

Novel Spiro-Fluorenes from Tandem Radical-Addition for Liquid Crystalline

Monodisperse Conjugated Oligomers

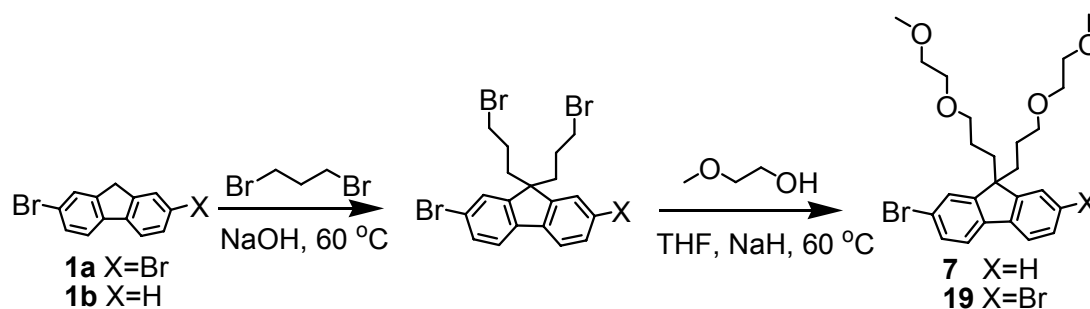
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Supporting Information

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Scheme S1. Synthesis route of fluorene derivatives **7** and **19**.



2,7-dibromo-9,9-bis(3-bromo-propyl)-fluorene

A mixture of 2,7-dibromo-fluorene (**1a**, 5.0 g, 15.4 mmol), sodium hydroxide (**1a**, 15 g, 0.38 mmol), tetrabutylammonium bromide (0.35 g, 1.1 mmol), 1,3-dibromo-propane (30 mL) and water (30 mL) was stirred for 8 h at 60 °C. The mixture was cooled to room temperature then poured into a large amount of brine for extraction with methylene chloride. The organic extracts were washed brine before dried over MgSO_4 . Upon evaporating off the solvent, the residue was purified by recrystallization with petroleum ether to afford the product (6.6 g, 77%) as a white solid. ^1H NMR (300 MHz, CDCl_3): δ (ppm) 7.51-7.58 (m, 6H), 3.15-3.19 (m, 4H), 2.15-2.20 (m, 4H), 1.12-1.22 (m, 4H). Anal. Calcd. for $\text{C}_{19}\text{H}_{18}\text{Br}_4$: C, 40.32; H, 3.21. Found: C, 40.42; H, 2.99. Molecular Mass: Calcd for $\text{C}_{19}\text{H}_{18}\text{Br}_4$: 565.96. Found: 565.72.

