, 24.1, 22.6, 14.1. Anal. Calcd for $C_{54}H_{65}N_3O_2$: C, 82.34; H, 8.26; N, 5.46. Found: C, 82.33; H, 8.33; N, 5.01.

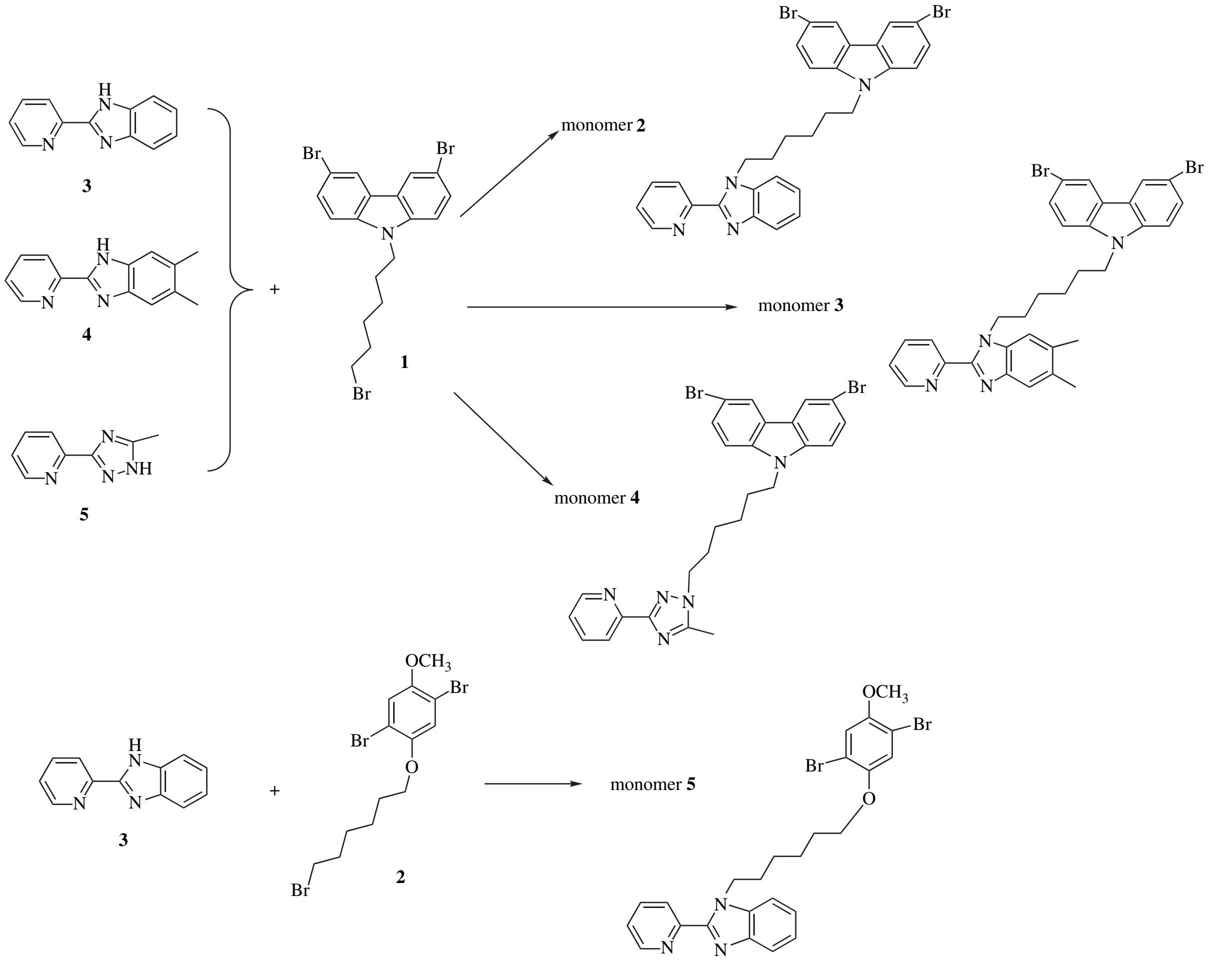
3. Results and discussion

3.1. Synthesis and structure characterization

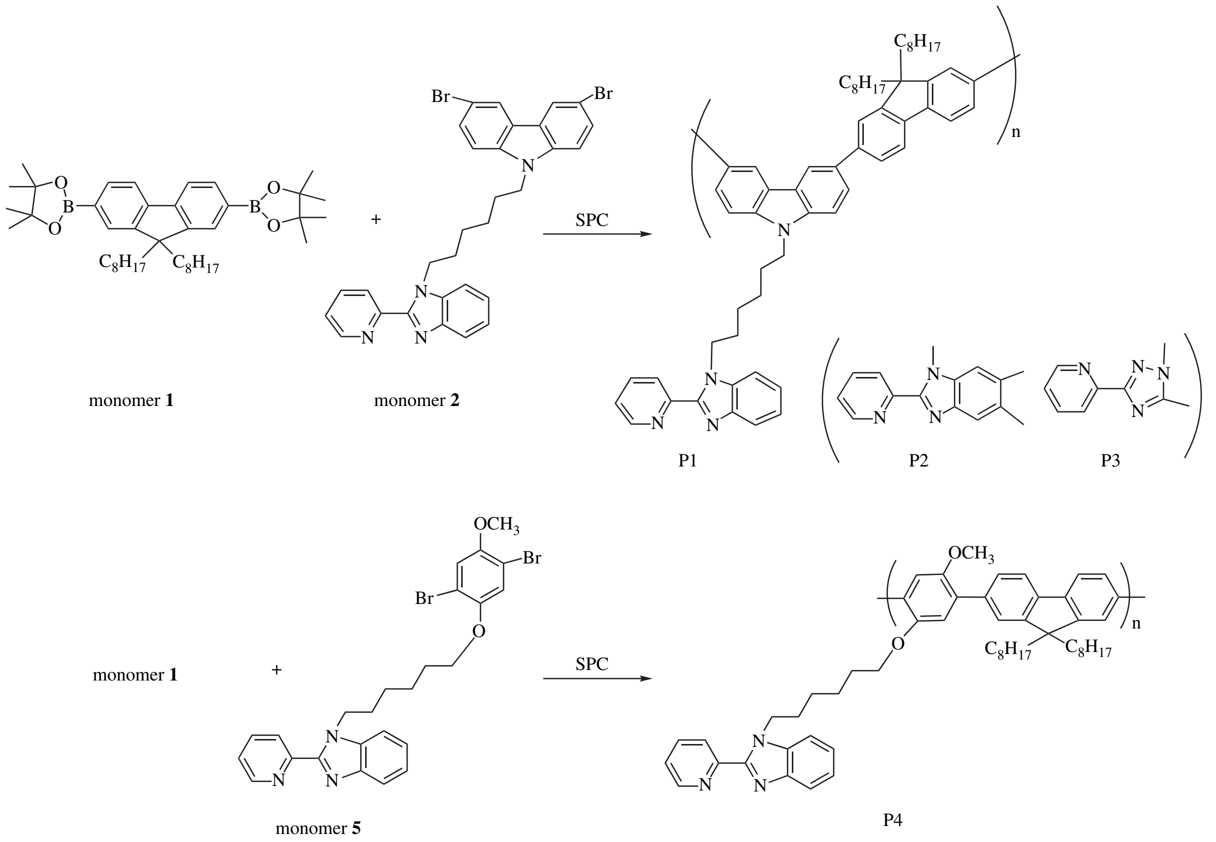
The synthetic routes of monomers are shown in Scheme 1. The monomer (**1**) 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene was prepared following the published procedure [20] and the obtained product was recrystallized from methanol to give a white solid in a yield of 50%. The monomer (**2**) 3,6-dibromo-9-(*N*-(2-(2′-pyridyl)-benzimidazole)-hexyl)-carbazole was synthesized by a coupling reaction between 2-(2′-pyridyl)-benzimidazole and 3,6-dibromo-9-(6′-bromohexyl)-carbazole in the presence of sodium hydroxide according to the published procedure [19]. The monomers (**3**–**5**) were obtained in the same way as a white solid. The polymers (P1–P4) were prepared from monomers **1** and **2**–**5** by using Suzuki polycondensation (Scheme 2). The feed ratios of monomer **1** to monomers (**2**–**5**) are 50:50 and the corresponding polymers are respectively named P1, P2, P3 and P4. The actual ratio of fluorene to receptor in polymers calculated from the elemental analysis is close to the feed ratio as listed in Table 1. Polymers are soluble in common organic solvents, such as chloroform, THF, toluene and xylene. The number-average molecular weight (M_n) and polydispersity (PDI) of polymers (P1–P4) are summarized in Table 1.

