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Polybinaphthyls incorporating chiral (*R*) or (*S*)-2,2′-binaphthyl and oxadiazole moieties by Stille reaction

Yixiang Cheng *, Lingwu Chen, Xiaowei Zou, Jinfeng Song, Wang Zhiliu

College of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, People's Republic of China

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Abstract

Chiral polymers **P-1** and **P-2** were prepared by the polymerization of (*R*)-3,3′-diiodo-2,2′-bisbutoxy-1,1′-binaphthyl ((*R*)-**M-1**) and (*S*)-3,3′-diiodo-2,2′-bisbutoxy-1,1′-binaphthyl ((*S*)-**M-1**) with 2,5-bis[(4-tributylstannyl)phenyl]-1,3,4-oxadiazole (**M-2**) via Pd(PPh_3)$_4$ catalyzed Stille coupling reaction. 1,3,4-Oxadiazole unit not only has high electron affinity, high thermal and oxidative stability, but also serves as a good chromophore. Polymers have strong blue fluorescence due to the efficient energy migration from the extended π-electronic structure of the polymers to the chiral binaphthyl core and can be expected to have potential application in the materials of fluorescent sensors. Circular dichroism (CD) spectra of polymers **P-1** and **P-2** are almost identical except that they gave opposite signals at each wavelength. The long wavelengths CD effect of **P-1** and **P-2** can be regarded as the more extended conjugated structure in the repeating unit and a high rigidity of the polymer backbone.

Keywords: (*R*)- and (*S*)-1,1′-binaphthol; Chiral polymers; 1,3,4-Oxadiazole

1. Introduction

The chirality of 1,1′-binaphthol (BINOL) and its derivatives is derived from the restricted rotation of the two naphthalene rings. (*R*) or (*S*)-1,1′-binaphthol (BINOL) have often been used as the starting materials for conjugated polymers that have a main chain chiral configuration [1–4]. The 2,2′-hydroxyl groups of BINOL can be easily converted to other groups (ethers, esters, PPh_2, etc.), and 3,3′- and 6,6′- positions of binaphthyl skeletal structure of BINOL can be selectively introduced by conjugated linkers, leading to a variety of polybinaphthyls with stable chiral configuration and high chiral induction. These chiral binaphthyl-based main chain polymers have exhibited potential applications in areas such as molecular recognition [5–7], asymmetric catalysis [8–10], optoelectronic materials [11–14].

Conjugated polymers containing oxadiazole derivatives are one of the most widely used electron transporting and hole blocking materials in LED devices and LED blends because 1, 3,4-oxadiazole unit not only has high electron affinity, high thermal and oxidative stability, but also serves as a good chromophore [15–18]. In our paper, the linker monomer **M-2**, 2,5-bis[(4-tributylstannyl)phenyl]-1,3,4-oxadiazole, was introduced into the chiral polymer backbone to maintain conjugation between the oxadiazole and binaphthyl segments so that the electron transporting properties of the polymers may be improved. These polymers are found to be blue light emitting materials with good fluorescence and also show high thermal stability. Pd-catalyzed Stille cross-coupling reaction was employed here for the creation of new C–C bond-formation since Stille reaction cannot only be done under mild conditions, but also tolerate many functional groups in the reagents and substrates [19–21]. This synthesis method has been investigated to synthesize conjugated or other functional polymers with unique structure and properties [22–24]. Herein, we report preliminary results of synthesis and structural characterization of two polymers based on 3,3′- positions of the chiral (*R*)- or (*S*)-1,1′-binaphthyl with 2,5-bis[(4-tributylstannyl)phenyl]-1,3,4-oxadiazole by Stille reaction.

2. Experimental part

2.1. Materials and measurements

(*R*) or (*S*)-1,1′-binaphthol were resolved from racemic 1,1′-binaphthol by (8*S*, 9*R*)-(−)-*N*-benzylcinchonidinium chloride according to the literature [25,26], both enantiomers could be obtained with 90.0% yield and >99.0% ee. (*R*) or

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* Corresponding author. Tel.: +86 25 83592709; fax: +86 25 83317761.
E-mail address: yxcheng@nju.edu.cn (Y. Cheng).

