

CPL Emission of Chiral BINOL-based Polymers *via* Chiral Transfer of the Conjugated Chain Backbone Structure

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Content

1. Experimental Section
2. ¹H NMR of compounds.

1. Experimental Section

Measurements and materials

NMR spectra were obtained using a 300-Bruker spectrometer 300 MHz for ^1H NMR and reported as parts per million (ppm) from the internal standard TMS. UV-*vis* spectra and Circular dichroism (CD) spectra were recorded on JASCO J-810 spectropolarimeter. Fluorescence spectra were obtained from a HITACHI F-7000 Fluorescence spectrophotometer. Circularly polarized luminescence (CPL) spectra were performed on a JASCO CPL-200 spectrofluoropolarimeter. Molecular weight was determined by 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.

Synthesis of **M-1**

A mixture of 3,7-dibromo-10-octyl-10H-phenothiazine (2.00 g, 4.26 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (149.6 mg, 213.1 μmol), CuI (40.6 mg, 213.1 μmol) and trimethylsilylacetylene (1.81 mL, 12.79 mmol) was dissolved in 70 mL Et_3N . The reaction mixture was stirred at 80 °C for overnight under N_2 atmosphere. After the solution cooled to room temperature, the Pd was filtered and washed with ethyl acetate. After removal of the solvent under reduced pressure, the residues were dissolved with 30 mL CH_2Cl_2 and 30 mL CH_3OH , then NaOH (0.68 g, 17.04 mmol) was added into the above solution. The mixture was stirred at room temperature for 4 h, the solvent was removed under reduced pressure, then poured into water (50 mL) and extracted

with CH₂Cl₂. After the solvent was removed, the residues were purified by column chromatography on silica gel (petroleum ether (60-90 °C)/ethyl acetate, v/v, 8:1) to give **M-1** as a yellow oil (1.08 g, 70%). **M-1**: ¹H NMR (300 MHz, CDCl₃): 7.78 (dd, 2H, *J* = 2.1, 8.4 Hz), 7.21 (d, 2H, *J* = 2.1 Hz), 6.75 (d, 2H, *J* = 8.4 Hz), 3.80 (t, 2H, *J* = 8.4 Hz), 3.04 (s, 2H), 1.76 (m, 2H), 1.26 (m, 10H), 0.86 (t, 3H, *J* = 5.7 Hz).

Synthesis of **R/S-M-2**

Compound BINOL-MOM (2.84 g, 7.58 mmol) was dissolved in 60 mL of anhydrous Et₂O, 10.6 mL of *n*-BuLi (2.5 mol/L in hexane, 26.53 mmol) was added by syringe injection at room temperature under N₂ atmosphere. The solution was stirred for 2 h at room temperature, and then the solution of iodine (7.7 g, 30.32 mmol in 30 mL of THF) was slowly injected to the mixed solution at 0 °C under N₂ atmosphere. The mixture was then stirred overnight while the temperature was gradually warmed to room temperature. The reaction was quenched with 10% aqueous Na₂S₂O₃ (30 mL). After removal of the 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 residues were purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/ ethyl acetate, v/v, 30:1) to give a yellow solid **R/S-M-2** (1.52 g, 32%). $[\alpha]_D^{25}$ of **R/S-M-2** (*c* = 1.0, CH₂Cl₂) are -42.0 and +40.8, respectively; **R/S-M-2**: ¹H NMR (300 MHz, CDCl₃): 8.54 (s, 2H), 7.78 (d, 2H, *J* = 8.4 Hz), 7.16-7.45 (m, 6H), 4.81 (d, 2H, *J* = 5.7 Hz), 4.70 (d, 2H, *J* = 5.7 Hz), 2.60 (s, 6H).