3.2. Optical properties

UV–vis absorption spectra of polymers in solid film are depicted in Fig. 1(a). The absorption peaks of polymers (P1–P3) around 346 nm can be assigned to the π–π* transition of conjugated backbone. The absorption peak of P4 at 372 nm can be assigned to the π–π* transition of conjugated backbone and the absorption peaked at 317 nm can be due to the pendant 2-(2′-pyridyl)-benzimidazole group by comparison with the absorption data of 2-(*N*-(2′-pyridyl)-hexyl)-benzimidazole, respectively. The absorption and emission data of polymers (P1–P4) are summarized in Table 2. In comparison with P4



Scheme 1. Synthetic routes of the monomers.



Scheme 2. Synthetic routes for polymers.

containing an almost linear conjugation chain structure, the blue shift ($\Delta\lambda = 30$ nm) of absorption peaks of P1–P3 is probably attributed to their zigzag chain structure [22]. The carbazole at the 3,6-linkage can effectively decrease the conjugation length of polymer backbone. From the similarity in absorption and emission spectra of polymers (P1–P3), it is observed that the introduction of different receptors in the side chain has little effect on the conjugation length of polymer backbone. Being consistent with the absorption spectra, the emission peaks of polymers (P1–P3) show the blue shift (about $\Delta\lambda = 13$ nm) compared with P4, which is a further evidence of the shorter conjugation length of the backbone.

3.3. Electrochemical properties

The electrochemical characteristics of the polymer thin films coated on Pt electrode were investigated by cyclic voltammetry (CV). The highest occupied molecular orbital (HOMO) levels were calculated according to the empirical formula $E_{\mathrm{HOMO}} = -e(E_{\mathrm{ox}} + 4.4)$, where E_{ox} is the onset oxidation potential vs. SCE. Because no reversible n-doping process was observed on the cyclic voltammograms, the LUMO levels were estimated from the HOMO values and values of optical band gaps (E_g^{opt}) by the empirical formula $E_{\mathrm{LUMO}} = E_{\mathrm{HOMO}} + E_g^{\mathrm{opt}}$. The optical band gap was obtained from the equation $E_g^{\mathrm{opt}} = 1240/\lambda_{\mathrm{edge}}$, where λ_{edge} is the onset value of absorption spectrum of solid film in long wavelength direction [20]. The electrochemical data of polymers are summarized in Table 2. The carbazole-based polymers (P1–P3) with different functional groups attached at the side chain have similar HOMO and LUMO levels. The HOMO levels increase and the LUMO levels of polymers (P1–P3) decrease compared with polyfluorene (PFO), owing to the introducing of the electron-rich carbazole moiety on the backbone [21,22].

Table 1
Structural characterization of the polymers

Polymer	M_n ($\times 10^3$)	PDI	Fluorene/receptor content[a] (mol%)	
			In feed ratio	In polymers
P1	6.8	1.74	50:50	54:46
P2	6.9	1.72	50:50	55:45
P3	12	1.56	50:50	53:47
P4	23	1.63	50:50	53:47

[a] Determined from the data of elemental analyses of polymers.

3.4. Responsive properties on metal ions and H^+

Polymers had no response upon addition of alkali and alkaline earth metal ions (up to 100 ppm) for absorption and fluorescence spectra due to the poor coordination ability of the receptors with these metal ions. No obvious change in the absorption spectra upon the addition of transition metal ions (up to 100 ppm) was observed, which was not as apparent as that of those materials containing acceptors directly in conjugated

