Electronic Supplementary Information

Far-Red/Near-Infrared Fluorescent Conjugated Polymer Nanoparticles with Size-Dependent Chirality and Cell Imaging Applications

Chunhui Dai,[a] Dongliang Yang,[b] Wenjie Zhang,[a] Biqing Bao,[b] Yixiang Cheng*[a] and Lianhui Wang*[b]

[a]Key Lab of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

[b]Key Laboratory for Organic Electronics and Information Displays and Institute of Advanced Materials, Nanjing University of Posts and Telecommunications, Nanjing 210023, China.

E-mail: *yxcheng@nju.edu.cn; iamlhwang@njupt.edu.cn*

Contents:

ESI 1. Synthesis procedures of key intermediates

Synthesis of 2

2,7-dibromo-9*H*-fluorene (2.17 g, 5.2 mmol) was dissolved in 40 mL dry DMF, and (*S*)-1-bromo-2-methylbutane (2.35 g, 15.6 mmol) was added to the solution. After that, *t*-BuOK (1.46 g, 13.0 mmol) was added and the resulting mixture was heated to 40 °C for 35 min. After the reaction finished, the mixture was poured into water and extracted with ethyl acetate (3×50 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and then concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with pure petroleum ether to get **2** (R_f = 0.9) as a white solid (1.52 g, 63 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54–7.46 (m, 5H), 7.45–7.44 (t, 1H), 2.08–2.00 (m, 2H), 1.86–1.77 (m, 2H), 0.97–0.74 (m, 4H), 0.63–0.56 (m, 8H), 0.30–0.24 (m, 6H); MS (EI, *m/z*): 464.21 (M^+); anal. calcd for $C_{23}H_{28}Br_2$: C, 59.37; H, 5.92. Found: C, 59.50; H, 6.08%.

Synthesis of 5

3,5-dimethyl-1*H*-pyrrole-2-carbaldehyde (**4**) (6.16 g, 50.0 mmol), 85% hydrazine hydrate (7.53 mL, 300 mmol) were added in 100 mL ethanol. Then 10 drops of glacial acetic acid were added dropwise. After about 2 minutes, a yellow precipitate emerged and the resulting mixture was further stirred for 1 h. The precipitate was filtrated and washed with cold ethanol. The product was dried under vacuum to give **5** as a bright yellow solid (1.20 g, 84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.62 (brs, 2H), 8.37 (s, 2H), 5.81 (s, 2H), 2.26 (s, 6H), 2.17 (s, 6H). MS (EI, *m/z*): 243.1 (M^++1); anal. calcd for $C_{14}H_{18}N_4$: C, 69.48; H, 7.62; N, 23.01. Found: C, 69.39; H, 7.49; N, 23.13%.

Synthesis of 6

5 (2.42 g, 10.0 mmol), 25 mL of triethylamine were added in 50 mL toluene and the resulting mixture was stirred for 10 minutes. Then $BF_3{\cdot}Et_2O$ (30 mL) was added by syringe and the mixture was heated to reflux overnight. After cooling to room temperature, the residue was concentrated to dryness under reduced pressure and the product was purified by column chromatography on silica gel (petroleum ether/dichloromethane, 1/1, v/v) to get **6** (R_f = 0.8) as a yellow solid (2.46 g, 73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 (s, 2H), 6.18 (s, 2H), 2.50 (s, 6H), 2.33 (s, 6H); MS (EI, *m/z*): 361.13 (M^+); anal. calcd for $C_{14}H_{16}B_2F_4N_4$: C, 49.60; H, 4.59; N, 16.61. Found: C, 49.76; H, 4.77; N 16.58%.

Synthesis of 9

A mixture of 2-thienylboronic acid (**7**) (1.28 g, 1.0 mmol), 4,7-dibromo-2,1,3-benzothidiazole (**8**) (0.88 g, 3.0 mmol), [$Pd(PPh_3)_4$] (57.8 mg, 0.05 mmol) was added in Schlenk tube. After the tube was evacuated under vacuum and flushed with Ar three times, 2 M aqueous Na_2CO_3 (15 mL), benzene (30 mL) and ethanol (8 mL) were added by syringe. The mixed solution was stirred at 85 °C for 15 h under Ar atmosphere. After the reaction finished, the mixture was cooled to room temperature and extracted with dichloromethane (3×50 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether as the eluent) to get **9** (R_f = 0.6) as a bright yellow solid (0.95 g, 32%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12 (d, J = 3.7 Hz, 2H), 7.88 (s, 2H), 7.46 (d, J = 5.1 Hz, 2H), 7.23–7.20 (m, 2H); MS (EI, *m/z*): 300.45 (M^++1); anal. calcd for $C_{14}H_8N_2S_3$: C, 56.10; H, 2.75; N, 9.51. Found: C, 55.97; H, 2.68; N, 9.32%.