Synthesis of **R/S-P**

A mixture of **M-1** (75.0 mg, 0.21 mmol), **M-2** (130.6 mg, 0.21 mmol), Pd(PPh₃)₄ (24.1 mg, 0.02 mmol) and CuI (4.0 mg, 0.02 mmol) was dissolved in 10 mL THF and 4 mL Et₃N. The solution was stirred at 70 °C for 3 d under N₂ atmosphere and cooled to room temperature, and then filtered through a short silica gel column. After the solvent was removed, the mixture was dissolved in 2 mL CH₂Cl₂, and then added into 50 mL CH₃OH to precipitate conjugated polymer. The polymer was filtered and washed with methanol several times. **R/S-P** was dried in vacuum to give yellow solids in 76% yield. $[\alpha]_D^{25}$ of **R/S-P** (*c* = 0.2, CH₂Cl₂) are -484.0 and +445.0, respectively; GPC: *M*_w=14320, PDI=1.51, *n*=13; ¹H NMR (300 MHz, CDCl₃): 8.18 (s, 2H), 7.86 (m, 4H), 7.39 (m, 4H), 7.33 (m, 4H), 6.81 (d, 2H), 5.16 (d, 2H), 4.94 (d, 2H), 3.83 (m, 2H), 6.81 (d, 2H), 2.52 (s, 6H), 1.75 (m, 2H), 1.26 (m, 10H), 0.87 (m, 3H).

2. ¹H NMR of compounds.

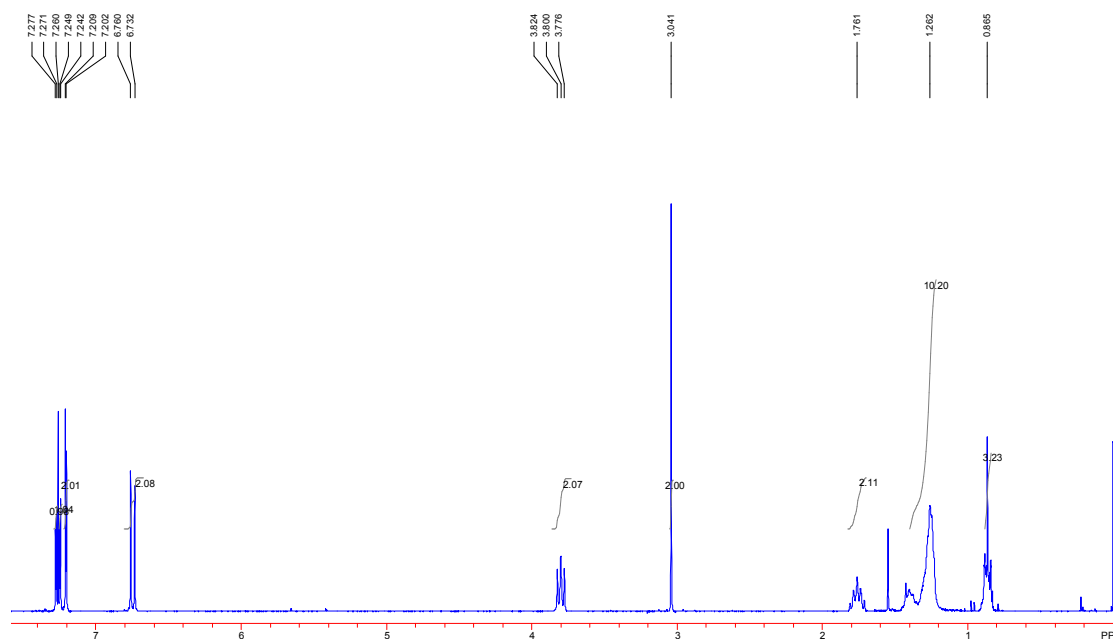


Fig. S1. ¹H NMR of **M-1** (CDCl₃, 300 MHz).