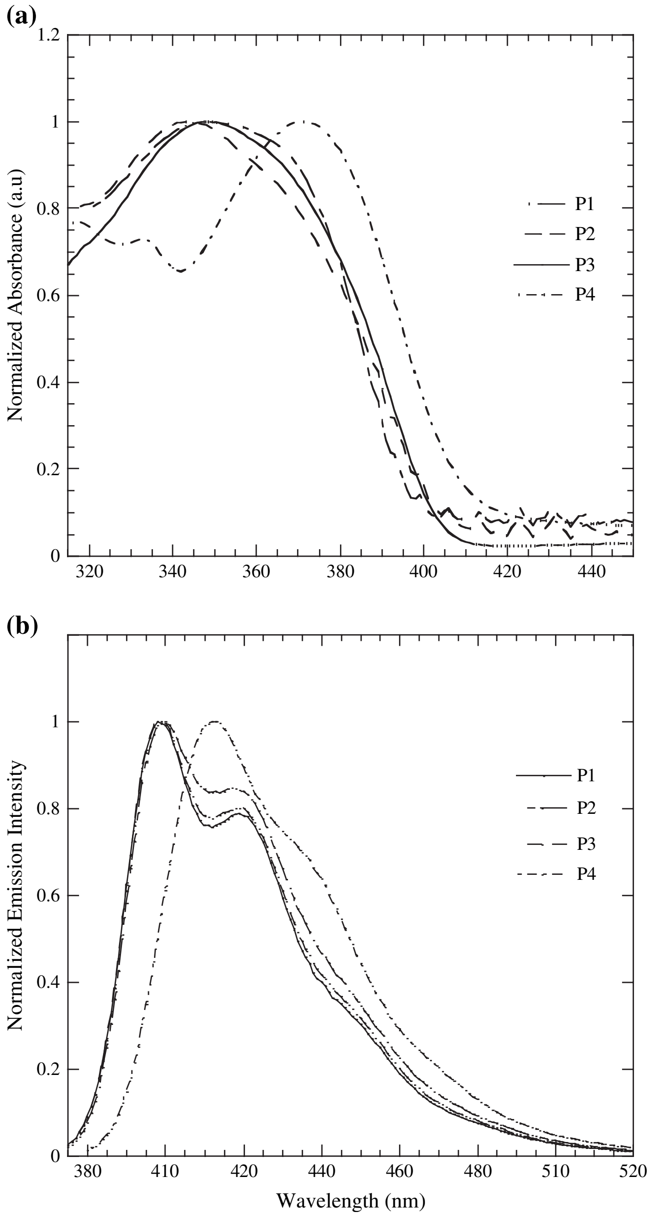


Fig. 1. The absorption spectra of polymers in film (a) and emission spectra of polymers in THF (b).

main chain, because the interaction of metal ions with receptors in the side chain had little effect on the electronic structure of the backbone [14].

Table 2
Optical and electrochemical properties of the polymers

Polymer	$\lambda_{max(abs)}$[b] (nm)	$\lambda_{max(PL)}$[a] (nm)	E_g^{opt}[b] (eV)	E_{ox} (V)	HOMO (eV)	LUMO[c] (eV)
PFO	386	417	2.85	1.38	−5.77	−2.22
P1	346	400	2.98	0.96	−5.36	−2.38
P2	348	400	2.98	0.98	−5.38	−2.40
P3	348	399	3.02	1.0	−5.41	−2.39
P4	317, 372	413	2.88	1.28	−5.68	−2.80

[a] Determined from the PL spectra in THF solution.
[b] Determined from the absorption spectra in film.
[c] Calculated from $E_{LUMO} = E_{HOMO} + E_g^{opt}$.

Table 3
Fluorescence emission response of the polymers to metal ions[a]

Ion	(I_0/I)[b]			
	P1	P2	P3	P4
–	s/1[c]	s/1	s/1	s/1
Ag^+	w/37	q/67	w/15	w/15
Co^{2+}	q/110	q/558	w/40	w/44
Ni^{2+}	q/111	q/561	q/110	w/38
Cu^{2+}	s/1.3	s/1.1	s/1.2	s/1.1
Sn^{2+}	m/6	q/15	s/1.0	m/12
Zn^{2+}	s/1.0	s/1.1	s/1.2	s/1.2
Pb^{2+}	s/1.1	s/1.2	s/1.3	s/1.1
Mn^{2+}	s/1.7	s/1.4	s/1.2	s/1.2
Cd^{2+}	m/3.5	w/11	s/1.1	s/1.2
Al^{3+}	w/24	q/262	s/3.2	w/29
Fe^{3+}	q/67	q/560	w/11	q/300

[a] The polymer (5.0×10^{-6} M) and metal ions (1.0×10^{-4} M) in THF solution. Metal salts used: $NiCl_2$, $AgNO_3$, $CoCl_2$, $FeCl_3$, $CuSO_4$, $SnCl_2$, $ZnSO_4$, $Al_2(SO_4)_3$, $Pb(OAc)_2$, $MnCl_2$, and $CdCl_2$.
[b] I_0: original emission intensity, I: emission intensity upon the addition of metal ions.
[c] The emission intensity: s, strong (hardly quenched); m, medium (slightly quenched); w, weak (efficiently quenched); q, quenched (completely quenched).

