Electronic Supplementary Information

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

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Synthesis of 2
2,7-dibromo-9H-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 MgSO₄ 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 (Rf = 0.9) as a white solid (1.52 g, 63 %). ¹H NMR (300 MHz, CDCl₃): 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 C₂₃H₂₈Br₂: C, 59.37; H, 5.92. Found: C, 59.50; H, 6.08%.

Synthesis of 5
3,5-dimethyl-1H-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%). ¹H NMR (300 MHz, CDCl₃): 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 C₁₄H₁₈N₄: 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 BF₃·Et₂O (30 mL) was added by syringe and the mixture was heated to reflux overnight. After cooling to room temperature, the residue was concentrated under reduced pressure and the product was purified by column chromatography on silica gel (petroleum ether/dichloromethane, 1/1, v/v) to get 6 (Rf = 0.8) as a bright yellow solid (2.46 g, 73%). ¹H NMR (300 MHz, CDCl₃): δ 7.94 (s, 2H), 6.18 (s, 2H), 2.50 (s, 6H), 2.33 (s, 6H); MS (EI, m/z): 361.13 (M⁺+1); anal. calcd for C₁₄H₁₆B₂F₄N₄: 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-benzothiadiazole (8) (0.88 g, 3.0 mmol), [Pd(PPh₃)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 Na₂CO₃ (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 MgSO₄ 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 (Rf = 0.6) as a bright yellow solid (0.95 g, 32%). ¹H NMR (300 MHz, CDCl₃): 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 C₁₄H₁₄B₂F₂N₃S: 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$_3$): $\delta$ 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$_6$Br$_2$N$_2$S$_3$: 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$_3$](image-url)