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(*S*)-2,2′-bismethoxymethoxy-1,1′-binaphthyl and (*R*) or (*S*)-3,3′-diiodo-2,2′-binaphthol were synthesized according to the literature (Scheme 1) [27–29]. 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 was freshly distilled on sodium-benzophenone, DMF was distilled from CaH_2, CH_2Cl_2 and CH_3CN were distilled from P_2O_5.

^{1}H, ^{13}C NMR spectra measurements (all in $CDCl_3$) were recorded on a 300-Bruker spectrometer with TMS as internal standard. FT-IR spectra were taken in KBr plates on a Nexus 870 FT-IR spectrometer. UV–vis spectra were carried out on a Perkin–Elmer Lambda 25. Fluorescent spectra were carried out on a 48000 DSCF spectrometer. DSC–TGA was determined on a Perkin–Elmer Pyris-1 under N_2 atomsphere. MS was determined on a micromass GCT. Circular dichroism (CD-) spectra were carried on a 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.

2.2. Preparation of (R)-3,3′-diiodo-2,2′-bisbutoxy-1,1′-binaphthyl [(R)-M-1]

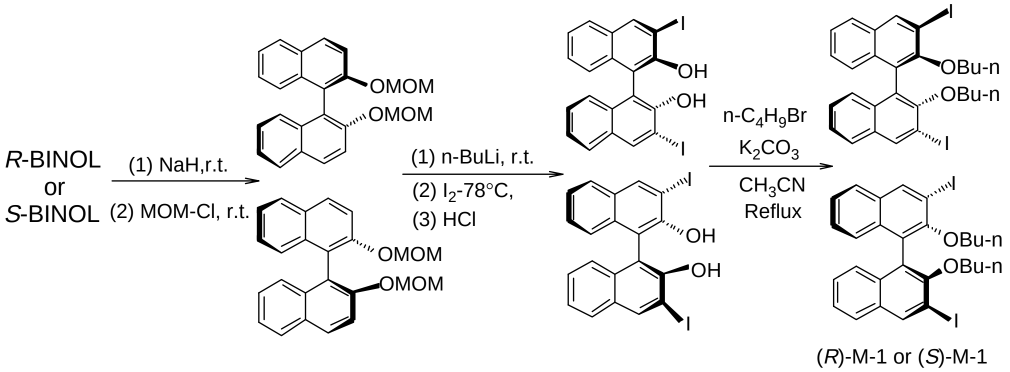
A mixture of (*R*)-3,3′-diiodo-2,2′-binaphthol (6.1 g, 10.9 mmol), K_2CO_3 (14.0 g, 0.1 mol), 1-bromobutane (4.5 g, 32.7 mmol) and NaI (0.3 g, 2 mmol) in 180 mL CH_3CN was refluxed for 4 h under N_2 before the second portion of K_2CO_3 (7.0 g, 0.05 mol) and 1-bromobutane (2.2 g, 16.4 mmol) was added. The solution was stirred and kept refluxing for 10 h. The mixture was poured into 5% aqueous NaOH (200 mL) and extracted with CH_2Cl_2 (2×75 mL). The combined organic layer was washed with saturated brine twice and then dried over anhydrous $MgSO_4$. After the solvent was removed under the reduced pressure, the residue was purified by chromatography on silica with petroleum ether as eluent or recrystallized from ethanol. (*R*)-**M-1** was obtained as a pale yellow crystal product in 90% yield (7.46 g). Mp: 125–126 °C; $[\alpha]_D = -71.8$ (*c* 0.5, THF); MS *m/z*: 650 (M^+, 8.2), 538 (65.8), 520 (68.5), 127 (100); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.50 (t, $J=7.3$ Hz, 6H), 0.71–0.75 (m, 2H), 0.89–0.94 (m, 2H), 1.20–1.32 (m, 4H), 3.27–3.34 (m, 2H), 3.78–3.85 (m, 2H), 7.13 (d, $J=4.1$ Hz, 2H), 7.27 (t, $J=8.2$ Hz, 2H), 7.40 (t, $J=8.0$ Hz, 2H), 7.79 (d, $J=4.1$ Hz, 2H), 8.53 (s, 2H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 13.84, 18.95, 32.05, 73.71, 93.41, 125.80, 125.97, 126.30, 127.28, 132.42, 134.32, 139.93, 154.50; ν_{max} (KBr)/cm^{-1}: 3050.4, 2953.0, 2927.5, 2868.0, 1557.0, 1560.8, 1229.6, 1011.3, 755.4.

