

## Synthesis and Characterization of Polybinaphthyls Incorporating Chiral (*R*) or (*S*)-2,2'-Binaphthyl Entities by Heck Reaction

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**ABSTRACT:** Four chiral conjugated polymer-1 (**P-1**), polymer-2 (**P-2**), polymer-3 (**P-3**) and polymer-4 (**P-4**) were obtained by the polymerization of (*S*)-6,6'-dibromo-2,2'-bisbutoxy-1,1'-binaphthyl ((*S*)-**M-1**) and (*R*)-6,6'-dibromo-2,2'-bisbutoxy-1,1'-binaphthyl ((*R*)-**M-1**) with 1,4-divinyl-2,5-dibutoxybenzene (**M-2**) and 1,3,4-oxadiazole-2,5-bis(4-vinylbenzene) (**M-3**) under Pd-catalyzed Heck reaction respectively. Both monomers (*S*)-**M-1**, (*R*)-**M-1**, **M-2**, **M-3** and polymers were analyzed by NMR, MS, FT-IR, UV, fluorescent spectroscopy, polarimetry, GPC, circular dichroism (CD-) spectra. Four polymers can emit stronger green-blue fluorescence and are expected to have the potential application in the polarized light-emitting sensors. [DOI 10.1295/polymj.37.355]

**KEY WORDS** (*R*)- and (*S*)-1,1'-Binaphthol / Chiral Polymers / Fluorescence / Heck Reaction /

Chiral conjugated polymers are optically active materials made of organic fragments such as aromatic rings and unsaturated carbon or heteroatom bonds with delocalizable  $\pi$ -electronic system.<sup>1–4</sup> (*R*) or (*S*)-1,1'-binaphthol (BINOL) have often been used as the starting materials for obtaining chiral binaphthyl compounds. The 2,2'-hydroxyl groups of BINOL can be easily converted into other functional groups and the 3,3'-and 6,6'-positions of binaphthyl skeletal structure of BINOL can be selectively functionalized at the well-defined molecular level, leading to a variety of binaphthyl derivatives which can exhibit remarkably stable chiral configuration as well as high chiral induction in molecular recognition,<sup>5–9</sup> asymmetric processes.<sup>10–15</sup> These rigid and sterically chiral polybinaphthyl polymers also represent a new generation of materials for applications in chiral sensors, polarized light emission and nonlinear optical materials.<sup>16–20</sup>

Conjugated polymers with rigid  $\pi$ -systems often possess poor solubility, which seriously inhibits full structural elucidations and property investigations. We choose **M-2** and **M-3** as the conjugated molecular bridge linkers. Oxadiazole derivatives have been widely used as electron transporting/hole blocking materials in LED devices and LED blends because oxadiazole unit has many excellent properties on the better chromophore, high thermal and oxidative stability, and the good charge injection and transporting building blocks.<sup>21–23</sup> In our paper, **M-3**, 1,3,4-oxadiazole-2,5-bis(4-vinylbenzene) is introduced into the chiral polymers main chain backbone to maintain conjugation between the oxadiazole and binaphthyl segments so that the electron transporting properties of the poly-

mers may be improved. In addition, by introducing oxadiazole, an electron deficient moiety into the main chain, the electron density may shift away from the vinyl bond, which could increase the stability of the resulting chiral polymers.<sup>24,25</sup> To make soluble conjugated polymers, the alkyl groups substituents on the phenyl and binaphthyl rings as side chain of the polymers can improve solubility in organic solvents and facile electro-optical sensors. Heck, Suzuki, Stille and Sonogashira reactions are the most important C–C coupling reactions in organic chemistry synthesis. Herein, we present preliminary results of synthesis and properties of four polymers based on the chiral unit 1,1'-binaphthyl structure. The four chiral polymers containing vinylene linkages between naphthyl and phenyl groups can reduce steric hindrance between backbone rings and groups, and also have a beneficial effect on delocalizable  $\pi$ -electronic conjugation structure of polymers. These polymers are green-blue light emitting materials with very good fluorescence quantum efficiencies.

### EXPERIMENTAL

#### General

<sup>1</sup>H, <sup>13</sup>C NMR spectra measurements (all in CDCl<sub>3</sub>) were recorded on a 300-Bruker spectrometer with TMS as internal standard. FT-IR spectra were taken in KBr plates on Nicolet-170SX spectrometer. UV-vis spectra were carried out on PerkinElmer Lambda 25. Fluorescent spectra were carried out on 48000 DSCF spectrometer. MS was determined on Micro-mass GCT. Elemental analyses were carried out by

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HN-O-RAPID instrument. Circular dichroism (CD-) spectra were carried on JASCO J-810 spectropolarimeter. Molecular weight was determined by gel permeation chromatography (GPC) on Waters-244 HPLC pump and THF used as solvent and relative to polystyrene standards. All solvents and reagents were purchased from commercial A.R. grade. All reactions were performed under nitrogen atmosphere using Schlenk tube techniques. In experiments requiring dried solvents, THF and toluene was distilled from sodium-benzophenone, DMF was distilled from CaH<sub>2</sub>, and CH<sub>2</sub>Cl<sub>2</sub> was distilled from P<sub>2</sub>O<sub>5</sub>.

