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Fluorescent Chemosensory Conjugated Polymers Based on Optically Active Polybinaphthyls and 2,2′-Bipyridyl Units

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ABSTRACT: Chiral conjugated polymers **P-1** and **P-2** were synthesized by the polymerization of (*S*)-6,6′-di-(4-methylphenyl)-3,3′-diiodo-2,2′-bisoctoxy-1,1′-binaphthyl (***S*-M-2**) and (*S*)-6,6′-dibromo-3,3′-di(4-methylphenyl)-2,2′-bisoctoxy-1,1′-binaphthyl (***S*-M-3**) with 5,5′-divinyl-2,2′- bipyridine (**M-1**) under Heck cross-coupling reaction, respectively. The chiral polymers **P-1** and **P-2** can show strong blue-green fluorescence. The responsive properties of chiral polymers on transition metal ions and H^+ were investigated by fluorescent spectra. Cu^{2+} and Ni^{2+} lead to nearly complete fluorescent quenching of two polymers, and Zn^{2+}, Cd^{2+}, and H^+ can cause slight fluorescent quenching. Such distinct ion responsive behaviors revealed the obvious difference of coordination abilities of transition metal ions with 2,2′-bipyridyl ligand receptors. The obvious quenching effect of **P-1** and **P-2** also suggested that the chiral conjugated polymers backbone structure and the efficiencies of energy or electron transfer between backbone and receptor ions in the main chain play important roles in fluorescence quenching. The results show that the chiral conjugated polybinaphthyls incorporating the 2,2′-bipyridyl moiety as the recognition site can act as promising active materials for application as fluorescent chemosensors.

1. Introduction

Investigations on highly sensitive and selective fluorescent chemosensory materials have received much attention in recent years. In particular, numerous efforts have focused on the design of chemosensory systems with unique electrical and optical properties that are capable of detecting metal ions in both a real-time and reversible fashion.[1] The conjugated polymers incorporating molecular recognition moieties are that they can make use of the high sensitivity of conjugated polymers to external structural perturbations and to electron density changes within the conjugated polymer main backbone, when they can interact and form complexes with transition metal ions.[2] Sensitive detection methods employed for sensing metal ions involve the design of “turn-on” fluorescent chemosensors based on the photoinduced electron transfer and energy migration mechanism in conjugated polymer main backbone. Swager et al. reported that the delocalizable π-electronic conjugated “molecular wire” polymer can greatly amplify the fluorescence quenching due to facile energy migration along the polymer backbone upon the light excitations.[3]

Optically active 1,1′-binaphthol (BINOL) has often been used as the starting material for the preparation of conjugated polymers that have a main-chain chiral configuration. The skeletal structure of BINOL at the 3,3′- or 6,6′-positions of binaphthyl can be selectively functionalized at the well-defined molecular level and lead to a variety of binaphthyl derivatives which can exhibit efficient and stable chiral configuration as well as high chiral induction and chiral discrimination in molecule recognition[4] and asymmetric catalysis.[5] These rigid and regular chiral binaphthyl-based polymers also represent a new generation of materials for potential applications in areas such as fluorescence sensors in chiral molecule recognition, polarized light emission materials, and nonlinear optical materials.[6] In this paper, we report synthesis and fluorescent chemosensory material of chiral polybinaphthyls incorporating 2,2′-bipyridyl moieties in the polymer main chain by Pd-catalyzed Heck reaction. An electron-deficient heterocyclic ligand 2,2′-bipyridine as the conjugated molecular bridge linker and a metal chelating ligand are introduced into the chiral polybinaphthyl’s main-chain backbone to maintain conjugation between bipyridyl and naphthyl segments so that the electron transporting properties of the polymers may be improved and the electron density may shift away via vinylene bridge, which could increase the stability of the resulting chiral polymers.[7] This neutral chelating bipyridyl ligand in the π-conjugated polymers main chain can directly coordinate with different metal ions to form polymer complexes. In this paper, two chiral conjugated polymers **P-1** and **P-2** have strong blue-green fluorescence. Two conjugated polymers have been found to be highly sensitive to a wide variety of metal ions, and their fluorescence is efficiently or completely quenched on the addition of different metal ions and H^+. The result shows that Cu^{2+} and Ni^{2+} can lead to complete fluorescent quenching of two polymers, and Zn^{2+}, Cd^{2+}, and H^+ can cause slight fluorescent quenching. Such distinct ion responsive behaviors revealed the obvious difference of coordination abilities of transition metal ions with 2,2′-bipyridyl ligand receptors in the chiral conjugated polymer main-chain backbone. They are expected to be used as special fluorescent chemosensors for the appropriate detection of the sensitive and selective sense of metal ions.

2. Experimental Section

2.1. General. ^1H and ^{13}C NMR spectra measurements (all in $CDCl_3$) were recorded on a 300-Bruker spectrometer with TMS as an internal standard. FT-IR spectra were recorded on a Nexus 870 FT-IR spectrometer. UV−vis spectra were obtained from a Perkin-Elmer Lambda 25 spectrometer. DSC−TGA was performed on a Perkin-Elmer Pyris-1 instrument under a N_2 atmosphere. Fluorescent spectra were obtained from a 48000 DSCF spectrometer. MS was determined on a Micromass GCT. C, H, and N of elemental analyses were performed on an Elementar Vario MICRO analyzer. The circular dichroism (CD) spectrum was determined with a Jasco

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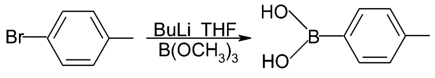
Scheme 1. Synthesis Procedure of 4-Methylphenylboronic Acid



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J-810 spectropolarimeter. Molecular weight was determined by gel permeation chromatography (GPC) with Waters-244 HPLC pump and THF was used as solvent and relative to polystyrene standards. All solvents and reagents were commercially available A.R. grade. (*S*)-1,1′-Binaphthol (BINOL) were purchased from Aldrich and directly used without purification. All reactions were performed under N_2 using Schlenk tube techniques. THF and Et_3N were purified by distillation from sodium in the presence of benzophenone. CH_2Cl_2 and CH_3CN were distilled from P_2O_5.

Metal Ion Titration. Each metal ion titration experiment was started with 4.0 mL of polymer in THF solution with a known concentration (1.26×10^{-5} M). Solutions of metal salt (acetate or chloride, 2.52×10^{-3} M) and hydrochloric acid (3.60×10^{-3} M) were used for the titration. Polymer−metal complexes were produced by adding aliquots of a solution of the selected metal salt to a THF solution of the chiral polymer (4.0 mL). The mixture was stirred constantly during the titration. Steady-state fluorescent spectra were monitored 15 min after addition of the metal salt to the polymer solutions.

2.2. Synthesis of Monomers. 2.2.1. Synthesis of 4-Methylphenylboronic Acid (Scheme 1).[8] 7.0 mL of *n*-BuLi (2.5 M in hexane, 17.5 mmol) was slowly injected to a solution of 4-bromotoluene (2.5 g, 14.6 mmol) in THF (25 mL) at −78 °C under a N_2 atmosphere. After being stirred at −78 °C for 20 min, a solution of $B(OMe)_3$ (2.28 g, 22.0 mmol in 10 mL of THF) was added to the above solution. The mixture was then stirred overnight while the temperature was gradually warmed to room temperature. The reaction was quenched with 2 N HCl (24 mL) at 0 °C for 3 h. Upon being evaporated to dryness, the residue was extracted with ethyl acetate and washed with aqueous $NaHCO_3$ and brine twice and then dried over anhydrous Na_2SO_4. The solution was evaporated under reduced pressure, and the crude product was recrystallized by H_2O to afford a white solid 4-methylphenylboronic acid **1** (1.6 g, 80.6% yield); mp: 256−263 °C. ^{1}H NMR (DMSO): δ 7.93 (s, 2H), 7.66−7.68 (d, 2H, J = 7.7 Hz), 7.12−7.14 (d, 2H, J = 7.3 Hz), 2.31 (s, 3H).