2.3. Preparation of (S)-3,3′-diiodo-2,2′-dibutoxy-1,1′-binaphthyl [(S)-M-1]

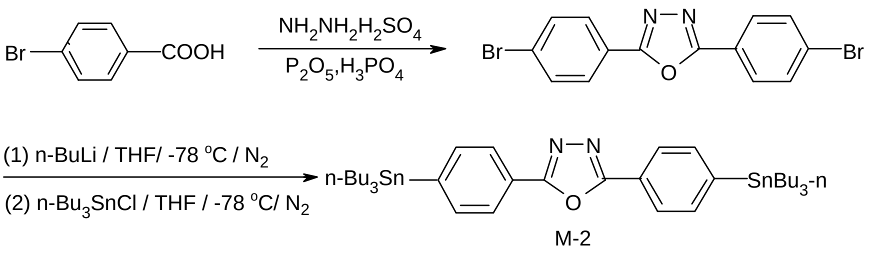
(*S*)-**M-1** was synthesized as the same procedure of (*R*)-**M-1**, and the yield of (*S*)-**M-1** was 91%. Mp: 125–126 °C; $[\alpha]_D = +71.5$ (*c* 0.5, THF); MS *m/z*: 650 (M^+, 1.0), 538 (5.9), 520 (30.7), 127 (100); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.50 (t, $J=7.3$ Hz, 6H), 0.70–0.75 (m, 2H), 0.89–0.93 (m, 2H), 1.20–1.32 (m, 4H), 3.27–3.34 (m, 2H), 3.78–3.84 (m, 2H), 7.13 (d, $J=4.1$ Hz, 2H), 7.27 (t, $J=8.2$ Hz, 2H), 7.40 (t, 2H, $J=8.0$ Hz), 7.79 (d, 2H, $J=4.1$ Hz), 8.53 (s, 2H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 13.84, 18.95, 32.05, 73.71, 93.41, 125.80, 125.97, 126.30, 127.28, 132.42, 134.32, 139.93, 154.50; ν_{max}(KBr)/cm^{-1}: 3050.1, 2953.1, 2927.3, 2867.8, 1557.1, 1560.9, 1229.6, 1011.2, 755.4.

2.4. Preparation of 1,3,4-oxadiazole-2,5-bis(4-tributylstannylbenzene) (M-2)

2,5-Di(4-bromophenyl)-1,3,4-oxadiazole (1.5 g, 4.0 mmol) was dissolved in dry anhydrous THF (30 mL) under N_2, the solution was cooled to −78 °C before 3.8 mL of *n*-butyllithium (2.2 M in hexane, 8.3 mmol) was added into the above solution. The mixture was stirred at −78 °C for 90 min, and then 2.6 mL of tributylstannyl chloride (9.5 mmol) was added dropwise. The reaction mixture was gradually warmed to room temperature and kept stirring for 8 h. The reaction was quenched with saturated aqueous NH_4Cl, and then the mixture was extracted with ether twice. The combined organic layer was washed with water and dried over anhydrous $MgSO_4$, and the solvent was evaporated under reduced pressure to give a viscous liquid. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 10:1, v/v) as the eluent to afford a colorless liquid **M-2** (2.2 g, 69.7%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.92 (t, $J=7.23$ Hz,



Scheme 1. Synthesis procedures of (*R*)-**M-1** and (*S*)-**M-1**.