### Monomer Syntheses

**Preparation of (S)-6,6'-Dibromo-2,2'-dibutoxy-1,1'-binaphthyl ((S)-**M-1**).** A mixture of (S)-6,6'-dibromo-1,1'-binaphthol (6.08 g, 13.7 mmol), K<sub>2</sub>CO<sub>3</sub> (14 g, 0.1 mol) and 1-bromobutane (6.48 g, 48.6 mmol) in 180 mL CH<sub>3</sub>CN was refluxed for 4 h under N<sub>2</sub>. The second portion of K<sub>2</sub>CO<sub>3</sub> (7 g, 0.05 mol) and 1-bromobutane (3.24 g, 24.3 mmol) was added to ensure the complete reaction. The solution was stirred and continued to keep refluxing for 10 h. The mixture was poured into 5% aqueous NaOH (200 mL). The solution was extracted by ethyl acetate (150 mL). The organic layer was washed with saturated brine for two times and then dried over anhydrous MgSO<sub>4</sub>. After the solvent was removed under the reduced pressure, the residue was purified by chromatography on silica with petroleum ether as eluent. (S)-**M-1** was obtained as a pale yellow viscous product in 98% yield (7.46 g). [ $\alpha$ ]<sub>D</sub> = -19.5 (c = 0.1, THF); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.68 (t, 6H, *J* = 7.36 Hz), 1.03 (m, 4H), 1.43 (m, 4H), 3.98 (m, 4H), 7.01 (d, 2H, *J* = 9.00 Hz), 7.27 (dd, 2H, *J* = 9.01, 2.01 Hz), 7.43 (d, 2H, *J* = 9.00 Hz), 7.86 (d, 2H, *J* = 9.00 Hz), 8.02 (d, 2H, *J* = 1.94 Hz); <sup>13</sup>C NMR (300 MHz,  $\delta$  CDCl<sub>3</sub>): 13.49, 18.70, 31.25, 69.17, 116.37, 117.17, 120.02, 127.09, 128.35, 129.40, 129.72, 130.16, 132.57, 154.76;  $\delta$   $\nu_{\max}$  (KBr)/cm<sup>-1</sup>: 2956.6, 2930.9, 1584.1, 1493.2, 1327.7, 1269.2, 1244.1, 1070.5, 875.0, 809.3.

**Preparation of (R)-6,6'-Dibromo-2,2'-dibutoxy-1,1'-binaphthyl ((R)-**M-1**).** (R)-**M-1** was synthesized as the same procedures of (S)-**M-1**, and the final yield was 96%, [ $\alpha$ ]<sub>D</sub> = +18.8 (c = 0.1, THF); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.68 (t, 6H, *J* = 7.37 Hz), 1.02 (m, 4H), 1.42 (m, 4H), 3.97 (m, 4H), 6.99 (d, 2H, *J* = 9.04 Hz), 7.28 (dd, 2H, *J* = 9.00, 2.02 Hz), 7.42 (d, 2H, *J* = 9.03 Hz), 7.85 (d, 2H, *J* = 9.01 Hz), 8.02 (d, 2H, *J* = 1.92 Hz);  $\delta$   $\nu_{\max}$  (KBr)/cm<sup>-1</sup>: 2957.0, 2931.4, 2870.7, 1584.9, 1493.7, 1327.9, 1270.0, 1242.9, 1070.3, 875.8, 807.9.

**Preparation of 1,4-Dibutoxybenzene (**1**).** A mixture of hydroquinone (5 g, 45.4 mmol), 1-bromobutane (13.7 g, 100 mmol) and NaOH (4.8 g, 120 mmol) in

50 mL ethanol was refluxed 12 h under N<sub>2</sub> and then poured into water. The precipitate was filtered and washed with water (3  $\times$  100 mL). The crude solid was recrystallized from 95% ethanol (2  $\times$  60 mL) to give a white product **1** in 82% yield (8.3 g). Mp: 49–51 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.99 (t, 6H, *J* = 7.4 Hz), 1.44–1.57 (m, 4H), 1.72–1.81 (m, 4H), 3.93 (t, 4H, *J* = 6.5 Hz), 6.85 (s, 4H);  $\nu_{\max}$  (KBr)/cm<sup>-1</sup>: 1511.07, 1472.13, 1399.24, 1288.90, 1239.26, 1123.60, 1072.15, 1043.19, 1013.90, 974.16, 828.42.

**Preparation of 1,4-Bis(bromomethyl)-2,5-dibutoxybenzene (**2**).** A mixture of **1** (4 g, 18 mmol), (HCHO)<sub>n</sub> (3 g, 180 mmol), saturated aqueous HBr (8 mL) and H<sub>3</sub>PO<sub>4</sub> (4 mL) in 50 mL AcOH was heated to 90 °C for 3 h under N<sub>2</sub>, and then the mixture was poured into water (300 mL). The precipitate was filtered and washed by water (3  $\times$  200 mL) and recrystallized over petroleum ether to give a white product **2** in 76% yield (5.60 g). Mp: 108–110 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.01 (t, 6H, *J* = 7.4 Hz), 1.49–1.63 (m, 4H), 1.77–1.87 (m, 4H), 4.55 (s, 4H), 6.87 (s, 2H).