2.2.2. Preparation of 5,5′-Divinyl-2,2′-bipyridine (M − 1) (Scheme 2).[1a,7b,9] 5,5′-Dimethyl-2,2′-bipyridine was synthesized under the catalysis of Raney Ni from the starting product 3-methylpyridine according to the literature.[9] The yield was 11%; mp: 116−118 °C. ^{1}H NMR ($CDCl_3$): δ 8.48 (s, 2H), 8.22−8.25 (d, 2H, J = 8.0 Hz), 7.59−7.62 (d, 2H, J = 8.2 Hz), 2.37 (s, 6H).

5,5′-Dimethyl-2,2′-bipyridine (3.5 g, 19 mmol) was dissolved in 40 mL of benzene. 7.1 g of *N*-bromosuccinimide (NBS, 40 mmol) and 2,2′-azobis(isobutyronitrile) (AIBN, 0.1 g) were added to the above solution. After being refluxed for 8 h, the solution was cooled to room temperature, and the reaction was quenched with $NaHSO_3$. The solution was extracted with CH_2Cl_2 (2×40 mL). The combined organic layers were washed with $NaHSO_3$ and saturated brine twice and dried over anhydrous Na_2SO_4. After removal of solvent, the crude product 5,5′-bis(bromomethyl)-2,2′- bipyridine was recrystallized by CH_2Cl_2 to afford a light yellow solid. Yield was 33.7% (1.55 g); mp: 193−194 °C. ^{1}H NMR ($CDCl_3$): δ 8.74 (s, 2H), 8.54−8.56 (d, 2H, J = 8.4 Hz), 7.94−7.97 (dd, 2H, J = 8.2, J = 2.3 Hz), 4.56 (s, 4H).

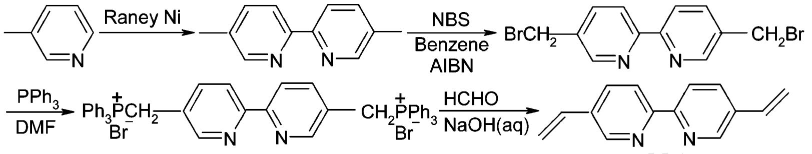
5,5′-Bis(bromomethyl)-2,2′-bipyridine (2.5 g, 7.3 mmol) and PPh_3 (5.0 g, 19 mmol) were dissolved in 40 mL of DMF. The reaction mixture was stirred at 90 °C for 8 h and produced the light yellow bisphosphonium salt deposition. The precipitate was filtered and washed with ether and then transferred into a 100 mL three-necked flask for **M-1** synthesis. A mixture of CH_2Cl_2 (40 mL) and 40% aqueous HCHO (12 mL) was added to the former flask. The solution was cooled to −5 °C and stirred vigorously. 10% aqueous NaOH (20 mL) was added dropwise over 1 h with constant stirring under N_2. The resulting mixture was stirred at room temperature overnight, and then 50 mL of water was added to the above solution. The resulting solution was extracted with CH_2Cl_2 (3×30 mL). The combined organic layers were washed with saturated brine twice and dried over anhydrous $MgSO_4$. The solvent was removed to dryness under reduced pressure to afford the mixtures. The mixtures were purified on silica column using the mixed solvents of petroleum ether and ethyl acetate (20:1, v/v) as an eluent to afford a light yellow solid **M-1** (1.3 g, 98% yield). **M-1** needs to be kept in the dark at −4 °C before using; mp: 56−58 °C. MS (EI, *m/z*): 208 (M^+, 100), 180 (32). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.68−8.69 (d, 2H, J = 1.9 Hz), 8.37−8.39 (d, 2H, J = 8.3 Hz), 7.87−7.91 (dd, 2H, J = 8.3, J = 2.2 Hz), 6.74−6.83 (dd, 2H, J = 17.7, J = 11.0 Hz), 5.89−5.95 (d, 2H, J = 17.6 Hz), 5.42−5.46 (d, 2H, J = 11.0 Hz). ^{13}C NMR ($CDCl_3$): δ 155.34, 148.17, 133.94, 133.67, 133.42, 121.85, 116.82. Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.82; N, 13.45. Found: C, 80.76; H, 5.75; N, 13.37. FT-IR (KBr, cm^{-1}): 3001.9, 1628.8, 1589.4, 1542.1, 1467.9, 1366.9, 1250.4, 1023.3, 911.1, 845.9, 749.8.

2.2.3. Preparation of *S*-M-2 (Scheme 3).[10,11] (*S*)-6,6′-Dibromo-1,1′-binaphthol and (*S*)-6,6′-dibromo-2,2′-bis(methoxymethoxy)-1,1′- binaphthyl (**2**) were prepared and purified as reported in the literature.[10]

The product **3** was synthesized according to the general Suzuki coupling reaction. **2** (1.8 g, 3.38 mmol) and $Pd(PPh_3)_4$ (390 mg, 0.338 mmol) were mixed in DME (25 mL) under a N_2 atmosphere. **1** (1.61 g, 11.8 mmol) and 2 M K_2CO_3 solution (8.8 mL) were added to the above the solution. The resulting mixture was stirred and refluxed for 10 h under a N_2 atmosphere. The mixture was cooled to room temperature, and the solution was filtered through a short column of silica gel with ethyl acetate as an eluent. After removal of solvents under reduced pressure, the residue was extracted by CH_2Cl_2 (2×40 mL) and washed with water and brine twice and dried over anhydrous Na_2SO_4. After removal of solvent, the crude product (*S*)-6,6′-di(4-methylphenyl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl (**3**) was purified on silica column using the mixed solvents of petroleum ether and ethyl acetate (10:1, v/v) as an eluent to afford a pale yellow solid **3** (1.41 g, 75.2% yield); mp: 59−62 °C; $[\alpha]_D = +113.3$ (*c* 0.28, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 8.09 (s, 2H), 8.03 (d, 2H, J = 9.1 Hz), 7.59−7.65 (m, 6H), 7.52 (d, 2H, J = 8.7 Hz), 7.20−7.28 (m, 6H), 5.13−5.15 (d, 2H, J = 6.9 Hz), 5.02−5.05 (d, 2H, J = 6.8 Hz), 3.21 (s, 6H), 2.42 (s, 6H). FT-IR (KBr, cm^{-1}): 3021.4, 2952.4, 2899.4, 1594.4, 1518.4, 1494.2, 1477.8, 1345.8, 1241.5, 1185.5, 1149.9, 1074.0, 1038.5, 1020.4, 921.6, 811.0.