Scheme 2. Synthesis procedures of the monomers **M-2**.

6H), 1.13 (t, $J=7.8$ Hz, 4H), 1.32–1.42 (m, 4H), 1.53–1.63 (m, 4H), 7.66 (d, $J=8.1$ Hz, 4H), 8.08 (d, $J=8.1$ Hz, 4H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 10.10, 14.53, 27.38, 29.46, 123.79, 126.19, 137.41, 148.48, 165.20; IR, ν_{max}(KBr)/cm^{-1}: 2956.2, 2926.0, 2870.8, 2832.4, 1599.6, 1535.7, 1483.7, 1463.4, 1052.1, 1015.4, 825.7, 735.0; MS (*m/z*): 801 ($M^{+\cdot}+H$, 100), 362 (27).

2.5. Polymer synthesis of *P-1*

A mixture of (*R*)-**M-1** (0.878 g, 1.35 mmol) and **M-2** (1.081 g, 1.35 mmol) was dissolved in 15 mL mixed solvent of THF and DMF (v/v 1:1). After the solution was bubbled with N_2 for 15 min, $Pd(PPh_3)_4$ (0.016 g, 0.0125 mmol) was added. The reaction solution was kept at 85 °C for 50 h under N_2. After cooled to room temperature, the solution was filtered through a short silica gel column into methanol (200 mL) to remove palladium black from the solution and precipitate out the crude product **P-1**, which was washed several times with methanol. Further purification could be conducted by dissolving the polymer in CH_2Cl_2 to precipitate in methanol again. Seven hundred and fifty-seven milli gram **P-1** was obtained in 91% yield. $[\alpha]_D^{25}=-274$ (*c* 0.05, THF), ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.27–0.43 (m, 6H), 0.78–1.12 (m, 4H), 1.40–1.78 (m, 4H), 3.01–3.37 (m, 4H), 7.09–7.23 (m, 4H), 7.34–7.37 (m, 2H), 7.72–7.81 (m, 4H), 7.90–7.97 (m, 4H), 8.17–8.23 (m, 4H); ν_{max}(KBr)/cm^{-1}: 3053.7, 2954.1, 2928.8, 2868.6, 1612.1, 1574.2, 1493.9, 1482.4, 1429.0, 1404.5, 1194.2, 1064.4, 1017.7, 845.0, 829.9, 750.0, 734.8.