**Preparation of 1,4-Divinyl-2,5-dibutoxybenzene (**M-2**).** A solution of **2** (4 g, 9.75 mmol) and triphenylphosphate (5.6 g, 21.4 mmol) in 40 mL toluene was refluxed for 4 h and produced **3** (8.4 g). The precipitate was filtered and washed with petroleum ether, and then transferred into a 100 mL three-necked flask for **M-2** synthesis. A mixture of CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and aqueous HCHO (12 mL) were added into the former flask. The solution was cooled down to -15 °C and stirred vigorously. 10% aqueous NaOH (20 mL) was added dropwise over 1 h with constant stirring under N<sub>2</sub>. The resulting mixture was stirred at room temperature overnight, and then 50 mL water was added to the above solution. The resulting solution was extracted three times with dichloromethane (20 mL). The combined organic layers were washed with saturated brine twice and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed to dryness under the reduced pressure. The colorless crystal product **M-2** was obtained as a colorless crystal in 63% yield (1.69 g) by the recrystallization of 50% ethanol twice. Mp: 42–44 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.01 (t, 6H, *J* = 7.4 Hz), 1.48–1.61 (m, 4H), 1.77–1.86 (m, 4H), 4.00 (t, 4H, *J* = 6.4 Hz), 5.28 (dd, 2H, *J* = 10.9, 1.3 Hz), 5.76 (dd, 2H, *J* = 17.7, 1.3 Hz), 7.01 (s, 2H), 7.10 (dd, 2H, *J* = 8.9, 6.6 Hz); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  14.31, 19.78, 30.11, 31.95, 69.39, 110.90, 114.40, 127.57, 131.94, 151.03;  $\nu_{\max}$  (KBr)/cm<sup>-1</sup>: 2959.1, 2934.1, 2871.8, 1621.6, 1497.8, 1425.7, 1378.9, 1204.6, 1068.5, 1027.4, 994.3, 903.2; MS *m/z*: 274 (M<sup>+</sup>, 42.56), 162 (100).

**Preparation of 2,5-Bis(4-methylbenzene)-1,3,4-oxadiazole (**4**).** A mixture of orthophosphoric acid (1.5 mL) and phosphorus oxide (3.3 g, 23 mmol) was

heated to 120 °C under N<sub>2</sub>. After the solid was dissolved completely, hydrazine sulfate (0.72 g, 5.5 mmol) and *p*-toluic acid (1.5 g, 11.0 mmol) was added, and then the mixture was heated to 135 °C for 8 h. After cooling, the mixture was poured into water. White solid product was precipitated and filtered, the crude product **4** was washed with water, aqueous NaOH (pH = 9) and water respectively. A yellow crystal was obtained in 76% yield (1.05 g). Mp: 173–175 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 2.46 (s, 6H), 7.35 (d, 4H, *J* = 8.2 Hz), 8.04 (d, 4H, *J* = 8.1 Hz); ν<sub>max</sub> (KBr)/cm<sup>-1</sup>: 1614.96, 1552.30, 1495.61, 1072.07, 1016.01, 821.45, 735.41.

**Preparation of 2,5-Bis(4-bromomethylbenzene)-1,3,4-oxadiazole (5).** A mixture of **4** (0.6 g, 2.4 mmol), *N*-bromosuccinimide (0.98 g, 5.5 mmol) and benzoyl peroxide (10 mmg, 0.04 mmol) in 10 mL CCl<sub>4</sub> was refluxed for 6 h under N<sub>2</sub>. After cooling, the precipitate was filtered, the mixture was washed ether and water. The crude solid **5** was recrystallized from THF/CH<sub>3</sub>OH (1:1) to give a white product in 57% yield (0.55 g). Mp: 225–227 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 4.56 (s, 4H), 7.59 (d, 4H, *J* = 8.3 Hz), 8.14 (d, 4H, *J* = 8.3 Hz); ν<sub>max</sub> (KBr)/cm<sup>-1</sup>: 1551.92, 1493.40, 1227.01, 1072.84, 849.27, 710.95, 598.77.

**Preparation of 2,5-Bis(4-vinylbenzene)-1,3,4-oxadiazole (M-3).** A mixture of **5** (1.4 g, 3.43 mmol), triphenylphosphate (2.25 g, 8.58 mmol) in 20 mL DMF was refluxed for 10 h and produced **6** (3.5 g). The precipitate was filtered and washed with ether, and then transferred into a 100 mL three-necked flask for **M-3** synthesis. **M-3** was synthesized in the same procedures as **M-2**. The colorless product **M-3** yielded 51% (0.47 g). Mp: 127–129 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 5.43 (d, 2H, *J* = 10.9 Hz), 5.92 (d, 2H, *J* = 17.6 Hz), 6.80 (dd, 2H, *J* = 17.6, 10.9 Hz), 7.59 (d, 4H, *J* = 8.3 Hz), 8.12 (d, 4H, *J* = 8.3 Hz); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 116.21, 123.01, 126.78, 127.13, 135.87, 140.82, 164.36; ν<sub>max</sub> (KBr)/cm<sup>-1</sup>: 1625.1, 1577.3, 1492.9, 1411.9, 1080.7, 993.3, 901.9, 851.0, 717.9; MS *m/z*: 274 (M<sup>+</sup>, 82), 131 (100); *Elemental anal.* (%) Calcd. For C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>O: C 78.81; H 5.14; N 10.21; Found: C 78.67; H 5.17; N 10.05.