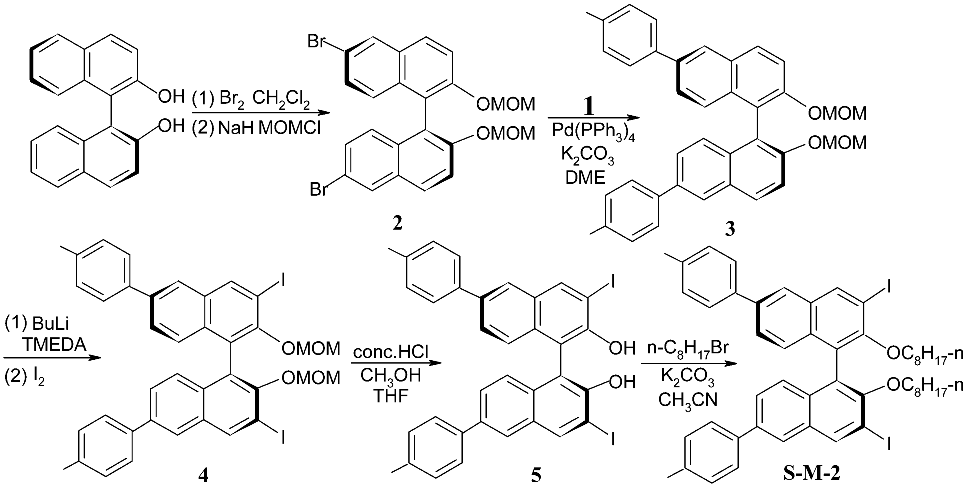
A solution of **3** (1.42 g, 2.56 mmol) and TMEDA (1.20 g, 10.2 mmol) was dissolved in 30 mL of THF. 4.1 mL of *n*-BuLi (2.5 M in hexane, 10.2 mmol) was added to the above solution at room temperature under a N_2 atmosphere. The solution was stirred for 6.5 h at room temperature, and then the solution of iodine (3.25 g, 12.8 mmol in 30 mL of THF) was slowly injected to the mixed solution at −78 °C under a N_2 atmosphere. The mixture was then stirred overnight while the temperature was gradually warmed to

Scheme 2. Synthesis Procedures of M-1

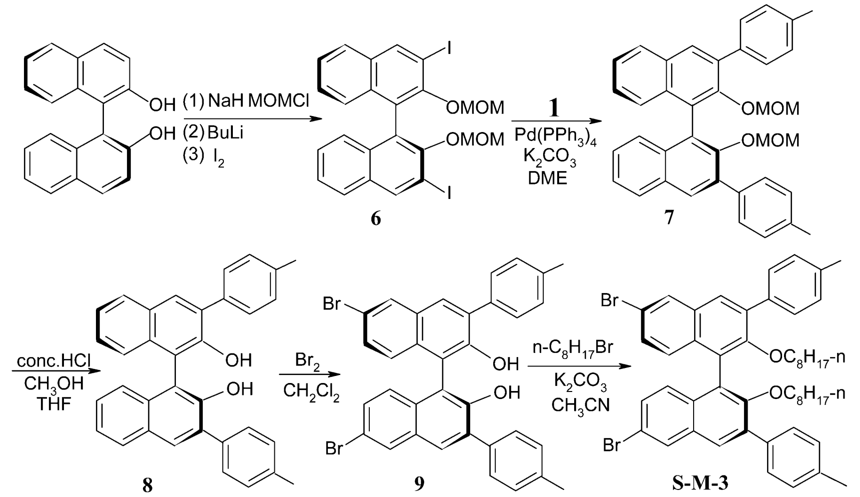


M-1

Scheme 3. Synthesis Procedures of *S*-M-2



Scheme 4. Synthesis Procedures of *S*-M-3



room temperature. The reaction was quenched with 10% aqueous $Na_2S_2O_3$ (40 mL). After removal of solvent under reduced pressure, the residue was extracted with ethyl acetate (2 × 50 mL), the combined organic layers were washed with water and brine twice. The solution was dried over Na_2SO_4 and concentrated to give a crude product. Purification was carried out by column chromatography (petroleum ether/ethyl acetate) (30:1 v/v) to afford a yellow solid product (*S*)-6,6′-di(4-methylphenyl)-3,3′-diiodo-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl (**4**) (0.92 g, 44.6% yield). The product **4** was dissolved in the mixed solvents of 30 mL of ether and 20 mL of methanol. 20 mL of HCl (12 M) solution was added to the above the solution. The solution was stirred at room temperature for 8 h. After the removal of solvent under reduced pressure, the residue was extracted with ethyl acetate (2 × 50 mL). The combined organic layers were washed with 10% aqueous Na_2CO_3 and brine twice and dried over anhydrous Na_2SO_4. After removal of solvent, an orange pure product (*S*)-6,6′-di(4-methylphenyl)-3,3′-diiodo-1,1′-binaphthol (**5**) was obtained in the yield of 96.4% (790 mg); mp: 105−108 °C. ^1H NMR ($CDCl_3$): δ 8.59 (s, 2H), 7.99 (s, 2H), 7.56−7.62 (m, 6H), 7.19−7.31 (m, 6H), 5.49 (s, 2H), 2.43 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 150.2, 141.1, 140.1, 139.9, 138.2, 137.9, 137.8, 131.5, 130.1, 128.2, 127.4, 125.4, 125.1, 77.8, 77.4, 77.0, 21.5.

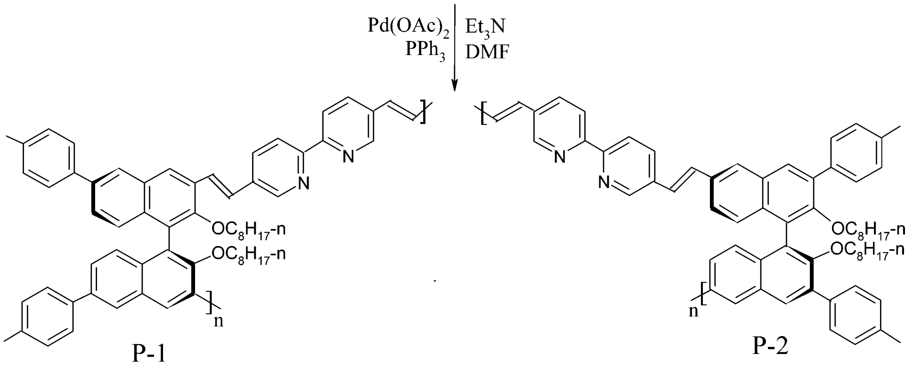
A mixture of **5** (200 mg, 0.28 mmol), K_2CO_3 (310 mg, 2.2 mmol), and *n*-$C_8H_{17}Br$ (210 mg, 1.1 mmol) was dissolved in 20 mL of CH_3CN. The solution was refluxed overnight. After being evaporated to dryness, the residue was extracted with petroleum ether (3 × 20 mL). The solution was washed with 5% aqueous NaOH (30 mL) and brine and then dried over anhydrous Na_2SO_4. After removal of solvent, the cruder product was purified by chromatography on silica gel with petroleum ether as an eluent to afford a viscous product (*S*)-6,6′-di(4-methylphenyl)-3,3′-diiodo-2,2′-bisoctoxy-1,1′-binaphthyl (***S*-M-2**) (250 mg, 95.2% yield); $[\alpha]_D = +19.53$ (*c* 0.26, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 8.55 (s, 2H), 7.95 (s, 2H), 7.51−7.57 (m, 6H), 7.19−7.28 (m, 6H), 3.81−3.88 (dd, 2H, $J = 14.3$, $J = 6.0$ Hz), 3.33−3.40 (dd, 2H, $J = 14.4$, $J = 6.6$ Hz), 2.40 (s, 6H), 1.05−1.23 (m, 24H), 0.83 (t, 6H, $J = 7.2$ Hz). ^{13}C NMR ($CDCl_3$): δ 154.5, 140.1, 138.4, 137.9, 137.8, 133.4, 132.8, 130.0, 127.4, 126.8, 125.9, 124.6, 93.9, 32.2, 30.1, 29.6, 29.4, 25.9, 23.1, 21.5, 14.5. Anal. Calcd for $C_{50}H_{56}I_2O_2$: C, 63.69; H, 6.00. Found: C, 63.62; H, 5.88.