The influences of various metal ions on the fluorescence emission response of the polymers are shown in Table 3. Ni^{2+}, Co^{2+}, Ag^+ and Fe^{3+} ions caused complete fluorescent quenching of all polymers, which was tentatively attributed to the energy or electron-transfer reactions between the polymer backbone and binding metal complexes in the side chain [15]. Cu^{2+} ion hardly quenched the fluorescence of all polymers even at a high concentration (100 ppm). However, for those oligopyridyl-functionalized conjugated polymers, the fluorescence could be completely quenched by Cu^{2+} at a very low concentration [8–13]. Such distinct ion responsive behaviors revealed the obvious difference of coordination abilities of Cu^{2+} between 2-(2′-pyridyl)-benzimidazole and 5-methyl-3-(pyridin-2-yl)-1,2,4-triazole, and oligopyridine receptors. As a result, the development of tailored sensory materials for selectively sensing of metal ions could be realized through appropriate alteration of receptors with various degrees of affinity toward metal ions [14]. The same result was observed by Mn^{2+} ion (Table 3). The responsive selectivities of P4 to metal ions are depicted in Fig. 2 and Table 3. The tested metal ions could be categorized into three groups according to the data of (I_0/I): (1) Cd^{2+}, Pb^{2+}, Zn^{2+}, Cu^{2+} and Mn^{2+}, slightly quenched; (2) Al^{3+}, Ag^+, Co^{2+}, Sn^{2+} and Ni^{2+}, efficiently quenched; (3) Fe^{3+}, completely quenched.

A Stern–Volmer fluorescence quenching analysis by Ni^{2+} ion in the P1 and P4 solutions is shown in Fig. 3. The concentrations of polymers were fixed at 5.0×10^{-6} M corresponding to receptor units. The polymers (P1 and P4) used 2-(2′-pyridyl)-benzimidazole unit as a receptor with the different backbone and P4 has longer conjugation length in comparison with P1 (see Fig. 1). P1 was more sensitive to Ni^{2+} ion compared with P4. The fluorescence of P1 was quenched to 50 (I_0/I) upon the addition of a Ni^{2+} solution of 3.2×10^{-6} M, whereas the fluorescence of P4 was only quenched to 22

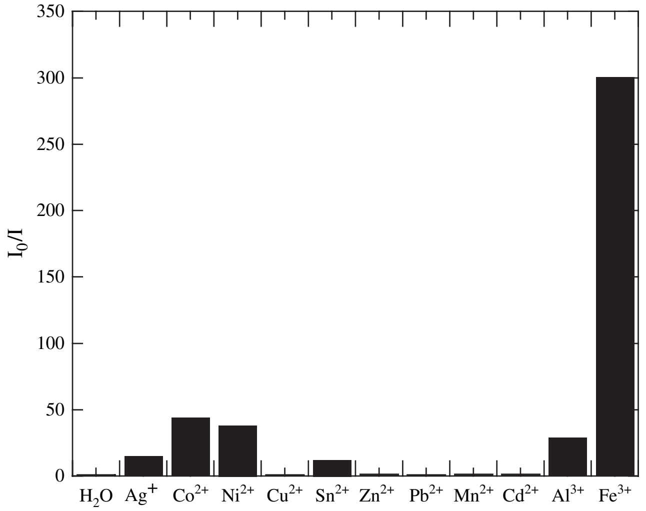


Fig. 2. The fluorescence emission response profiles of P4. The polymer concentration is 5.0×10^{-6} M corresponding to receptor unit and the metal ions concentration is 1.0×10^{-4} M in THF solution.