### Polymer Syntheses

**Preparation of P-1.** A mixture of (*S*)-**M-1** (382.6 mg, 0.688 mmol) and **M-2** (188.5 mg, 0.688 mmol) was dissolved in 8 mL DMF, and then 2% Pd(OAc)<sub>2</sub> (3.1 mg, 0.014 mmol) and 6% triphenylphosphate (21.7 mg, 0.083 mmol), 5 molar equivalent Et<sub>3</sub>N (0.85 mL)/(*S*)-**M-1** were added to the above mixture solution. The solution was stirred and heated at 115 °C for 10 h under N<sub>2</sub>, and then refluxed at 145 °C for an additional 2 h. The mixture was cooled down to room temperature. The solution was filtered

through a short silica gel column into methanol (200 mL) to precipitate out the polymer. The yellow crude polymer was washed with methanol several times. **P-1** was dried *in vacuo* and collected 294.2 mg in 64% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.66 (m, 12H), 1.00 (m, 8H), 1.41 (m, 8H), 3.96 (m, 8H), 7.16 (m, 2H), 7.24 (s, 2H), 7.50 (m, 6H), 7.90 (m, 6H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 13.57, 13.95, 18.78, 19.48, 31.44, 31.64, 69.33, 69.44, 110.58, 115.79, 116.75, 120.86, 122.76, 123.91, 125.92, 126.66, 127.08, 128.16, 129.48, 133.25, 133.84, 151.45, 154.83; ν<sub>max</sub> (KBr)/cm<sup>-1</sup>: 3048.9, 2955.6, 2930.7, 2869.1, 1608.5, 1589.3, 1494.8, 1463.7, 1272.2, 1244.8, 1202.6, 1066.3, 1028.1, 964.6.

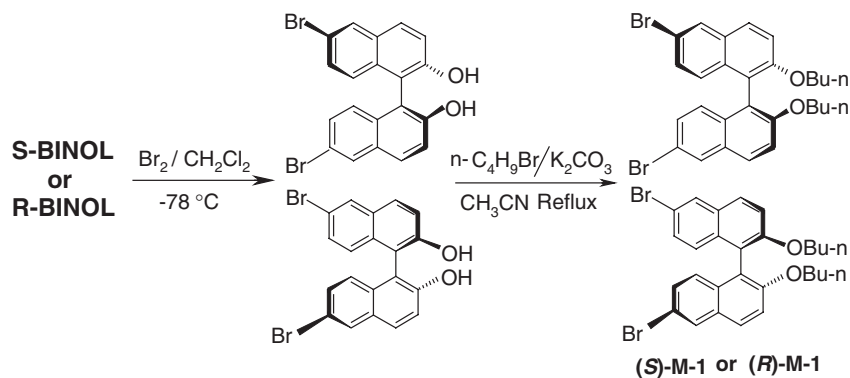
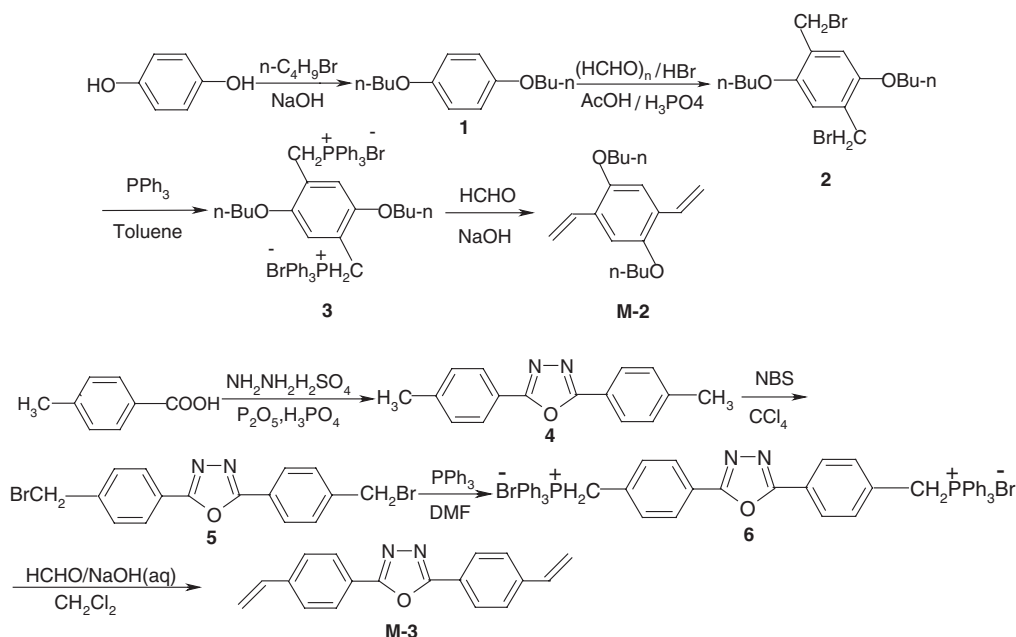
**Preparation of P-2, P-3 and P-4.** **P-2**, **P-3** and **P-4** were synthesized in the same way as **P-1**. The yields were 70% (**P-2**), 73% (**P-3**), 74% (**P-4**) respectively. **P-4** spectroscopic data: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.68 (m, 6H), 1.01 (m, 4H), 1.40 (m, 4H), 4.00 (m, 4H), 7.12 (m, 2H), 7.43 (m, 4H), 7.50 (m, 2H), 7.56 (m, 2H), 7.65 (m, 2H), 7.93 (m, 6H), 8.10 (m, 2H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 13.47, 18.70, 31.28, 69.30, 115.97, 117.15, 120.56, 123.02, 126.00, 126.84, 127.23, 128.20, 129.31, 129.54, 130.22, 131.88, 134.01, 135.87, 141.00, 155.04, 164.45; ν<sub>max</sub> (KBr)/cm<sup>-1</sup>: 3027.0, 2954.4, 2929.3, 2869.1, 1604.7, 1585.4, 1492.4, 1463.2, 1270.3, 1241.0, 1218.4, 1066.0, 1028.0, 960.5.