2-Bromo-9,9-bis(3-bromo-propyl)-fluorene

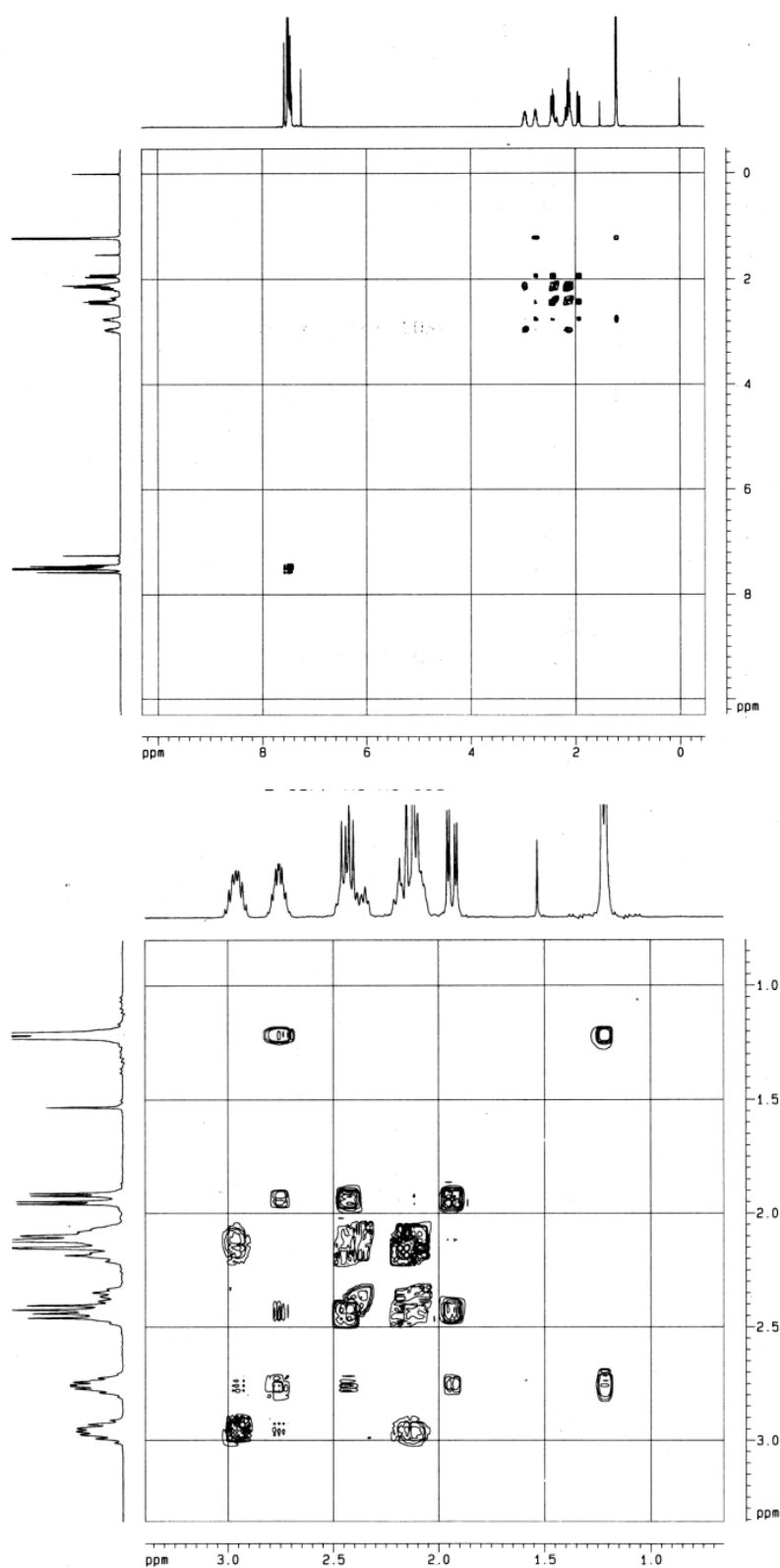
The procedure for the synthesis of 2,7-dibromo-9,9-bis(3-bromo-propyl)-fluorene from **1a** was followed to prepare the target from **1b** in a yield of 58%. ^1H NMR (300 MHz, CDCl_3): δ (ppm) 7.64-7.67 (m, 1H), 7.54-7.57 (m, 1H), 7.45-7.48 (m, 2H), 7.35-7.35 (m, 3H), 3.09-3.13 (m, 4H), 2.06-2.35 (m, 4H), 1.06-1.17 (m, 4H). Anal. Calcd. for $\text{C}_{19}\text{H}_{19}\text{Br}_3$: C, 46.85; H, 3.93. Found: C, 46.79; H, 3.74. Molecular Mass: Calcd for $\text{C}_{19}\text{H}_{19}\text{Br}_3$: 487.07. Found: 486.96.