2.2.4. Preparation of *S*-M-3 (Scheme 4).[11,12] (*S*)-2,2′-Bis(methoxymethoxy)-1,1′-binaphthyl and (*S*)-3,3′-diiodo-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl (**6**) were prepared and purified according to the literature.[11]

The synthesis of **7** was carried out by the same procedure as **3** according to the general Suzuki coupling reaction. **6** (1.2 g, 1.6 mmol) and $Pd(PPh_3)_4$ (187.7 mg, 0.16 mmol) were dissolved in DME (20 mL) at room temperature under a N_2 atmosphere. **1** (770 mg, 5.7 mmol) and 4.3 mL of aqueous Na_2CO_3 solution (2 M) were added to the above solution. The resulting mixture was stirred and refluxed for 10 h under a N_2 atmosphere. The solution was gradually cooled to room temperature, and the solution was filtered through a short column of silica gel with ethyl acetate as an eluent. After removal of solvents under reduced pressure, the residue was extracted with CH_2Cl_2 (2 × 40 mL) and washed with water and brine twice and then dried over anhydrous Na_2SO_4. After removal of solvent, the crude product (*S*)-3,3′-di(4-methylphenyl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl (**7**) was further purified by column chromatography (petroleum ether/ethyl acetate) (20:1 v/v)

Scheme 5. Synthesis Procedures of Polymer P-1 and P-2

M-1 + S-M-2 / S-M-3



to afford a pure solid product **7** (620 mg, 67% yield). The product **7** was dissolved in mixed solvents of 20 mL of ether and 10 mL of methanol. 12 mL of HCl (12 M) solution was added to the above the solution. The solution was stirred at room temperature for 8 h. After the removal of solvent under reduced pressure, the residue was extracted with ethyl acetate (2 × 30 mL) and washed with 10% aqueous Na_2CO_3 and brine twice and then dried over anhydrous Na_2SO_4. After removal of solvent, a brown pure product (*S*)-3,3′-di(4-methylphenyl)-1,1′-binaphthol (**8**) was obtained in the yield of 93.3% (490 mg); $[\alpha]_D = -53.7$ (*c* 0.13, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 8.02 (s, 2H), 7.92−7.95 (d, 2H, $J = 7.6$ Hz), 7.64−7.66 (d, 4H, $J = 8.0$ Hz), 7.23−7.43 (m, 10H), 5.37 (s, 2H), 2.45 (s, 6H). FT-IR (KBr, cm^{-1}): 3509.7, 3051.6, 3025.2, 2952.9, 2918.8, 2866.2, 1619.0, 1595.1, 1513.7, 1497.4, 1434.8, 1401.7, 1382.3, 1359.1, 1237.0, 1212.1, 1167.0, 1145.2, 1125.5, 1021.6, 896.1, 818.1, 748.6, 729.0.

8 (490 mg, 1.06 mmol) was dissolved in 10 mL of CH_2Cl_2 and cooled to −50 °C. Bromine (0.12 mL, 2.22 mmol in 10 mL of CH_2Cl_2) was slowly added to the solution. The reaction mixture was stirred overnight and gradually warmed to room temperature. The reaction was quenched with 10% aqueous $Na_2S_2O_3$ (40 mL). After removal of solvent under reduced pressure, the residue was extracted with ethyl acetate (2 × 40 mL); the combined organic layers were washed with 10% aqueous $Na_2S_2O_3$ and brine twice and then dried over Na_2SO_4. After removal of solvent, the crude product (*S*)-6,6′-dibromo-3,3′-di(4-methylphenyl)-1,1′-binaphthol (**9**) was recrystallized by CH_2Cl_2 in a 91% yield; $[\alpha]_D = -50.2$ (*c* 0.15, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 7.96 (s, 2H), 7.65 (s, 2H), 7.50−7.52 (d, 2H, $J = 8.2$ Hz), 7.27−7.34 (m, 10H), 6.09 (s, 2H), 2.45 (s, 6H). FT-IR (KBr, cm^{-1}): 3493.8, 3025.7, 2958.9, 2920.0, 2854.2, 1588.0, 1513.3, 1484.7, 1437.6, 1400.6, 1356.0, 1259.7, 1231.2, 1212.0, 1185.4, 1132.2, 1073.2, 1021.5, 935.5, 901.9, 818.9, 726.2.

A mixture of **9** (560 mg, 0.9 mmol), K_2CO_3 (1.0 g, 7.2 mmol), and *n*-C_8H_{17}Br (700 mg, 3.6 mmol) was dissolved in 30 mL of CH_3CN. The solution was refluxed overnight. After being evaporated to dryness, the residue was extracted with petroleum ether (3 × 30 mL). The solution was washed with 5% aqueous NaOH (30 mL) and brine twice and then dried over anhydrous Na_2SO_4. After removal of solvent, the cruder product was purified by chromatography on silica gel with petroleum ether as an eluent to afford a yellow viscous product (*S*)-6,6′-dibromo-3,3′-di(4-methylphenyl)-2,2′-bisoctoxy-1,1′-binaphthyl (***S*-M-3**) (500 mg, 67.7% yield); $[\alpha]_D = +26.1$ (*c* 0.38, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 8.02 (s, 2H), 7.81 (s, 2H), 7.61−7.63 (d, 4H, $J = 8.1$ Hz), 7.26−7.31 (m, 6H), 7.04−7.07 (d, 2H, $J = 8.7$ Hz), 3.37−3.39 (m, 2H), 3.07−3.09 (m, 2H), 2.42 (s, 6H), 0.69−1.12 (m, 30H). ^{13}C NMR ($CDCl_3$): δ 154.5, 137.6, 137.0, 136.0, 132.3, 132.2, 130.5, 130.3, 129.7, 129.5, 129.4, 128.4, 126.5, 119.1, 73.1, 30.1, 29.9, 29.5, 29.3, 25.9, 23.0, 21.7, 14.5. FT-IR (KBr, cm^{-1}): 3027.2, 2956.3, 2926.1, 2854.9, 1585.2, 1514.6, 1465.6, 1436.2, 1377.9, 1348.6, 1258.2, 1241.6, 1186.3, 1069.0, 1027.8, 900.6, 822.0, 724.1. Anal. Calcd for $C_{50}H_{56}Br_2O_2$: C, 70.75; H, 6.66. Found: C, 70.86; H, 6.57.

2.3. Preparation of Polymers P-1 and P-2 (Scheme 5). A mixture of ***S*-M-2** (157.6 mg, 0.16 mmol) and **M-1** (34.8 mg, 0.16 mmol) was dissolved in the mixed solvents of 6 mL of DMF and 0.2 mL of Et_3N. The solution was first bubbled with N_2 for 15 min before 5 mol % $Pd(OAc)_2$ (1.9 mg, 0.0084 mmol) and 25 mol % PPh_3 (11.0 mg, 0.042 mmol) were added to the above solution. The temperature of the mixture was kept at 130 °C for 12 h under N_2 and then refluxed at 140 °C for an additional 2 h. The mixture was cooled to room temperature and then was filtered through a short silica gel column in methanol (60 mL) to precipitate out the polymer. The resulting polymer was filtered and washed with methanol several times. Further purification could be conducted by dissolving the polymer in CH_2Cl_2 to precipitate in methanol again. **P-1** was dried in vacuum to give 125 mg in 83.4% yield. **P-1** spectroscopic data: $[\alpha]_D = +136.2$ (*c* 0.05, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): 0.79−1.17 (m, 30H), 2.44 (s, 6H), 3.48 (br, 2H), 3.75 (br, 2H), 7.29−7.63 (m, 12H), 7.80 (br, 2H), 8.08−8.17 (m, 6H), 8.38 (br, 2H), 8.47 (br, 2H), 8.89 (br, 2H). Anal. Calcd for $C_{64}H_{66}N_2O_2$: C, 85.91; H, 7.38; N, 3.13. Found: C, 82.62; H, 6.89; N, 3.05. FT-IR (KBr, cm^{-1}): 3020.8, 2953.2, 2920.1, 2851.0, 1589.7, 1465.5, 1434.4, 1261.3, 1227.0, 1095.7, 1019.2, 963.8, 807.9.