## RESULTS AND DISCUSSION

### Syntheses of the Monomers

(*R*) and (*S*)-1,1'-binaphthol were resolved from racemic 1,1'-binaphthol by (8*S*,9*R*)-(-)-*N*-benzylcinchonidinium chloride according to the literature, both enantiomers could be obtained with 90% yield and >99.9% e.e.<sup>26,27</sup> (*S*)-**M-1** and (*R*)-**M-1** were synthesized from (*S*) and (*R*)-BINOL (Scheme 1) respectively according to the literature.<sup>13,28</sup> (*S*)-**M-1** and (*R*)-**M-1** served as the monomers for the synthesis of the desired chiral polymers. They can also be used as the starting materials or building blocks to prepare the novel chiral catalysts, molecular recognition and the polarized light-emitting sensors. Attachment of the butoxy substituents on binaphthyl rings as side chain of the polymers cannot only modify the electronic properties and conjugated structure of chiral polymers, but can also dramatically improve solubility in organic solvents and convenient processability for electro-optical sensors.<sup>16,29–33</sup>

The syntheses of the two divinyl conjugated monomers **M-2** and **M-3** were carried out in a very mild condition by Wittig reaction. **M-2** and **M-3** were stable in the air, but it should be kept in heptane at -4 °C before using. **M-2** could be obtained from the starting

**Scheme 1.** Synthesis procedures of the monomer (S)-M-1 and (R)-M-1.**Scheme 2.** Synthesis procedures of the monomers M-2 and M-3.

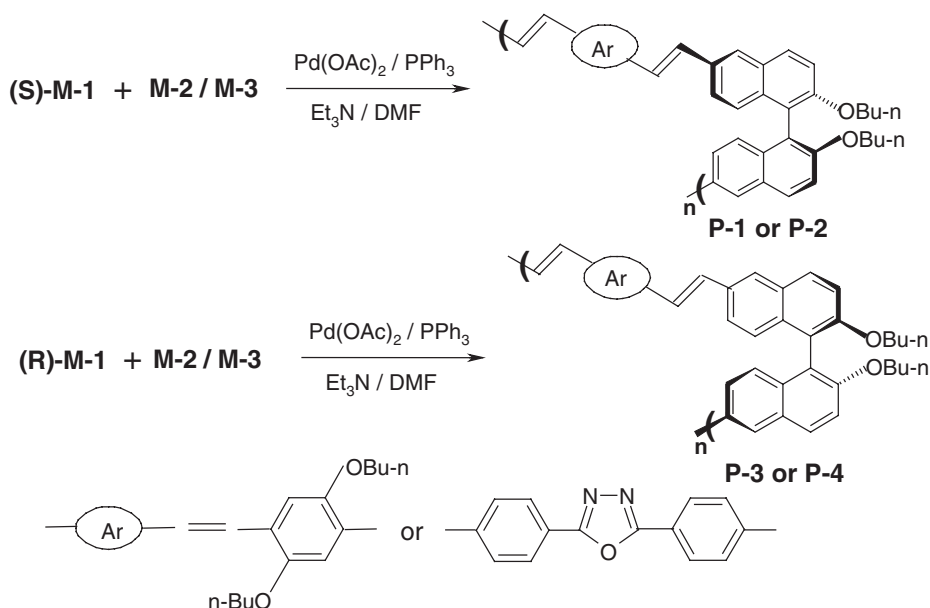
products of 1,4-hydroquinone (Scheme 2). The synthesis routes of **1–3** were carried out according to the literature.<sup>34,35</sup> **M-3** was synthesized by the starting products *p*-toluic acid (Scheme 2), and **4–6** were obtained according to the literature.<sup>36,37</sup> Bisphosphonium salts of **6** in refluxing toluene failed due to the poor solubility of the two salts. It only afforded the monophosphonium salts in the form of a white precipitate in a quantitative yield. Normally DMF was chosen as solvent. But **3** must be prepared in toluene because dibutoxy group can lead to higher solubility in DMF solution.