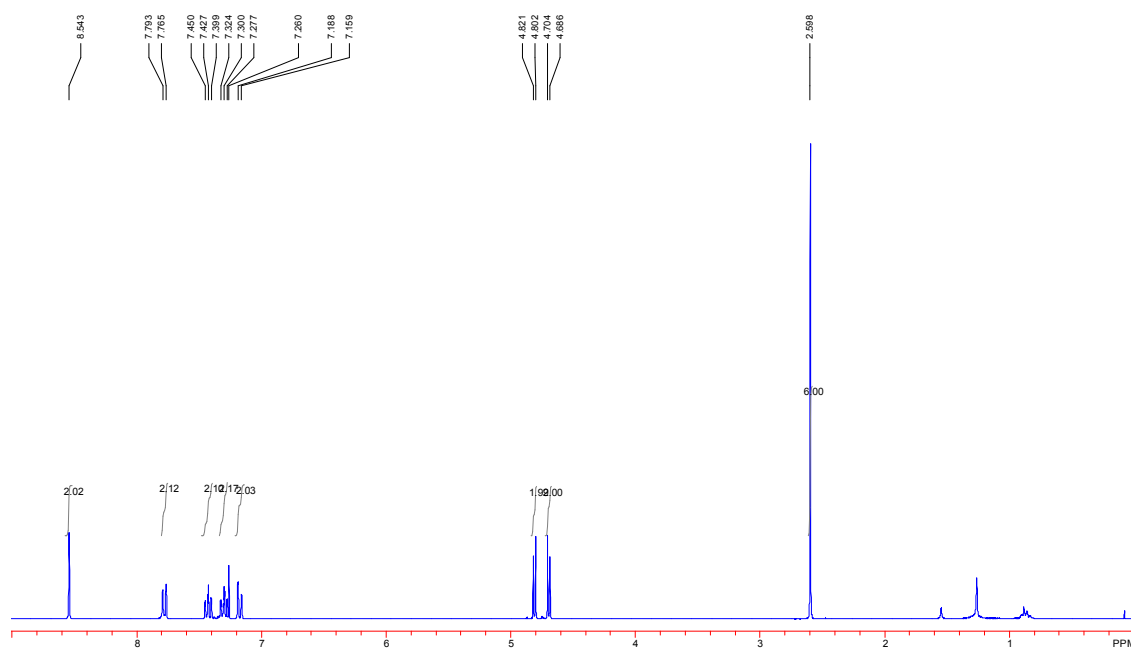


Fig. S2. ^1H NMR of *R/S*-**M-2** (CDCl_3 , 300 MHz).

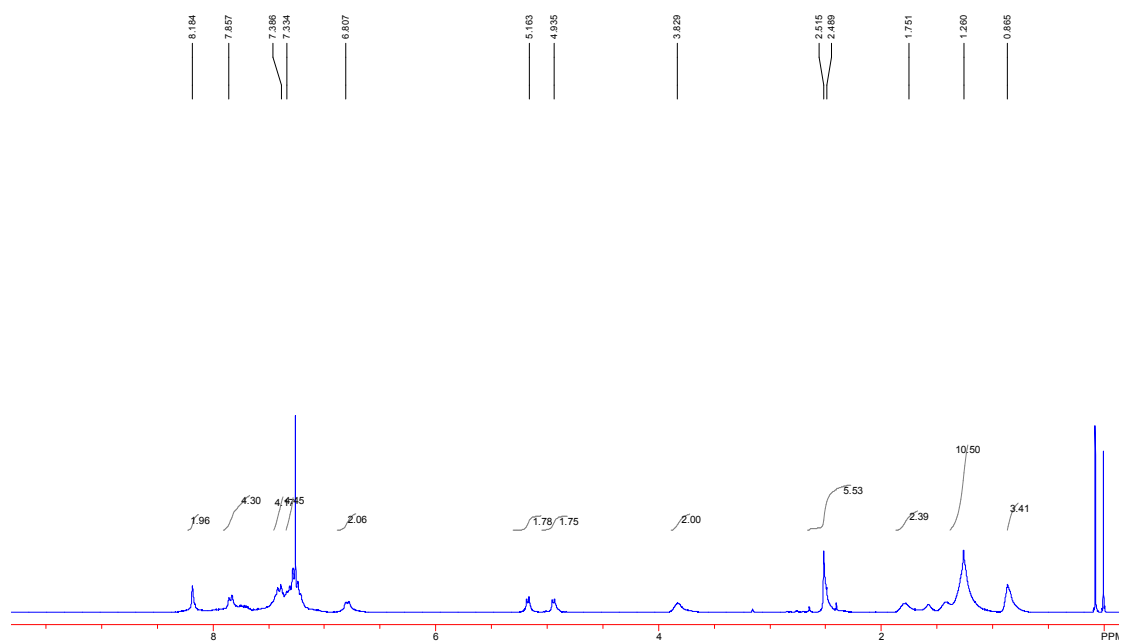


Fig. S3. ^1H NMR of *R/S*-**P** (CDCl_3 , 300 MHz).