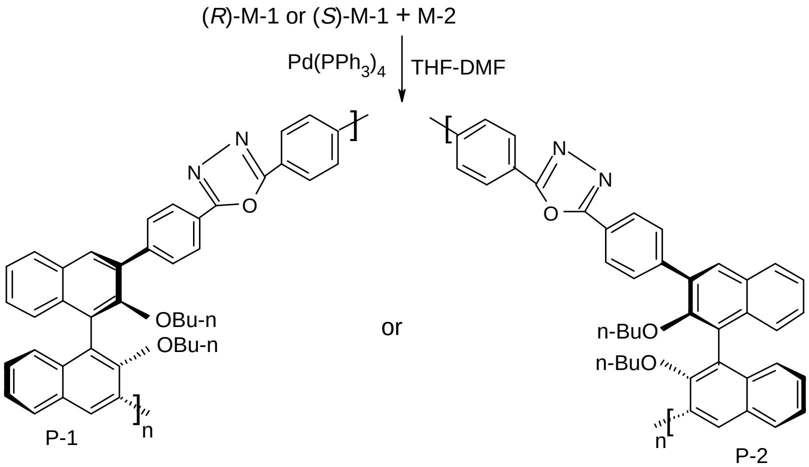
2.6. Polymer synthesis of *P-2*

P-2 was synthesized in the same way as **P-1**. The yield of **P-2** was 87%. $[\alpha]_D^{25}=+338$ (*c* 0.05, THF). **P-2** spectroscopic data: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.28–0.45 (m, 6H), 0.79–1.10 (m, 4H), 1.40–1.61 (m, 4H), 3.01–3.37 (m, 4H), 7.12–7.27 (m, 4H), 7.34–7.39 (m, 2H), 7.70–7.80 (m, 4H), 7.87–7.97 (m, 4H), 8.20–8.22 (m, 4H); ν_{max}(KBr)/cm^{-1}: 3054.2, 2955.3, 2929.1, 2869.5, 1613.0, 1571.3, 1494.8, 1483.4, 1428.2, 1405.6, 1195.3, 1065.5, 1018.5, 845.7, 830.9, 750.1, 735.3.

3. Results and discussion

3.1. Syntheses of polymers and characterization

In this paper, we chose **M-2**, 2,5-bis[(4-tributylstannyl) phenyl]-1,3,4-oxadiazole as the conjugated linker monomer. **M-2** was synthesized from 4-bromobenzoic acid (Scheme 2) according to the literature [30]. Synthesis of **M-2** should be handled under N_2 using Schlenk techniques with special care due to the toxicity of tributylstannyl chloride and side product hexa-*n*-butyldistannane. But the synthesis performance was easy. **M-2** was purified by chromatography and relatively stable when compared with most organometallic reagents. In addition, **M-2** is safe to be stored and used for the chiral polymer synthesis because **M-2** is not sensitive to either moisture or oxygen. A general Stille reaction condition was applied to the polymerization. The C–C cross coupling process was carried out by the polymerization of (*R*)-3,3′-



Scheme 3. Synthesis procedures of **P-1** and **P-2**.

Table 1
Polymerization results and characterization of **P-1** and **P-2**

	Yield (%)	M_w[a] ($\times 10^3$)	M_n[a] ($\times 10^3$)	PDI	$[\alpha]_D$[b]	T_g (°C)[c]	T_d (°C)[d]
P-1	91	4.0	1.6	2.57	−274	113	420
P-2	87	4.8	2.2	2.26	+338	115	422

[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 25 °C and solvent in THF (c 0.05).
[c] Determined by DSC at heating rate of 10 °C/min under N_2.
[d] Determined by TGA under N_2 at onset decomposition temperature.

diiodo-2,2′-bisbutoxy-1,1′-binaphthyl ((*R*)-**M-1**) and (*S*)-3,3′-diiodo-2,2′-bisbutoxy-1,1′-binaphthyl ((*S*)-**M-1**) with **M-2** in the presence of a catalytic amount (2% mol) of $Pd(PPh_3)_4$ at 85 °C under N_2 (Scheme 3). In order to synthesize higher molecular weight polymer and keep higher reaction temperature, the mixed solvents of THF–DMF (v/v 1:1) were chosen to improve the chiral polymer solubility in the reaction medium. The polymerization could be produced in a good yield (about 90%). The results of polymer's GPC showed it has moderate molecular weight (Table 1). GPC results of **P-1** and **P-2** using polystyrene as the standard are normally smaller than actual molecular weights of these polymers. The real molecular weights may be estimated by a factor of approximately 1.4–2.5 and lie in the range from 6000 to 10,000 (**P-1**) and 7000 to 12,000 (**P-2**) [31,32].

(*R*)-**M-1** and (*S*)-**M-1** can be used as the monomers to prepare the desired chiral polymers with predetermined luminescent properties. The chirality of binaphthyl compounds 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 important role in chiral induction. The dihedral angle between two naphthalene rings of a binaphthyl molecule ranges from 60 to 120°, which leads to the kinked or twisted polymer main chain backbone [1,11,33,34]. **P-1** and **P-2** showed good solubility in some common solvents such as THF, CH_2Cl_2, $CHCl_3$ and DMF. It can be attributed to the nonplanarity of the twisted polymers in the main chain backbone and the flexible alkyl substitutents on binaphthyl rings as side chain of the polymers.