P-2 was synthesized by using the same method as **P-1**. **P-2** spectroscopic data: $[\alpha]_D = +120.0$ (*c* 0.05, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): 0.80−1.14 (m, 30H), 2.45 (s, 6H), 3.17 (br, 2H), 3.40 (br, 2H), 7.28−7.43 (m, 6H), 7.52−7.75 (m, 12H), 7.87−8.12 (m, 4H), 8.44 (br, 2H), 8.81 (br, 2H). Anal. Calcd for $C_{64}H_{66}N_2O_2$: C, 85.91; H, 7.38; N, 3.13. Found: C, 81.47; H, 6.91; N, 2.97; FT-IR (KBr, cm^{-1}): 3025.8, 2949.1, 2922.1, 2852.4, 1588.4, 1465.6, 1431.9, 1376.6, 1246.2, 1215.3, 1199.6, 1021.4, 960.0, 821.2.

3. Results and Discussion

3.1. Syntheses and Features of Polymers. The chirality of 1,1′-BINOL and its derivatives is derived from the restricted rotation of the two naphthalene rings. The rigid structure and C_2 symmetry of the chiral binaphthyl molecules can play an important role in inherently chiral induction.[4a,6g,13] ***S*-M-2** and ***S*-M-3** were synthesized from (*S*)-BINOL by a six-step synthesis (Schemes 3 and 4, respectively). ***S*-M-2** and ***S*-M-3** can serve as the monomers for the synthesis of the desired chiral polymers. The octoxy and 4-methylphenyl group substitutents on binaphthyl rings as side chain of the polymers can improve solubility dramatically in common organic solvents but also modify the electronic properties and conjugated structure of chiral polymers. Two chiral conjugated polymers **P-1** and **P-2** containing a vinylene bridge between naphthyl and the 2,2′-bipyridyl group can reduce steric hindrance between backbone rings and groups and also have a beneficial effect on delocalizable π-electronic conjugation structure of polymers.[7b,f]

Heck coupling reaction is one of the most important C−C coupling reactions in organic chemistry synthesis.[14] Compared

Table 1. Polymerization Results and Characterization of P-1 and P-2

	yield (%)	M_w[a]	M_n[a]	PDI	$[\alpha]_D$[b]
P-1	83.4	7400	3600	2.06	+136.2
P-2	75.1	12000	3500	3.42	+120.0

[a] M_w, M_n, and PDI of **P-1** and **P-2** were determined by gel permeation chromatography using polystyrene standards in THF. [b] Temperature at 20 °C and solvent in CH_2Cl_2 ($c = 0.05$).

to other synthetic approaches, the Pd-catalyzed Heck reaction is relatively mild and gives an easy access to various monomers in the preparation of functionalized PPVs. In this paper, a typical Heck reaction condition was applied to the polymerization. The C−C cross-coupling process was easily carried out in DMF in the presence of a catalytic amount (5 mol %) of $Pd(OAc)_2$ with Et_3N and triphenylphosphate (PPh_3) under N_2. The polymerization went on quickly in a good yield. Instead of the Wittig method, the Heck synthetic route was used for the preparation of the chiral polymers because the Heck reaction directly produced the desired polymers with trans configuration.[1g,7b,15] Pu also reported the Heck coupling of the chiral binaphthyl monomers with the divinyl monomers. GPC analysis results of polymers indicated that neither the halogen atoms nor the size of the alkyl groups in the binaphthyl monomers had an effect on the molecular weight of the polymers.[15c] Minor-groove polymer **P-1** was obtained at the 3,3′-positions of ***S*-M-2** with **M-1**, and major-groove polymer **P-2** was obtained at the 6,6′-positions of ***S*-M-3** and **M-1**.[4a,5b,7f] The GPC results of the polymers **P-1** and **P-2** show the moderate molecular weight. GPC analysis and the specific rotation results of two polymers are listed in Table 1. Two chiral conjugated polymers show good solubility in some common solvents such as CH_2Cl_2, THF, and DMF, which can be attributed to the nonplanarity of the twisted polymers in the main-chain backbone and flexible octoxy and 4-methylphenyl group substitutents on binaphthyl units as side chain of the polymer.

The 2,2′-bipyridyl ligand has been used extensively as a neutral metal chelating ligand in a variety of approaches dealing with structural coordination chemistry or functional systems based on 2,2′-bipyridyl metal complexes due to its redox stability and ease of functionalization. There are a few reports on polymeric ligands with 2,2′-bipyridyl moiety and their corresponding polymer complexes with transition metal ions.[1a,f,2f,16] But so far, there are few reports on the bipyridyl unit as the precursor into the chiral conjugated polybinaphthyls main chain in a well-defined spatial arrangement.[7b] The chiral conjugated polymers have a strong fluorescence and can directly coordinate with metal ions to form polymer complexes. The introduction of metal ions may lead to the complete or efficient quench of polymer fluorescence. They are expected to be used as special chemosensory materials to detect some metal ions.

3.2. Thermal Analysis of Polymers. **P-1** and **P-2** are air stable solid with yellow-green color. Thermogravimetric analyses (TGA) of two polymers were carried out under a N_2 atmosphere at a heating rate of 10 °C/min (Figure 1). Both **P-1** and **P-2** show no glass transition temperature (T_g). According to Figure 1, the TGA plot of **P-1** is different from that of **P-2**, and **P-1** has a higher thermal stability than **P-2**. There is no loss weight before 225 °C for **P-1,** but there is about 1.5% loss of weight before 225 °C for **P-2**. Under a N_2 atmosphere, **P-1** appears an apparently one-step degradation at temperature ranging from 285 to 650 °C and tends to complete decomposition at 700 °C. A total loss of about 42% is observed when heated to 700 °C. But **P-2** exhibits a slow two-step degradation process: the first step degradation is observed at temperature ranging from 225 to 350 °C, and the second step degradation appears at temperature ranging from 350 to 620 °C. **P-2** tends to complete decomposition at 680 °C. A total loss of about 40% is observed when heated to 700 °C.

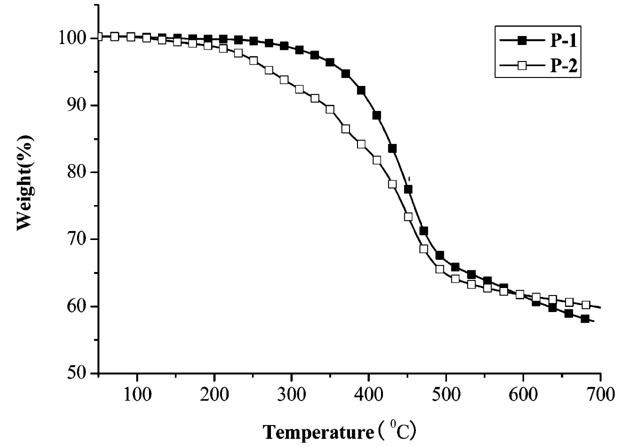


Figure 1. TGA curves of **P-1** and **P-2**.