#### Syntheses of the Polymers

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 (2% mol) of Pd(OAc)<sub>2</sub> with Et<sub>3</sub>N and triphenylphosphite under a N<sub>2</sub> atmosphere. The poly-

merization 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.<sup>38–43</sup> Pu also studied 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 effect on the molecular weight of the polymers.<sup>44</sup> In this paper, four chiral conjugated polymers were obtained by the polymerization of (S)-6,6'-dibromo-2,2'-bisbutoxy-1,1'-binaphthyl ((S)-**M-1**) and (R)-6,6'-dibromo-2,2'-bisbutoxy-1,1'-binaphthyl ((R)-**M-1**) with 1,4-divinyl-2,5-dibutoxybenzene (**M-2**) and 1,3,4-oxadiazole-2,5-bis(4-vinylbenzene) (**M-3**) under Pd-catalyzed Heck reaction respectively (Scheme 3). Four polymers are stable in air and show good solubility in THF, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, DMF. GPC analysis and





**Scheme 3.** Synthesis of the polymers **P-1**, **P-2**, **P-3** and **P-4**.

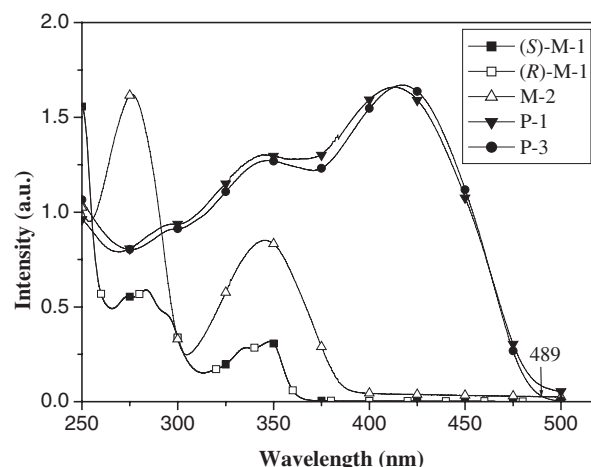
**Table I.** GPC analysis and specific optical rotation of four polymers

	$M_w$	$M_n$	PDI	Optical rotation $[\alpha]^{25}_D$ ( $c = 0.5$ , THF)
P-1	7900	5400	1.46	+358
P-2	7200	4200	1.71	+283
P-3	10360	5630	1.84	−345
P-4	11200	4500	2.49	−373

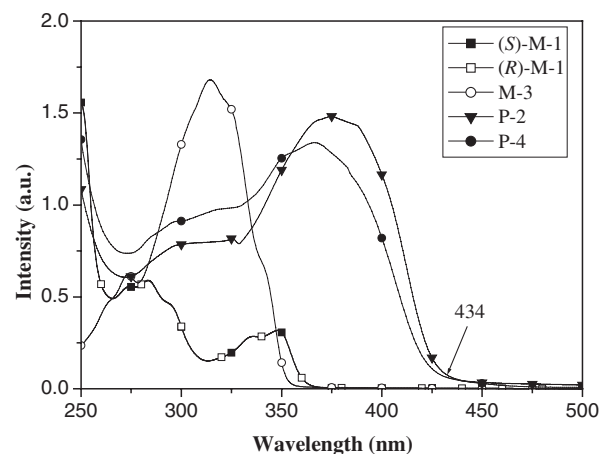
the specific optical rotation results of four polymers were listed in the Table I. The rigid structure and  $C_2$  symmetry of the chiral binaphthyl molecules play important role in chiral induction. The chirality of binaphthyl compounds is derived from the restricted rotation of the two naphthalene rings. The dihedral angle between two naphthalene rings of a binaphthyl molecule ranges from 60 to 120°. Four chiral polymers are made of optically pure binaphthyl units, when the divinyl conjugated monomers **M-2** and **M-3** are assumed to be coplanar, a helical structure should be generated. This kind chiral configuration of binaphthyls is remarkably stable.<sup>5,16,30,44</sup>

#### UV Absorption Spectra

UV spectra of monomers and polymers were determined in  $CH_2Cl_2$  solution. UV spectra of polymers **P-1**, **P-3** and polymers **P-2** and **P-4** are similar. Compared to monomers, both polymers' UV absorption spectra displayed great red shifts. The strongest absorption wavelength  $\lambda_{max}$  of **P-1** and **P-3** appeared at the region from 380 to 480 nm (Figure 1), and **P-2** and **P-4** are in the region from 340 to 420 nm (Figure 2). It can be concluded that there is a large



**Figure 1.** UV spectra of **(S)-M-1**, **(R)-M-1**, **M-2**, **P-1** and **P-3**.



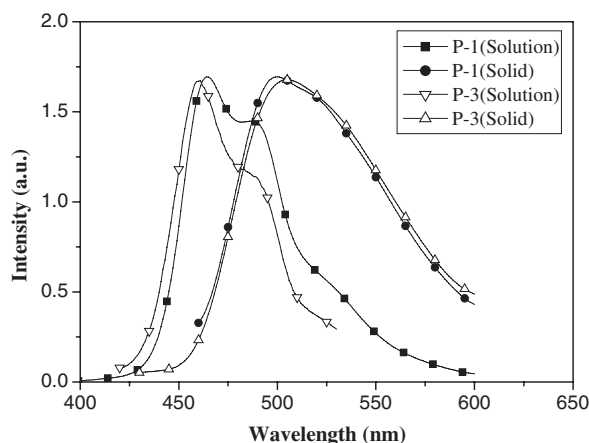
**Figure 2.** UV spectra of **(S)-M-1**, **(R)-M-1**, **M-3**, **P-2** and **P-4**.

red-shift in the electronic absorptions of the conjugated polymers due to the effective  $\pi$ - $\pi^*$  conjugated segment of the divinyl conjugated unit and naphthyl group in the main chain.<sup>5,8</sup>