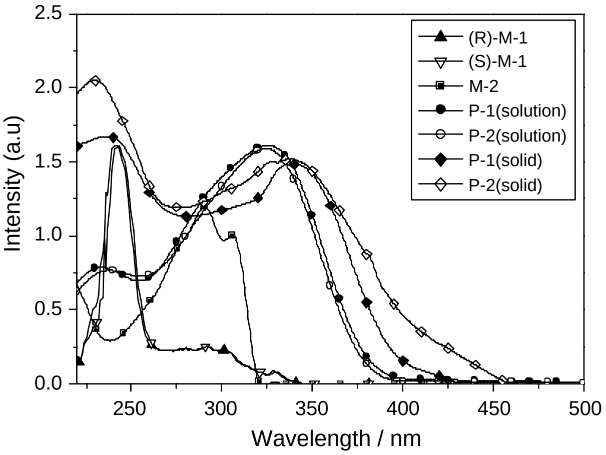


Fig. 1. UV spectra of monomers and polymers in THF solvent and thin films.

Table 2
Optical properties of **P-1** and **P-2**

	UV–vis λ_{max}, solution (nm)[a]	UV–vis λ_{max}, film (nm)[b]	PL λ_{max}, solution (nm)[a]	PL λ_{max}, film (nm)[b]	Φ_{PL}[c] solution
P-1	325	339	396	422	0.66
P-2	325	337	392	418	0.69

[a] Determined in THF solution.
[b] Determined in thin film.
[c] These values were estimated by using the quinine sulfate solution (ca. 1.0×10^{-5} M) in 0.12 M H_2SO_4 ($\Phi_f = 55\%$) as a standard.

3.2. Thermal analysis of polymers

Both **P-1** and **P-2** were air stable solid with pale color. **P-1** showed a glass transition temperature (T_g) at 113 °C, and the T_g of **P-2** was 115 °C. Thermogravimetric analyses (TGA) of **P-1** and **P-2** were carried out under N_2 atmosphere at a heating rate of 10 °C/min. The TGA plot of **P-1** is similar to that of **P-2**. Two polymers had good thermal stability and there is only about 8% of the loss weight from 260 to 380 °C due to the cleavage of the butyl group on the binaphthyl units [33,35,36]. Under N_2 atmosphere, an apparently one-step degradation was observed at temperature ranging from 420 to 500 °C. Both of them tended to complete decomposition at 520 °C. A total loss of 67% was observed when heated to 700 °C.

3.3. Optical properties

Fig. 1 illustrates the absorption spectra of monomers and polymers in THF solution and polymers as thin films. Optical properties of polymers **P-1** and **P-2** are summarized in Table 2. UV spectra of monomers (*R*)-**M-1**, (*S*)-**M-1** and polymers **P-1**, **P-2** are similar. Compared to monomers (*R*)-**M-1**, (*S*)-**M-1** and **M-2**, the polymers' UV absorption spectra displayed great red shifts. UV absorption maxima λ_{max} of (*R*)-**M-1** or (*S*)-**M-1** and **M-2** appeared at 242 and 291 nm respectively. The strongest absorption wavelength λ_{max} of **P-1** and **P-2** in THF solution appeared at 325 nm. **P-1** and **P-2** showed the stronger and broader absorption at the region from 270 to 370 nm (Fig. 1).