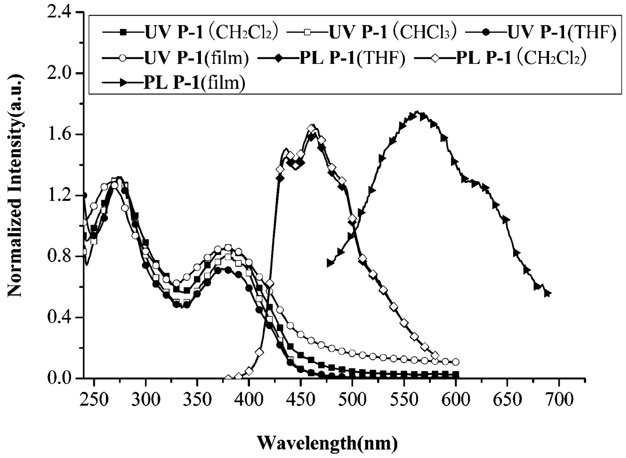


Figure 2. UV−vis and fluorescence spectra of **P-1** in solution and film.

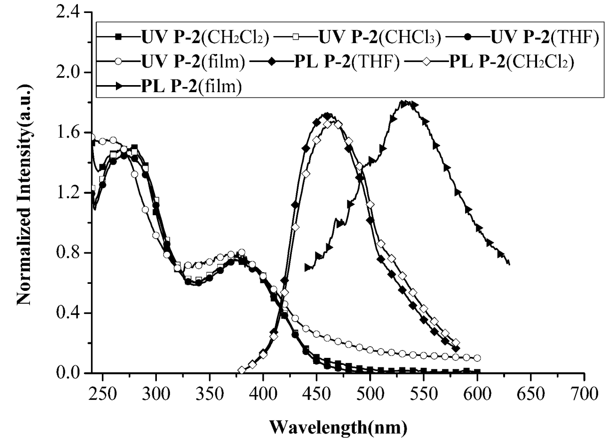


Figure 3. UV−vis and fluorescence spectra of **P-2** in solution and film.

3.3. Optical Properties. Figures 2 and 3 illustrate the UV−vis absorption spectra and fluorescent spectra of two polymers in different solvents and thin films, respectively. Optical properties of two polymers are summarized in Table 2. UV−vis spectra of both **P-1** and **P-2** are almost similar in the three different solvents. It can be concluded that solvent has no effect on the conjugation structure of polymer chain backbone. In addition, UV−vis spectra of the polymers **P-1** and **P-2** are

Table 2. Optical Properties of P-1 and P-2

			PL (λ_{max})					
	UV−vis (λ_{max})		solution (nm)[c]		film (nm)[b]			
	solution (nm)[a]	film (nm)[b]	λ_{ex}	λ_{em}	λ_{ex}	λ_{em}	Stokes shift (nm)[d]	Φ_{PL}[e] solution
***S*-M-2**	256		361	419				
***S*-M-3**	294		360	421				
M-1	272 (w), 320							
P-1	270, 376	267, 380	346	363, 381 (sh)			183	0.51
P-2	268, 378	266, 380	360	436, 462	363	563	152	0.49
			360	464	359	532		

[a] Determined in CH_2Cl_2 solution. [b] Determined in thin film. [c] Determined in CH_2Cl_2 solution. [d] Stokes shift = PL λ_{max} (nm) − UV−vis λ_{max} (nm). [e] These values were estimated by using the quinine sulfate solution (ca. 1.0×10^{-5} M) in 0.5 M H_2SO_4 ($\Phi_f = 55\%$) as a standard.

Table 3. CD Spectra Data of P-1 and P-2

	P-1 × 10^5 (in CH_2Cl_2)	**P-2** × 10^5 (in CH_2Cl_2)	**P-1** × 10^5 (in THF)	**P-2** × 10^5 (in THF)
[θ] (γ_{max} in nm)	−0.36 (253.8)	−0.37 (247.2)	−0.48 (253.8)	−0.56 (249.8)
	+0.93 (277.4)	+0.33 (271.3)	+1.19 (277.4)	+0.46 (269.4)
	−0.37 (313.2)	+0.38 (301.9)	−0.55 (313.9)	+0.49 (299.3)
	−0.24 (349.7)	−0.06 (368.2)	−0.36 (349.7)	−0.07 (354.6)
	+0.32 (397.6)	+0.09 (397.5)	+0.40 (397.6)	+0.11 (399.5)

similar due to the similar repeating units of the polymer backbone. Compared to the repeating unit 3,3′- or 6,6′-di(4-methylphenyl)-2,2′-bisoctoxy-1,1′-binaphthyl and **M-1**, UV absorption spectra of two conjugated polymers **P-1** and **P-2** display great red shifts. UV absorption maxima λ_{max} of 6,6′-di(4-methylphenyl)-2,2′-dioctoxy-1,1′-binaphthyl and **M-1** appeared at 255 and 320 nm. The strongest absorption wavelengths λ_{max} of **P-1** and **P-2** in CH_2Cl_2 solution appear at 270 and 268 nm. But both **P-1** and **P-2** show the stronger and broader absorption at the region from 325 to 450 nm. It can be concluded that there is a large red shift in the electronic absorptions of conjugated polymers due to the effective $\pi-\pi^*$ conjugated segment of the linker conjugated unit **M-1** and naphthyl group in the repeating unit of polybinaphthyls main chain.[4a,6d,7e,17] The UV absorptions of **P-1** and **P-2** in thin films show red shifts of about 4 and 2 nm relative to those measured in in CH_2Cl_2 solution, respectively. It can be attributed to a higher conjugated structure stacking of the repeating unit in the solid than in the solution.[2a,7f,18]

Fluorescent spectra of **P-1** and **P-2** were determined in CH_2Cl_2 and THF solution and in thin films (Figures 2 and 3). Both **P-1** and **P-2** can still emit blue-green light under ultraviolet light (361 nm) or sunlight even in low concentration (1×10^{-4} mol/L). The repeating units of 3,3′- or 6,6′-di(4-methylphenyl)-2,2′-dioctoxy-1,1′-binaphthyl and **M-1** do not show visible fluorescence. According to Figures 2 and 3, the fluorescent spectra have no effect on the solvent, but **P-1** and **P-2** have different fluorescent emission spectra. **P-1** shows two wavelength bands at 436 and 462 nm, and the maximum fluorescent wavelength λ^{F}_{max} of **P-2** appears at 464 nm. The PL efficiency (Φ_{PL}) of **P-1** and **P-2** is 0.51 and 0.49, respectively. Polymers show strong blue-green fluorescence due to the extended π-electronic structure between the chiral repeating unit and the conjugated linker unit via the vinylene bridge.[6d,7b,d,15c] But in the solid powder state, the fluorescent wavelengths λ^{F}_{max} of **P-1** and **P-2** show a red shift of 100 and 68 nm relative to those measured in CH_2Cl_2 solution state, which could be regarded as the conformational change from the degree of conjugation in the polymer backbone of the condensed state.[2a,7f,18] In addition, the rotation of two pyridyls is relatively free in the solution system; 2,2′-bipyridyl moieties in the conjugated polymer backbone may take either a transoid or cisoid conformation. In the solid state, two pyridyl groups can tend to coplanar structure and lead to a higher conjugated arrangement.[2f,3b,e,16c] The greatly enhanced fluorescence of chiral conjugated polybinaphthyls is expected to have the potential application in the polarized light-emitting materials and fluorescent chemosensor for the detection of the sensitive and selective sense of metal ions.