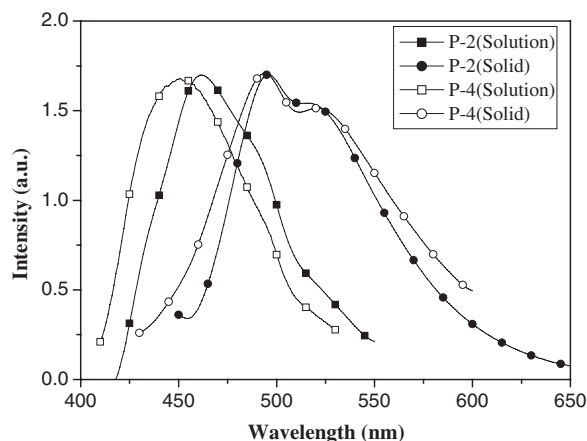
The absorption spectra edge of **P-1**, **P-3** and **P-2**, **P-4** were onset at 489 and 434 nm, which corresponded to band gaps at 2.54 and 2.80 eV respectively.<sup>19,45</sup> The band gap of **P-2** and **P-4** is larger than **P-1** and **P-3**, it can be mainly ascribed to well extended conjugation of **P-1** and **P-3** between the repeated units. The  $\sigma$ -band between the 1,3,4-oxadiazole unit and the phenyl unit will affect the conjugation effect of **P-2** and **P-4**. The larger red shift of UV spectra of **P-1** and **P-3** can also be attributed to the electron-donating effect of the butoxy-substituted moiety of **M-2** and the better coplanarity chain structure.

### Fluorescence Spectra

The fluorescent spectra of the four polymers in THF solution and in solid phase were shown in Figure 3 and Figure 4. The fluorescent spectra of polymers **P-1**, **P-3** and polymers **P-2** and **P-4** are almost similar due to the same chain structure except chiral center units. The polymers can emit very strong green-blue light under Ultraviolet light (366 nm) or sunlight even in the very low concentration. (*S*)-**M-1** and (*R*)-**M-1** cannot show visible fluorescence, and fluorescent wavelengths of **M-2** and **M-3** appeared at 383 and 389 nm respectively. The fluorescent intensity and wavelengths of the four polymers were dramatically increased over that of the monomers **M-2** and **M-3**, the maximum fluorescent wavelengths  $\lambda_{\text{max}}^{\text{F}}$  of **P-1** and **P-3** in THF solution showed two photoluminescent bands at 464, 487 nm and 460, 485 nm, and **P-2**, **P-4** showed 452 and 462 nm. The four polymers showed strong green-blue fluorescence due to the efficient energy migration from the extended  $\pi$ -electronic



**Figure 3.** Fluorescence spectra of **P-1** and **P-3** (**P-1**: Solution,  $\lambda_{\text{ex}} = 436$  nm; Solid,  $\lambda_{\text{ex}} = 440$  nm. **P-2**: Solution,  $\lambda_{\text{ex}} = 432$  nm; Solid,  $\lambda_{\text{ex}} = 438$  nm).

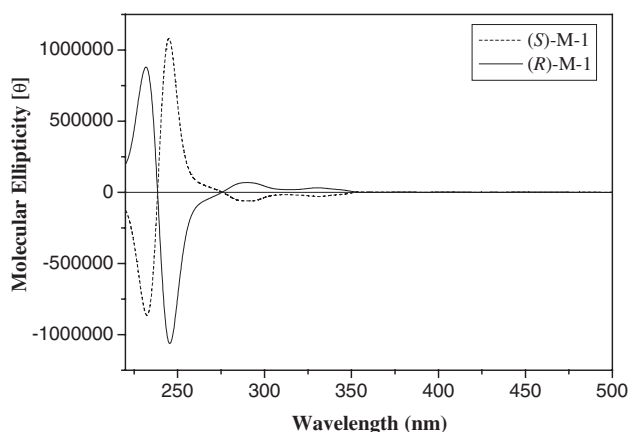


**Figure 4.** Fluorescence spectra of **P-2** and **P-4** (**P-2**: Solution,  $\lambda_{\text{ex}} = 425$  nm; Solid,  $\lambda_{\text{ex}} = 442$  nm. **P-4**: Solution,  $\lambda_{\text{ex}} = 422$  nm; Solid,  $\lambda_{\text{ex}} = 440$  nm).

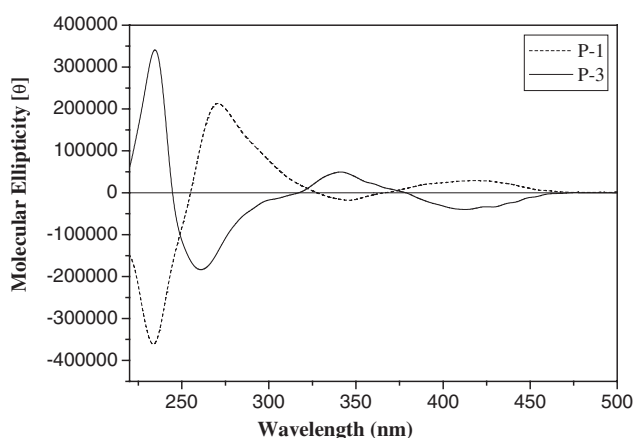
structure of the conjugated polymer main to the chiral binaphthyl core.<sup>5,8,17,43</sup> But in the solid powder state, the fluorescent wavelength  $\lambda_{\text{max}}^{\text{F}}$  of **P-1** and **P-3** appeared red shift to 500 nm, while **P-2** and **P-4** had a larger red shift to 496 and 519 nm. It can be attributed to more planar conformations of conjugated chains in the solid state than in solution.<sup>43,46,47</sup> The greatly enhanced fluorescence of chiral conjugated polymers are expected to have potential application in the polarized light-emitting molecular sensor.