2,7-Dibromo-9,9-bis(3-(2-methoxyethoxy)propyl)-fluorene (19)

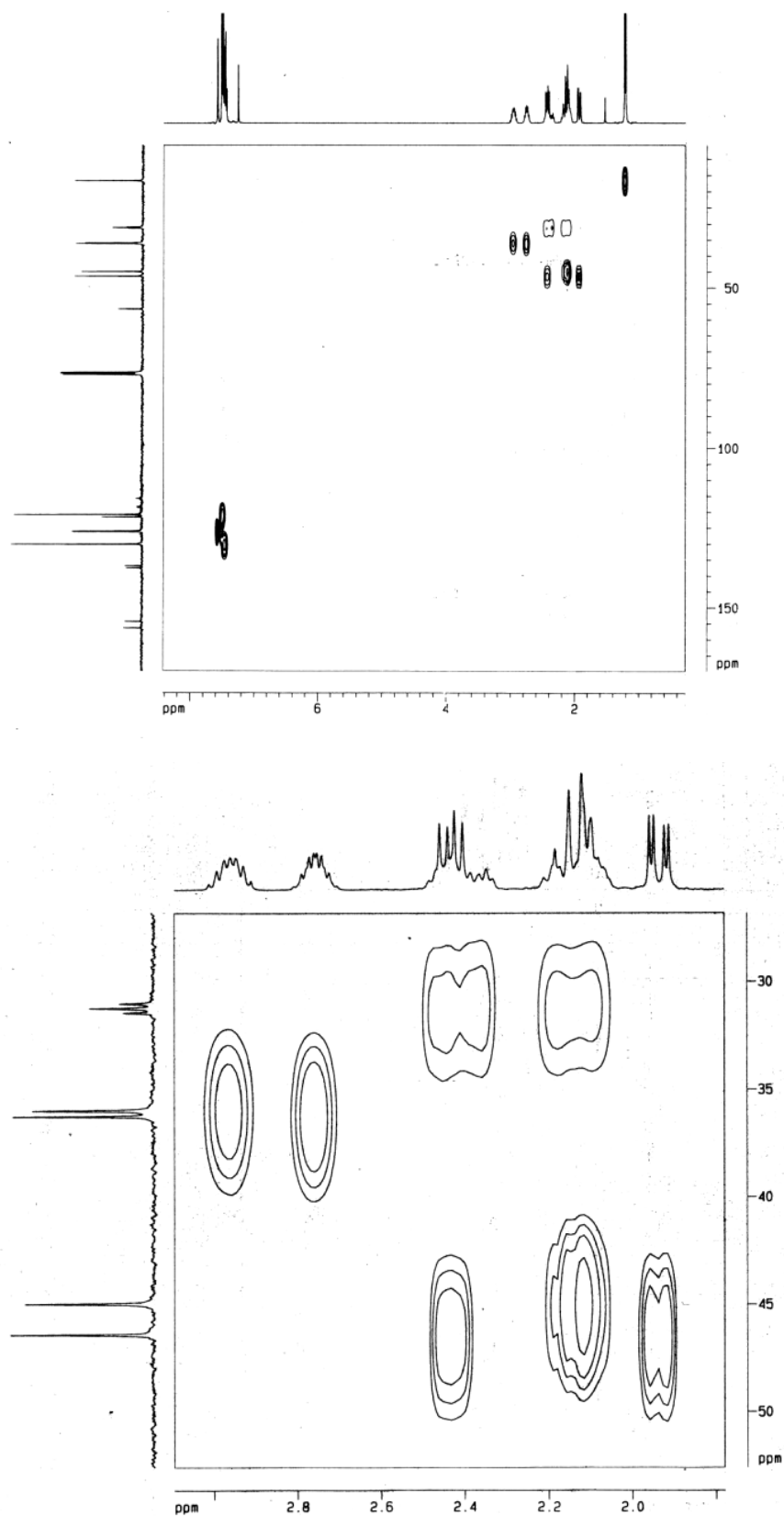
A solution of 2-methoxyethanol (2.28 g, 30.0 mmol) in dry THF (15 mL) was added dropwise to a stirred solution of sodium hydride (1.44 g, 30.0 mmol) in dry THF (20 mL) at room temperature. The mixture was reflux for 1 h and then cooled to room temperature, and then 2,7-dibromo-9,9-bis(3-bromo-propyl)-fluorene (2.83 g, 5.00 mmol) in dry THF (20 mL) was added dropwise. The reaction mixture was stirred over night at 75 °C. The mixture was cooled to room temperature then poured into a large amount of brine for extraction with ethyl ether. The organic extracts were washed with brine before dried over MgSO₄. Upon evaporating off the solvent, the residue was purified with column chromatography on silica gel with petroleum:ethyl ether (10:1) as the eluent to afford **19** (1.81 g, 68%) as a white solid. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.41-7.51 (m, 6H), 3.43-3.47 (m, 4H), 3.37-3.40 (m, 4H), 3.34 (s, 6H), 3.16-3.21 (m, 4H), 1.98-2.03 (m, 4H), 0.87-0.97 (m, 4H). Molecular Mass: Calcd for C₂₅H₃₂Br₂O₄: 556.33. Found: 556.13.