3.4. CD Spectra. The specific rotation value ($[\alpha]^{25}_{D}$) of the chiral repeating units 6,6′-di(4-methylphenyl)-2,2′-bisoctoxy-1,1′-binaphthyl is +88.2 (*c* 0.51, CH_2Cl_2), and $[\alpha]^{25}_{D}$ of their conjugated polymers **P-1** and **P-2** is +136.2 and +120.0, respectively. As a result, two chiral polymers **P-1** and **P-2** are made of optically pure binaphthyl units. The specific rotations of **P-1** and **P-2** are a little larger than that of their chiral center units (*S*)-6,6′-di(4-methylphenyl)-2,2′-bisoctoxy-1,1′-binaphthyl. According to our previous reports, if optically active polybinaphthyls do not have a propagating helical chain conformation in solution, the specific rotation and CD spectrum of this kind of polymer are very close to those of its monomeric model compound. That is, each unit in the polymer acts independently without an organized helical chain structure even though the 1,1-binaphthyl unit itself is helical. In this paper, **P-1** and **P-2** may form a zigzag chain configuration.[7f,19] CD spectra data of **P-1** and **P-2** in CH_2Cl_2 and THF are listed in Table 3, respectively. CD spectra of **P-1** and **P-2** have little change in two solvents, which demonstrates that **P-1** and **P-2** still keep the similar configuration in two different solvents. Both **P-1** and **P-2** exhibit intense CD signals with negative and positive Cotton effects in their CD spectra, and CD spectra of **P-1** and **P-2** are quite different from their position and intensity (Figure 4). The ^1L_a band intensity and position of **P-1** and **P-2** are almost similar, but the ^1B_b band of **P-1** is stronger than that of **P-2**. ^1B_b bands of **P-2** appear nearly the same magnitude as two split

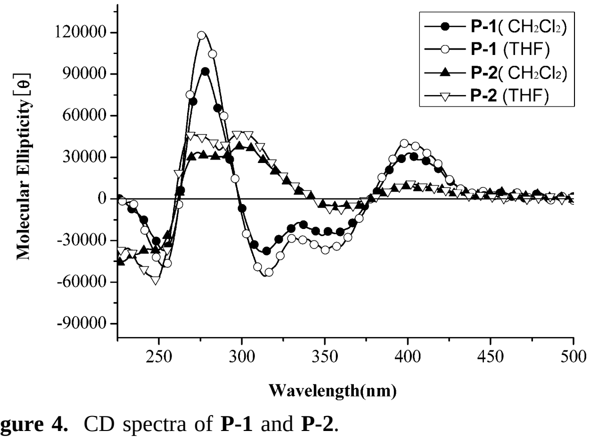


Figure 4. CD spectra of **P-1** and **P-2**.

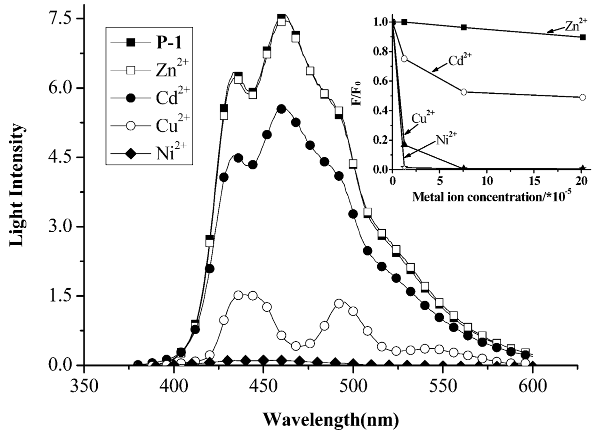


Figure 5. Quenching ability of metal ion for **P-1**.

Table 4. Quenching Ratio of the Transition Metal Ions to P-1 and P-2

	P-1 (n_{ion}:$n_{\mathbf{P-1}}$)			**P-2** (n_{ion}:$n_{\mathbf{P-1}}$)		
	1:1	6:1	16:1	1:1	6:1	16:1
Zn^{2+}	0.03%	3.61%	10.3%	15.7%	20.4%	26.3%
Cd^{2+}	24.9%	47.4%	51.0%	10.1%	36.5%	42.1%
Cu^{2+}	83.2%	99.5%	99.6%	53.3%	95.0%	95.2%
Ni^{2+}	98.7%	99.3%	99.4%	94.2%	94.7%	94.9%

peaks at about 270 and 300 nm; on the contrary, ^1B_b bands of **P-1** appear the reversed signals of two split peaks at about 277 and 313 nm. In addition, the long wavelength CD signal of **P-1** appears at about 398 nm, which can be regarded as the extended conjugated structure in the repeating unit and a high rigidity of polymer backbone.[4a,20] But **P-2** does not produce the long wavelength CD signal. This result may be attributed to the different polymer chain backbone configuration at 3,3′-position minor-groove polymer and 6,6′-position major-groove polymer.

3.5. Responsive Properties on Transition Metal Ions and H^+. The effects of the molecular recognition sites in optically active polybinaphthyl-based conjugated polymers **P-1** and **P-2** on metal ion sensing have been investigated. The influences of various metal ions on the fluorescence emission response of the polymers are shown in Table 4. The concentrations of polymers **P-1** and **P-2** were fixed at 1.26×10^{-5} M corresponding to 2,2′-bipyridyl receptor units. The concentrations of metal salts were fixed at 2.52×10^{-3} M. The fluorescence quenching behavior of **P-1** and **P-2** with various molar ratios of metal salts was also investigated to examine the effect of the chelating ability on the fluorescence quenching properties of the 2,2′-bipyridyl group in polymers. The fluorescence quenching ratios of **P-1** are 98.7, 82.3, 24.9, and 0.03% by Ni^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+} upon the 1:1 molar ratio addition of a metal salt solutions, while that of **P-2** are 94.2, 55.3, 10.1, and 15.7%, respectively. There was no obvious difference in the ion sensitivity for both **P-1** and **P-2** at the high metal salts concentration (Figures 5 and 6). Cu^{2+} and Ni^{2+} lead to nearly complete fluorescent quenching for two polymers, which can be attributed to the energy- or electron-transfer reactions between the polymer backbones and binding metal complexes in the conjugated polymer backbone.[1f,2d,g,16g] According to Table 4, the tested metal ions could be categorized into two groups according to the data of F_0/F, where F_0 and F are the fluorescent intensity of metal-free polymer and the metal-chelated polymer: (1) Zn^{2+} and Cd^{2+}, slight or efficiently fluorescent quenched; (2) Ni^{2+} and Cu^{2+}, completely quenched (Figures 5 and 6). Herein, metal ions with an open-shell electronic structure, which generally show the strong metal−ligand orbital interaction to form low-lying ligand-to-metal (LM) charge-transfer state, may exhibit a highly quenching response as in the case of and Ni^{2+} with d^8 electronic structure and Cu^{2+} with d^9 electronic structure. Metal ions with a full occupancy outer-shell orbital or half occupancy outer-shell orbital, which generally show the weak metal−ligand orbital interaction, may exhibit a low quenching response as in the case of Zn^{2+} (d^{10}) and Cd^{2+} (d^{10}). **P-1** and **P-2** still shows strong fluorescence upon the addition of the metal ions Zn^{2+} and Cd^{2+} even at a high concentration of 16:1 molar ratio, and that the emission wavelengths of the Zn^{2+} and Cd^{2+} polymer complexes did not produce an obvious change. But the fluorescent wavelengths and spectra of **P-1** and **P-2** show an obvious difference upon addition of a Cu^{2+} and Ni^{2+} solution. The maximum emission wavelengths λ^{F}_{max} of Cu^{2+}−polymer for **P-1** and **P-2** appear to blue-shift to 444 and 436 nm, and Ni^{2+}−polymer for **P-1** and **P-2** appear to blue-shift to 437 and 428 nm upon the 1:1 molar ratio addition of a metal salt solution, respectively. Wang and Wasielewski reported metal ion recognition-induced polymers incorporating the 2,2′-bipyridyl moiety in the conjugated polymer main chain.[3e] The ionochromic responses to 16 different di- and trivalent main-group and transition-metal ions and 6 trivalent lanthanide ions were measured in $CHCl_3$ solution. Both absorption and fluorescence emission bands of the polymer−metal complexes showed a great change, depending on the different metal ions present and the polymers used. The results indicated that the groups of Ag^+, Al^{3+}, Cd^{2+}, Hg^{2+}, Zn^{2+}, and the lanthanide ions induced red shifts in the emission spectra while Pb^{2+}, Fe^{3+}, Fe^{2+}, Cu^+, and Sb^{3+} induced blue shifts. As postulated by the authors, the red-shifting of the absorption and emission bands could be ascribed to electron density changes caused by the complexation of cationic mono-, di-, or trivalent metal ions or to conformational changes in the polymer's backbone as a result of the chelation. Blue shifts caused by the coordination of specific metal ions were attributed to a deconjugation effect on the polymer's backbone.