### CD Spectra

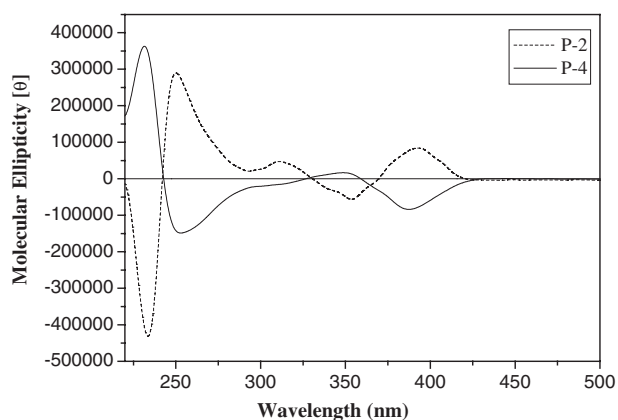
Although the optical rotation values ( $[\alpha]_{\text{D}}^{25}$ ) of monomers (*S*)-**M-1** and (*R*)-**M-1** are  $-19.5$  and  $+18.8$ , their conjugated polymers of **P-1**, **P-2**, **P-3** and **P-4** are  $+358$ ,  $+283$ ,  $-345$  and  $-373$  respectively. The absolute values of the optical rotation ( $[\alpha]_{\text{D}}^{25}$ ) of four polymers are much larger than the monomers (*S*)-**M-1** and (*R*)-**M-1**. Both monomers (*S*)-**M-1**, (*R*)-**M-1** and four polymers exhibit stronger CD signals with positive and negative Cotton Effects in their CD spectra (Figures 5–7). Monomers (*S*)-**M-1**, (*R*)-**M-1** and polymers **P-1**, **P-3** and polymers **P-2**, **P-4** have opposite signs for their optical rotation and CD spectra, but their position and intensity is almost identical. The molecular ellipticity of (*S*)-**M-1** is:  $[\theta]_{\lambda} = -8.63 \times 10^5$  (232 nm),  $+1.08 \times 10^6$  (245 nm),  $-6.47 \times 10^4$  (290 nm), and the molecular ellipticity of (*R*)-**M-1** is:  $[\theta]_{\lambda} = +8.84 \times 10^5$  (232 nm),  $-1.06 \times 10^6$  (245 nm),  $+7.35 \times 10^4$  (290 nm). The molecular ellipticity of **P-1** is:  $[\theta]_{\lambda} = -3.62 \times 10^5$  (234 nm),  $+2.15 \times 10^5$  (271 nm),  $-1.91 \times 10^4$  (346 nm),  $+2.86 \times 10^4$  (417 nm), the molecular ellipticity of **P-2** is:  $[\theta]_{\lambda} = -4.32 \times 10^5$  (233 nm),  $+2.89 \times 10^5$  (250 nm),  $+4.88 \times 10^4$  (312 nm),  $-5.60 \times 10^4$  (354 nm),  $+8.59 \times 10^4$  (392 nm), the molecular ellipticity of **P-3** is:  $[\theta]_{\lambda} = +3.40 \times 10^5$  (234 nm),



**Figure 5.** CD spectra of (S)-M-1 and (R)-M-1 (in THF).



**Figure 6.** CD spectra of P-1 and P-3 (in THF).



**Figure 7.** CD spectra of P-2 and P-4 (in THF).

$-1.84 \times 10^5$  (261 nm),  $+4.88 \times 10^4$  (342 nm),  $-4.10 \times 10^4$  (417 nm), and the molecular ellipticity of **P-4** is:  $[\theta]_D = +3.62 \times 10^5$  (231 nm),  $-1.49 \times 10^5$  (253 nm),  $-1.69 \times 10^4$  (312 nm),  $+1.62 \times 10^4$  (348 nm),  $-8.32 \times 10^4$  (388 nm). The long wavelength CD effect of polymers can be regarded as the more extended conjugated structure in the polymer chain. Cotton effect of the CD spectra of four

polymers are consistent with their UV absorption position.<sup>7,48,49</sup>

## CONCLUSIONS

Pd-catalyzed Heck reaction was found to offer a simple access to the four chiral polymers. Four chiral polymers can emit very strong green-blue fluorescence even in very low concentration. The polymer showed strong green-blue fluorescence due to the efficient energy migration from the extended  $\pi$ -electronic structure of the conjugated polymer main to the chiral binaphthyl core. There exists greatly difference from fluorescence spectra in the solid and solution state. The polymers exhibit stronger CD signals with positive and negative Cotton Effect in its CD spectra. The major differences between monomers and polymers are that a long wavelength Cotton Effect is observed for the polymer due to its more extended conjugation. Cotton effect of the CD spectra of four polymers are consistent with their UV absorption position.

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