2-Bromo-9,9-bis(3-(2-methoxyethoxy)propyl)-fluorene (7)

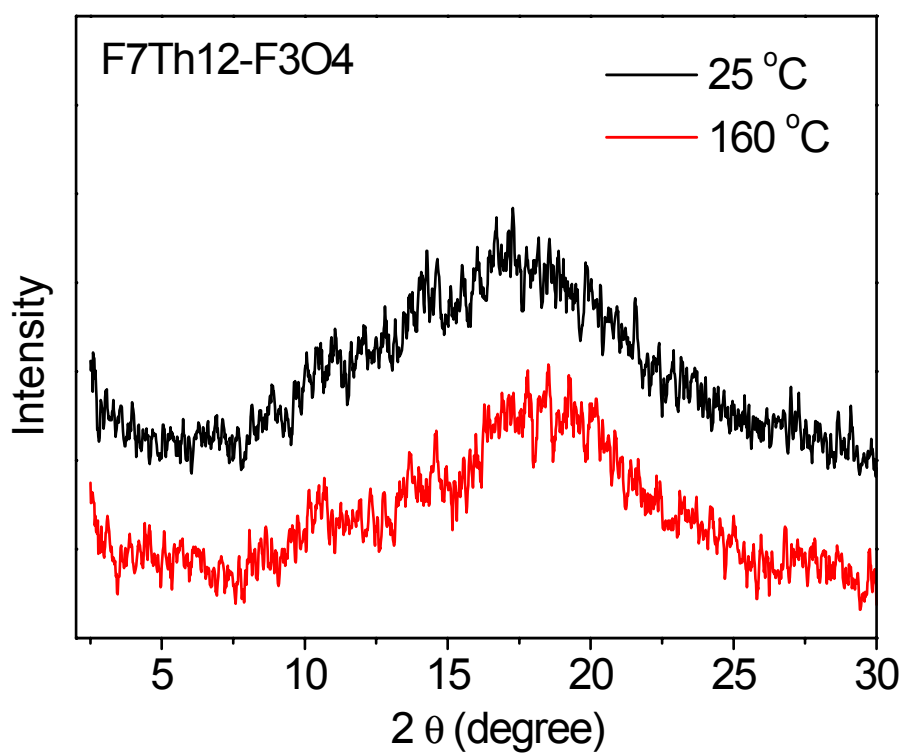
The procedure for the synthesis of **19** was followed to prepare **7** in a yield of 90%. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.64-7.69 (m, 1H), 7.53-7.60 (m, 2H), 7.40-7.49 (m, 2H), 7.32-7.35 (m, 2H), 3.43-3.47 (m, 4H), 3.37-3.40 (m, 4H), 3.38 (s, 6H), 3.20-3.23 (m, 4H), 1.98-2.03 (m, 4H), 0.87-0.97 (m, 4H). Molecular Mass: Calcd for C₂₅H₃₃BrO₄: 477.43. Found: 476.17.



H-C HMQC spectrum of compound **1**



H-C HMQC spectrum of compound 1



Wide angle X-ray diffraction (WAXD) patterns of **F7Th12-F3O4** at 25 and 160 °C on heating scan.