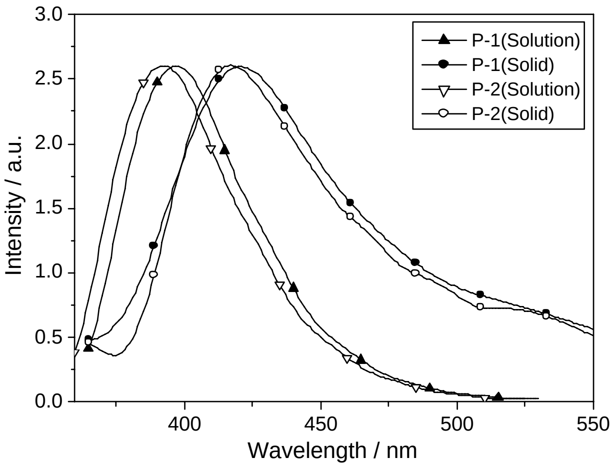


Fig. 2. Fluorescence spectra of **P-1** and **P-2** (**P-1**: solution, $\lambda_{ex} = 367$ nm; solid, $\lambda_{ex} = 360$ nm. **P-2**: solution, $\lambda_{ex} = 368$ nm; solid, $\lambda_{ex} = 365$ nm).

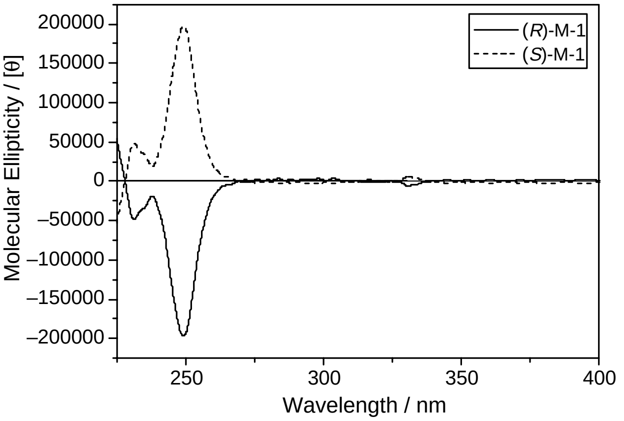


Fig. 3. CD spectra of (*R*)-**M-1** and (*S*)-**M-1** (in THF).

But the UV absorption of thin films of **P-1** and **P-2** showed red-shifts of 14 and 12 nm relative to those measured in solution state (Table 2). Pu synthesized a series of chiral conjugated polymers incorporating polybinaphthyls in the main chain and compared their UV absorption wavelengths of the polymers with their corresponding repeating units, and found there is almost no extended conjugation across the 1,1′-bond of the binaphthyl units in the backbone of such polymers [1,35,36]. In this paper, a large red-shift in the electronic absorptions of the conjugated polymers **P-1** and **P-2** can be attributed to the effective π–π* conjugated segment of the linker conjugated unit **M-2** and naphthyl group in the main chain [37,38].

The fluorescent spectra of the two polymers were determined in THF solution and in solid phase respectively (Fig. 2). The fluorescent spectra of polymer **P-1** and **P-2** are similar due to the same chain structure except chiral center units. The polymers can emit blue light under Ultraviolet light (361 nm) or sunlight even in low concentration (1×10^{-4} M). (*R*)-**M-1**, (*S*)-**M-1** and **M-2** did not show visible fluorescence. PL efficiency (Φ_{PL}) of **P-1** and **P-2** are 0.66 and 0.69, respectively. The maximum fluorescent wavelengths λ^{F}_{max} of **P-1** and **P-2** in THF solution showed photoluminescent bands at 396 and 392 nm. Two polymers showed blue fluorescence due to the efficient energy transfer or exciton migration from the extended π-electronic structure of the polymer to the chiral binaphthyl core [1,37,39]. But in the solid powder state, the fluorescent wavelength λ^{F}_{max} of **P-1** and **P-2** showed red-shift of 26 nm relative to those measured in solution state. It can be attributed to a higher conjugated chain stacking in the solid than in the solution [23,38,40].