(I_0/I) in a Ni^{2+} solution of 5.0×10^{-6} M. Based on Fig. 3, the corresponding Stern–Volmer constants (K_{sv}) were calculated at 1.7×10^7 and 4.05×10^6 for P1 and P4, respectively. The observed higher K_{sv} of P4 suggested that the backbone structure and the efficiencies of energy or electron transfer between backbone and receptor ions in the side chain play important roles in fluorescence quenching [4]. The effects of the chelating ability of the 2-(2′-pyridyl)-benzimidazole and 6,7-dimethyl-2-(2′-pyridyl)-benzimidazole groups in polymers on the fluorescence quenching properties were investigated (Fig. 3). There was no obvious difference in the ion sensitivity between P1 and P2 in the low Ni^{2+} concentrations. However, the receptor-dependent response of the polymers to Al^{3+} was obvious between P2 and P3, containing different receptors in the side chain and the same conjugated backbone. The fluorescence of P2 was quenched to 262 (I_0/I) whose quenching ratio was above 99.7% upon the addition of a Al^{3+} solution of 1×10^{-4} M, while the fluorescence of P3 was quenched only to 3.2 (I_0/I) in the same concentration (Table 3). The receptor-dependent response of the polymers to Sn^{2+} was also obvious. The fluorescence of P3 was hardly quenched by Sn^{2+} ion, whereas the fluorescence of P2 was efficiently quenched. There was poor selectivity of P2 to metal ions when the quencher concentration was as high as 100 ppm. However, P2 showed good selectivity to Ni^{2+} when the quencher concentration was as low as 5 ppm, probably owing to the different chelating ability of receptor with ion [9]. The fluorescence was quenched to 1% of its initial intensity in the presence of Ni^{2+}, while the quenching was hardly observed in the presence of Fe^{3+}, Al^{3+}, Pb^{2+}, Zn^{2+}, Cu^{2+}, Ag^+, Sn^{2+} and Mn^{2+} ions in the same condition, as shown in Fig. 4.

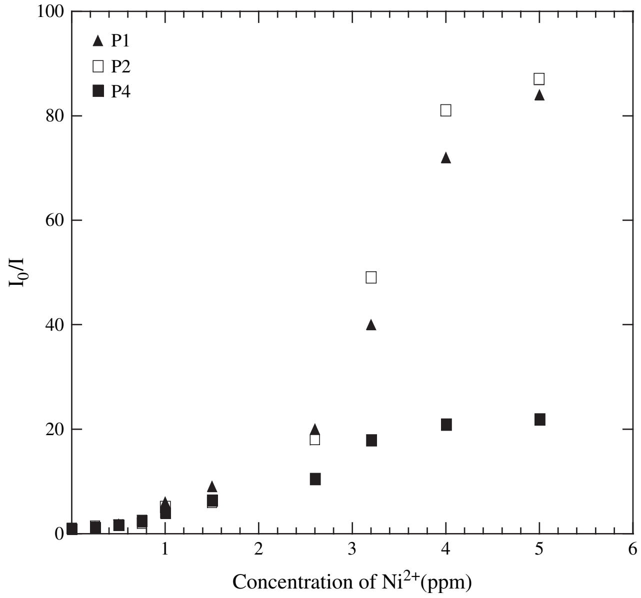


Fig. 3. The Stern–Volmer plots of the polymers emission quenched by Ni^{2+} in THF solution at room temperature.