Synthesis of M3

9 (0.30 g, 1.0 mmol), NBS (0.39 g, 2.2 mmol) were dissolved in 20 mL chloroform. The mixture was stirred for 48 h at room temperature. Then the residue was poured into water and extracted with chloroform (3×50 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and solvent was removed under reduced pressure. The residue was then recrystallized from chloroform to give **M3** as a red solid (0.24 g, 52%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 (d, J = 4.0 Hz, 2H), 7.80 (s, 2H), 7.16 (d, J = 4.0 Hz, 2H); MS (EI, *m/z*): 458.21 (M^+); anal. calcd for $C_{14}H_6Br_2N_2S_3$: C, 36.69; H, 1.42; N, 6.03. Found: C, 36.70; H, 1.32; N, 6.11%.

ESI 2. ^{1}H NMR spectra of the chiral conjugated polymer

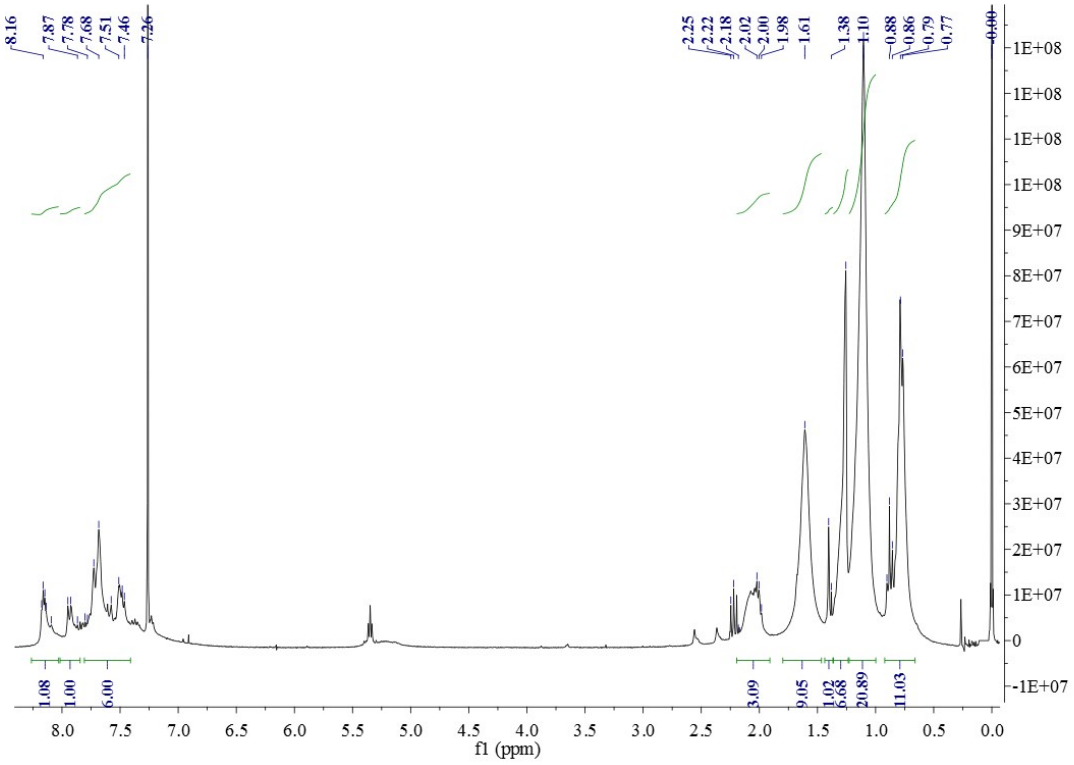

Figure S1. ^{1}H NMR of the chiral conjugated polymer in $CDCl_3$