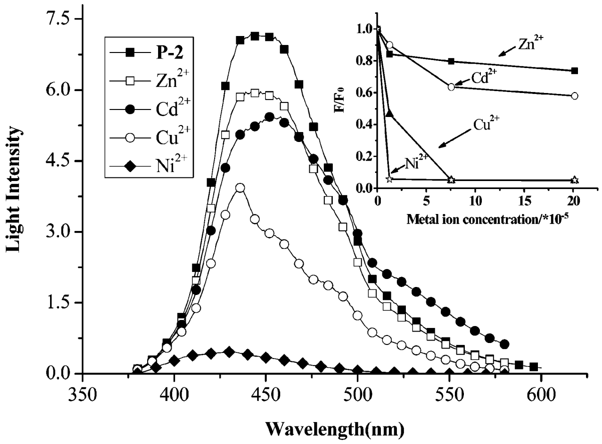


Figure 6. Quenching ability of metal ion for **P-2**.

Such distinct ion responsive behaviors revealed the obvious difference of coordination abilities of transition metal ions with 2,2′-bipyridyl ligand receptors. The obvious quenching effect of **P-1** and **P-2** suggested that the chiral conjugated polymers backbone structure and the efficiencies of energy or electron transfer between backbone and receptor ions in the main chain play important roles in fluorescence quenching. As a result, the design of the novel fluorescent polymers for selectively sensing of metal ions could be realized through appropriate alteration of receptors with various degrees of affinity toward metal ions. It was demonstrated that the chiral conjugated polybinaphthyls

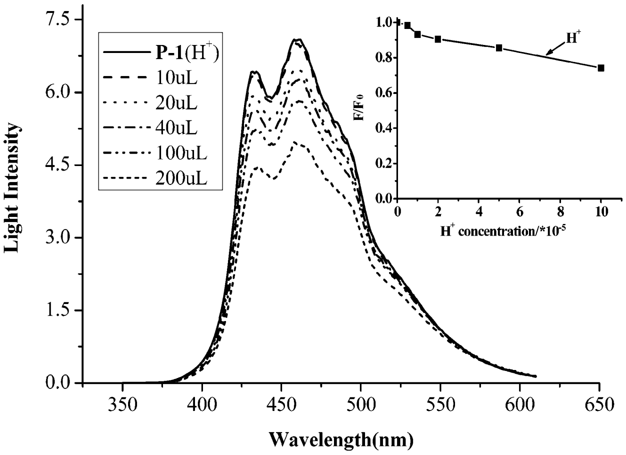


Figure 7. Quenching effect of H^+ for **P-1**.

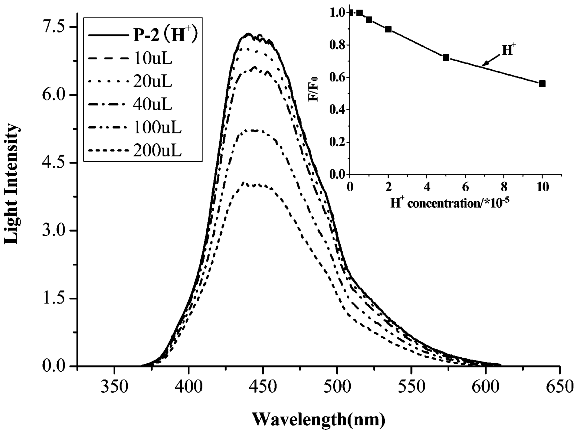


Figure 8. Quenching effect of H^+ for **P-2**.

Table 5. Quenching Ratio of the Hydrochloric Acid to P-1 and P-2

H^+ (μL)	P-1 (%)	P-2 (%)	H^+ (μL)	P-1 (%)	P-2 (%)
10	1.57	0.14	100	14.5	27.8
20	6.77	4.32	200	25.9	43.9
40	9.64	10.3			

incorporating the 2,2′-bipyridyl moiety can act as promising active materials for application as fluorescent chemosensors.

The fluorescence quenching analysis of **P-1** and **P-2** by the hydrochloric acid in different ratios is shown in Table 5. The emission intensities obviously decreased as the acid concentration increased (Figures 7 and 8). The fluorescence of **P-1** and **P-2** was quenched to 74.1 and 56.1% upon the 14:1 molar ratio addition of an acid solution. But the fluorescent wavelengths of both **P-1** and **P-2** do not produce difference from their initial polymer spectra. The quenching effect should be attributed to the hydrogen-bonding interactions between the receptors of 2,2′-bipyridine and H^+.

4. Conclusions

The Pd-catalyzed Heck reaction was found to offer a simple access to two chiral polymers. The chiral polymers and the polymer complexes show good solubility in some organic solvents due to the nonplanarity of the twisted polymers in the main-chain backbone and flexible octoxy and 4-methylphenyl group substitutents on binaphthyl units as side chain of the polymers. Polymers **P-1** and **P-2** exhibit intense CD signals with negative and positive Cotton effects in their CD spectra. Polymers show strong blue-green fluorescence due to the extended π-electronic structure between the chiral repeating unit and the conjugated linker unit via the vinylene bridge. Cu^{2+} and Ni^{2+} can form nonradiative metal-to-ligand charge-transfer complexes with the polymers, and Zn^{2+} and Cd^{2+} can cause slight fluorescent quenching. Such distinct ion responsive behaviors revealed the obvious difference of coordination abilities of transition metal ions with 2,2′-bipyridyl ligand receptors. This quenching effect can be attributed to an energy transfer from the π-conjugated chiral polymers to the metal complexes. A better understanding of energy-transfer processes in conjugated polymer sensors would provide critical information for the interpretation of increased quenching selectivity and the design of new, more sensitive, chemosensory materials. They are also expected to be used as special chemosensory materials to detect some metal ions.

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References and Notes

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