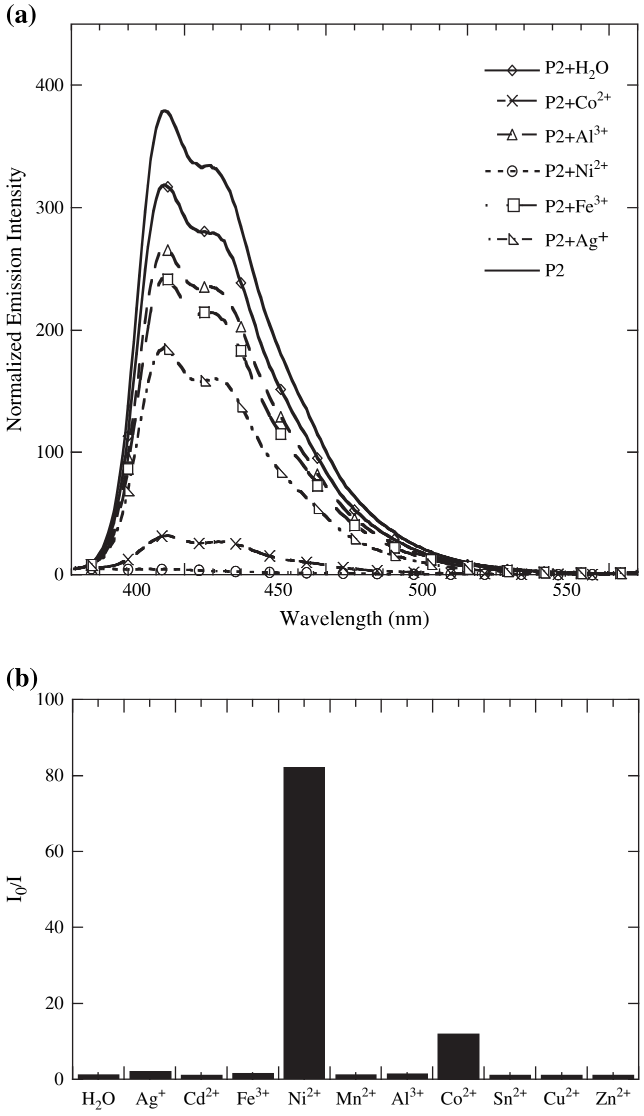


Fig. 4. Emission quenching of P2 (5.0×10^{-6} M) by different metal ions (5.0×10^{-6} M) (a) and fluorescence emission response profiles of P2 in THF solution (b).

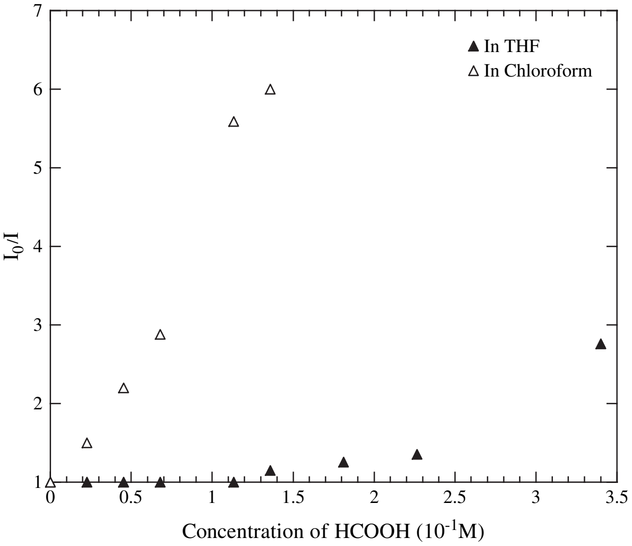


Fig. 5. The Stern−Volmer plots of the P4 (5.0×10^{-6} M) emission quenched by HCOOH in THF and $CHCl_3$ solution.

A Stern−Volmer fluorescence quenching analysis of P4 by the formic acid in different solution is shown in Fig. 5. The emission obviously decreased in chloroform solution and hardly changed in THF solution in the range of H^+ concentration from 0 to 0.15 M. The decreased quenching effect should be attributed to the hydrogen-bonding interactions between the THF and formic acid molecules [23]. The hydrogen-bonding effect weakens the interactions between the receptors and the analytes, which was also observed in polyfluorenes with phosphonate groups in the side chain as chemosensors for sensing Fe^{3+} [15]. The similar results were also shown by other polymers (P1−P3) (not listed).

4. Conclusions

The fluorescences of polymers (P1−P4) were efficiently quenched upon the transition metal ions such as Co^{2+}, Ni^{2+}, Fe^{3+} and Ag^+ due to the enhanced electronic communication properties of the conjugated polymers. The fluorescences of P1 and P4 were quenched to 50 (I_0/I) and to 22 (I_0/I) upon the addition of a Ni^{2+} solution of 3.2×10^{-6} M, as well as 5.0×10^{-6} M, respectively, owing to the different conjugated backbone. The fluorescences of P2 and P3 were completely and hardly quenched, respectively, upon the addition of a Al^{3+} solution of 1.0×10^{-4} M, owing to the different receptors in the side chain. P2 showed good selectivity to Ni^{2+} in the range of quencher concentration as low as 5 ppm, owing to the different chelating ability of receptor with ion. Cu^{2+} and Mn^{2+} ions hardly quenched the fluorescences of polymers (P1−P4), which was different from the oligopyridyl-functionalized conjugated polymers. It was demonstrated that the polymers containing 2-(2′-pyridyl)-benzimidazole and 5-methyl-3-(pyridin-2-yl)-1,2,4-triazole groups might act as promising active materials for application as fluorescent chemosensors.

Acknowledgments

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