3.4. CD spectra

Although the special rotation values ($[\alpha]^{25}_{D}$) of monomers (*R*)-**M-1** and (*S*)-**M-1** are −71.5 and +71.8, their conjugated polymers of **P-1** and **P-2** are −274 and +338, respectively. The absolute values of the special rotation ($[\alpha]^{25}_{D}$) of two polymers are much larger than two monomers (*R*)-**M-1** and (*S*)-**M-1**. Both **P-1** and **P-2** exhibited intense CD signals with negative and positive cotton effects in their CD spectra (Fig. 4). Monomers (*R*)-**M-1** and (*S*)-**M-1**, polymers **P-1** and **P-2** have opposite signals for their optical rotation and on their CD spectra, and their position and intensity is almost identical. The molecular ellipticity of (*R*)-**M-1** is: $[\theta]_{\lambda}=-4.81\times10^{4}$ (231 nm), -1.97×10^{5} (249 nm), and the molecular ellipticity of (*S*)-**M-1** is: $[\theta]_{\lambda}=+4.80\times10^{4}$ (232 nm), $+1.98\times10^{5}$ (249 nm). The molecular ellipticity of **P-1** is: $[\theta]_{\lambda}=-2.25\times10^{5}$ (235 nm), $+6.46\times10^{4}$ (269 nm), -8.79×10^{5} (340 nm), the molecular ellipticity of **P-2** is: $[\theta]_{\lambda}=+2.24\times10^{5}$ (235 nm), -6.46×10^{4} (270 nm), $+8.76\times10^{5}$ (339 nm). We can find great difference from CD spectra of (*R*)-**M-1**, (*S*)-**M-1** and **P-1**, **P-2** (Figs. 3 and 4). $^{1}B_{b}$ band of (*R*)-**M-1** and (*S*)-**M-1** appeared at 249 nm, but **P-1** and **P-2** showed blue shift to 235 nm even though their molar ellipicities are nearly the same magnitude as monomers (*R*)-**M-1** and (*S*)-**M-1**. **P-1** and **P-2** have $^{1}L_{a}$ bands at 269 and 270 nm respectively. R-**M-1** and S-**M-1** did not have $^{1}L_{a}$ electronic transition in their CD spectra [41,42]. The long wavelengths CD effect of polymer **P-1** appeared at 340 nm, and **P-2** appeared at 339 nm, which can be regarded as the more extended conjugated structure in the repeating unit and a high rigidity of polymer backbone [34,43,44].

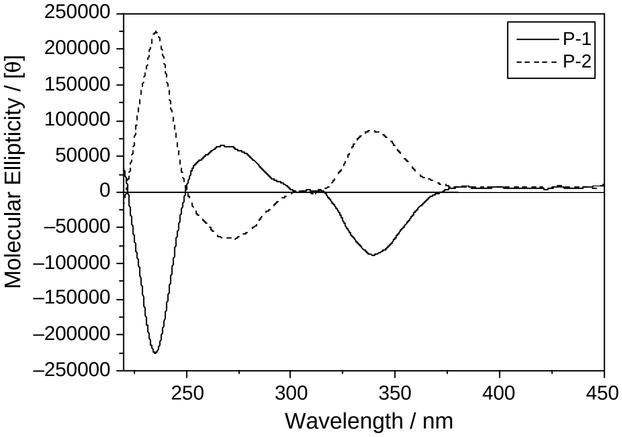


Fig. 4. CD spectra of **P-1** and **P-2** (in THF).

4. Conclusion

Pd-catalyzed Stille reaction was found to offer a simple access to the desired chiral polymers. **P-1** and **P-2** showed good solubility in some common solvents due to the nonplanarity of the twisted polymers in the main chain backbone and flexible alkyl substitutents on binaphthyl rings as side chain of the polymers. Polymers have strong blue fluorescence due to the efficient energy migration from the extended π-electronic structure of the polymers to the chiral binaphthyl core and are expected to have potential application in the materials of fluorescent sensors. The polymers exhibit strong CD signals with positive and negative cotton effect in their CD spectra. The major difference between monomers and polymers is that a long wavelength cotton effect is observed for the polymers due to their more extended π electron in the repeating unit and a high rigidity of the polymer backbone.

Acknowledgements

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