

Synthesis of Anthradithiophene-Based Liquid Crystals and Their Applications in Organic Thin Film Transistors

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Experimental Section

Material synthesis

The synthetic routes of anthradithiophene-based organic semiconductor materials are shown in scheme 1.

2-(4-Pentylphenyl)thiophene (1a) and 2-(4-dodecylphenyl)thiophene (1b)

Compounds 1a and 1b were prepared by similar methods. The synthetic procedures of compound 1b are described below. To a 250 mL round bottom flask was introduced 2-(tributylstannyl)thiophene 3.2 g (8.57 mmol), 1-bromo-4-dodecylbenzene 1.86 g (5.71 mmol), tetrakis(triphenylphosphine)palladium (0) 0.1 g (0.1 mmol), and degassed toluene (70 mL). The mixture was heated to 90 °C under argon gas for 16 h. After cooling to room temperature, the mixture was washed twice with brine. The organic layer was dried with anhydrous magnesium sulphate. After the solvent was removed, the crude product was purified by column chromatography (silica gel, hexane as eluent) and recrystallization in ethanol to yield 1.26 g (67 %) of white crystals. Compound 1a was synthesized by a similar method, and the yield was 75 %.

Trimethyl(5-(4-pentylphenyl)thiophen-2-yl)stannane (2a), (5-(4-dodecylphenyl)thiophen-2-yl)trimethylstannane (2b), and (5-dodecylthiophen-2-yl)trimethylstannane (2c)

Compounds 2a–2c were prepared by similar methods. The synthetic procedures of compound 2a are described below. Compound 1a 3.3 g (19.1 mmol) was dissolved in dry THF (50 mL) and cooled to -78 °C. To the mixture, 2.5 M *n*-butyl lithium (9.5 mL, 23.8 mmol) was added and stirred for 30 min at -78

°C. The reaction was then stirred at room temperature for 30 min. 28.7 mL trimethyltin chloride (28.65 mmol) was added to the reaction mixture at -78 °C. The reaction mixture was allowed to stir at room temperature for 16 h. The solvent was then removed, and the residue was washed with brine for three times. The organic layer was dried with anhydrous magnesium sulphate. After the solvent was removed, 7.0 g (93 %) of light yellow liquid was obtained. Compounds 2b and 2c were synthesized by similar methods, and their yields are 33 and 47 %, respectively.

((2-Bromo-5-(5-(4-pentylphenyl)thiophen-2-yl)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) (3a), ((2-bromo-5-(5-(4-dodecylphenyl)thiophen-2-yl)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) (3b), and ((2-bromo-5-(5-dodecylthiophen-2-yl)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) (3c)

Compounds 3a-3c were prepared by similar methods. The synthetic procedures of compound 3a are described below. To a 250 mL round bottom flask was introduced compound 2a 0.5 g (1.3 mmol), ((2,5-dibromo-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) 1.86 g (5.71 mmol), tetrakis(triphenylphosphine)palladium (0) 0.1 g (0.1 mmol), and degassed toluene (70 mL). The mixture was heated to 90 °C under argon gas for 16 h. After cooling to room temperature, the mixture was washed twice with brine. The organic layer was dried with anhydrous magnesium sulphate. After the solvent was removed, the crude product was purified by column chromatography (silica gel, hexane as eluent) and recrystallization in ethanol to yield 0.15 g (20 %) of yellow solid. Compounds 3b and 3c were synthesized by similar methods, and their yields are 43 and 36 %, respectively.

((2-(5-(4-Pentylphenyl)thiophen-2-yl)-5-(thiophen-2-yl)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) (4a), ((2-(5-(4-dodecylphenyl)thiophen-2-yl)-5-(thiophen-2-yl)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) (4b), and ((2-(5-dodecylthiophen-2-yl)-5-(thiophen-2-yl)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) (4c)

Compounds 4a-4c were prepared by similar methods. The synthetic procedures of compound 4a are described below. To a 150 mL round bottom flask was introduced compound 3a 0.15 g (0.25 mmol), 2-(tributylstannyl)thiophene 0.1 g (5.71 mmol), tetrakis(triphenylphosphine)palladium (0) 0.1 g (0.1 mmol), and degassed toluene (30 mL). The mixture was heated to 90 °C under argon gas for 16 h. After cooling to room temperature, the mixture was washed twice with brine. The organic layer was dried with anhydrous magnesium sulphate. After the solvent was removed, the crude product was purified by column chromatography (silica gel, hexane as eluent) and recrystallization in methanol to yield 0.06 g (39 %) of yellow solid. Compounds 4b and 4c were synthesized by similar methods, and their yields are 22 and 44 %, respectively.

2-(2,5-Diethynyl-4-(thiophen-2-yl)phenyl)-5-(4-pentylphenyl)thiophene (5a), 2-(2,5-diethynyl-4-(thiophen-2-yl)phenyl)-5-(4-dodecylphenyl)thiophene (5b), and 2-(2,5-diethynyl-4-(thiophen-2-yl)phenyl)-5-dodecylthiophene (5c)

Compounds 5a-5c were prepared by similar methods. The synthetic procedures of compound 5b are described below. To a 150 mL round bottom flask was introduced compound 4b 0.6 g (0.88 mmol), potassium carbonate 0.73 g (5.2 mmol), and cosolvent of methanol (8 mL) and tetrahydrofuran (3 mL). The reaction mixture was allowed to stir at room temperature for 16 h. After the solvent was removed, the mixture was washed twice with brine, and the organic layer was dried with anhydrous magnesium sulphate. The crude was purified by column chromatography (silica gel, hexane as eluent) to yield 0.5 g

(98 %) of yellow solid. Compounds 5a and 5c were synthesized by similar methods, and their yields are 95 and 97 %, respectively.

2-(4-Pentylphenyl)-6,12-dihydroanthra[1,2-b:5,6-b']dithiophene (5PADT), 2-(4-dodecylphenyl)-6,12-dihydroanthra[1,2-b:5,6-b']dithiophene (12PADT), and 2-dodecyl-6,12-dihydroanthra[1,2-b:5,6-b']dithiophene (12ADT)

Compounds 5PADT, 12PADT, and 12ADT were prepared by similar methods. The synthetic procedures of compound 5PADT are described below. To a 150 mL round bottom flask was introduced compound 5a 0.45 g (1.03 mmol), platinum(II) chloride 0.03g (0.11 mmol), and dry toluene (10 mL) under nitrogen. The reaction mixture was allowed to stir at 120 °C for 24 h. After the solvent was removed, the mixture was washed twice with brine, and the organic layer was dried with anhydrous magnesium sulphate. The crude was further purified by column chromatography (silica gel, hexane as eluent) to yield 0.05 g (11 %) of yellow solid. Compounds 12PADT and 12ADT were synthesized by similar methods, and their yields are 13 and 25 %, respectively.

Fabrication of OTFT Devices

Heavily doped Si wafers were used as the substrates and gate electrodes, followed by thermally growing 300 nm SiO₂ as gate insulators. The substrates were then dipped in 1 % SAM solution in toluene for 3 h to modify the surface. Subsequently, the substrates were cleaned by isopropyl alcohol (IPA), and the residual solvent was removed using a hotplate at 150 °C for 1 h. A solution containing the organic semiconductor (5 mg in 1 mL chloroform) was spin-coated on the substrates, followed by thermal annealing using a hotplate. Spin coating rate of 4000 rpm is used. The thickness of the organic film is

~50 nm. Gold was thermally deposited on the organic semiconductor layers under vacuum to serve as the source and drain electrodes.