Red Color CPL Emission of Chiral 1,2-DACH-based Polymers via

Chiral Transfer of the Conjugated Chain Backbone Structure

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1. Experimental Section

Measurements and materials

NMR spectra were obtained using a 300-Bruker spectrometer 300 MHz for ¹H NMR and 75 MHz for ¹³C NMR and reported as parts per million (ppm) from the internal standard TMS. UV-vis spectra were obtained from a Perkin-Elmer Lambda 25 spectrometer. Fluorescence spectra were obtained from a RF-5301PC spectrometer. Circular dichroism (CD) spectra were recorded on JASCO J-810 spectropolarimeter. 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 R/S-M-1

1 (1.00 g, 7.68 mmol) and (R,R)/(S,S)-1,2-DACH (439 mg, 3.84 mmol) were dissolved in EtOH (20 mL). The mixture was stirred for 4 hours at room temperature, and then the solvent was removed by rotary evaporation. The residue was recrystallize with acetone and petroleum ether to give a light yellow powder identified as **M-1** (1.24 g, 95%). **M-1**:¹H NMR (300 MHz, CDCl₃): δ 8.16 (s, 2H), 7.55 (d, *J* = 8.4 Hz, 4H), 7.45 (d, *J* = 8.4 Hz, 4H), 3.41 (m, 2H), 3.15 (s, 2H), 1.90-1.87 (m, 6H), 1.53-148 (m, 2H); ¹³C NMR(75 MHz, CDCl₃): δ 160.1, 136.4, 132.1, 127.6, 123.8, 83.3, 78.7, 73.7, 32.7, 24.3; ESI-MS: m /z: 339.15 [M + H]⁺.

Synthesis of R/S-M-2

M-1 (800 mg, 2.36 mmol) was dissolved in MeOH (15 mL), then NaBH₄ (537 mg, 14.18 mmol) was added to the solution slowly. The mixture was stirred for 2h at ice bath, and then the solvent was concentrated under reduced pressure. The mixture was extracted with CH₂Cl₂ (3×50 mL), and then dried over Na₂SO₄. The residues were purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/ dichloromethane:10:1) to give a yellow oil **M-2** (680 mg, 84%). **M-**2:¹H NMR (300 MHz, CDCl3): δ 7.40 (d, *J* = 8.4 Hz, 4H), 7.21 (d, *J* = 8.4 Hz, 4H), 3.80 (d, *J* = 12.5 Hz, 2H), 3.53 (d, *J* = 12.5 Hz, 2H), 3.06 (s, 2H), 2.22-2.00 (m, 4H), 1.92 (s, 2H), 1.70-1.60 (m, 2H), 1.19-0.88 (m, 4H); ¹³C NMR(75 MHz, CDCl3): δ 142.0, 132.0, 127.9, 120.4, 83.7, 77.2, 60.7, 50.4, 31.4, 24.9; ESI-MS: m/z: 343.15 [M + H]⁺.

Synthesis of R/S-P-1

A mixture of **R/S-M-1** (72.1 mg, 0.21 mmol), M-3 (150 mg, 0.21 mmol), Pd(PPh₃)₄ (12.3 mg, 0.01 mmol) and CuI (2.1 mg, 0.01 mmol) was dissolved in 12 mL THF and 7 mL Et₃N. The solution was stirred at 70 °C for 2 days under N₂ atmosphere. The mixture was cooled to room temperature and was 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 the polymer. The polymer was filtered and washed with methanol several times. The polymer was dried in vacuum to give 147 mg as a deep purple solid with 87% yield. GPC: $M_W = 13960$, PDI = 1.35, n=13; ¹H NMR (300 MHz, CDCl3): δ 8.16 (m, 2H), 7.56-7.51 (m, 4H), 7.51-7.47 (m, 1H), 7.47-7.37 (m, 4H), 7.10 (m, 2H), 7.01 (d, 1H), 3.97 (t, 2H), 3.41 (s, 2H), 2.70-2.67 (m, 6H), 1.87 (m, 6H), 1.58-1.48 (m, 10H), 1.28-1.16 (m, 10H), 0.89-0.77 (m, 3H).

Synthesis of R/S-P-2

A mixture of **R/S-M-2** (72.9 mg, 0.21 mmol), **M-3** (150 mg, 0.21 mmol), Pd(PPh₃)₄ (12.3 mg, 0.01 mmol) and CuI (2.1 mg, 0.01 mmol) was dissolved in 12 mL THF and 7 mL Et₃N. The solution was stirred at 70 °C for 2 days under N₂ atmosphere. The mixture was cooled to room temperature and was 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 the polymer. The polymer was filtered and washed with methanol several times. The polymer was dried in vacuum to give 143 mg as a dark solid with 85% yield. GPC: $M_W = 14520$, PDI = 1.32, n=14; ¹H NMR (300 MHz, CDCl3): δ 7.48-7.40 (m, 1H), 7.40-7.38 (m, 6H), 7.38-7.33 (m, 2H), 7.12 (s, 2H), 7.02 (s, 1H), 3.99 (m, 3H), 3.75 (m, 3H), 2.70 (s, 6H), 2.60-2.00 (m, 4H), 1.77 (s, 3H), 1.61 (s, 6H), 1.40-0.99 (m, 15H), 0.91-0.81 (m, 3H).

2. CD spectra of R/S-M-1, R/S-M-2 and R/S-P-2.



Fig. S1. CD spectra of R/S-M-1, R/S-M-2 and R/S-P-2 in THF (1.0×10⁻⁵ mol/L corresponding to BODIPY unit in the chiral polymer).

3. CPL spectra of R/S-P-1.



Fig. S2. CPL spectra of **R/S-P-2** in THF $(1.0 \times 10^{-5} \text{ mol/L corresponding to BODIPY unit in the chiral polymer).$

4. ¹H MR and ¹³C NMR spectra of compounds.



Fig. S3. 1 H NMR of **1** (CDCl₃, 300 MHz).



Fig. S4. ¹H NMR of M-1 (CDCl₃, 300 MHz).







Fig. S6. ¹H NMR of **M-2** (CDCl₃, 300 MHz).











Fig. S9. ¹H NMR of **P-1** (CDCl₃, 300 MHz).



Fig. S10. 1 H NMR of **P-2** (CDCl₃, 300 MHz).

5. MS of compounds.

+E-\lems-data\chengyixiang\ligit2013.4.26\ligit4-1.ledLine#:1 R.Time:0.333(Scan#21) MassPeaks+60 Spectrum Mode:Averaged 0.233-0.400(15-25) BasePeak:339.15(1169113) BG Mode:Averaged 0.033-0.867(3-53) Segment 1 - Event 1 Intensity 100 9(20 -365.2010-380.20 -267.15 600 150 200 250 300 350 400 500 550 650 100 450





Fig. S12. MS of **M-2**.

6. Time-resolved fluorescence decays (τ) of **P-1** and **P-2** in THF.



Fig. S13. Time-resolved fluorescence decays (τ) of **P-1** in THF (1.0×10⁻⁵ mol/L corresponding to BODIPY unit in the chiral polymer).



Fig. S14. Time-resolved fluorescence decays (τ) of **P-2** in THF (1.0×10⁻⁵ mol/L corresponding to BODIPY unit in the chiral polymer).