SUPPLEMENTAL MATERIAL

Nematic Liquid Crystals with Bent-Rod Shapes:
Mesomorphic Thiophenes with Lateral Dipole Moments

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^{1}H NMR (250 MHz) spectra were recorded in ppm using TMS as an internal standard. ^{13}C NMR (125.8 MHz) spectra were in ppm relative to the solvent peak to $CHCl_3$.

Synthesis of 2,5-di(4-methoxyphenyl)thiophene 1. Palladium tetrakis-(triphenylphosphine) (119 mg, 0.103 mmol), 4-methoxyphenylboronic acid (692.6 mg, 4.56 mmol) and sodium carbonate (1.76 g, 16.6 mmol) were placed in a 200 ml-Schlenk flask equipped with a septum cap. The air in the flask was replaced with argon gas. Into the flask, 2,5-dibromothiophene (0.233 ml, 500 mg, 2.07 mmol) was added using a syringe. Toluene (40 ml), and ethanol (2 ml) were added through a cannula. Water (8.4 ml) was added using a syringe. The solution was refluxed (oil bath, 85-90 °C) for 48 h. After cooling, 1*N* hydrochloric acid (50 ml) was added and the solution was stirred for 10 min. The organic phase was dried over $MgSO_4$ and filtered with silica gel (5 g), and the silica gel was washed with tetrahydrofuran (50 ml). The combined filtrates were concentrated to give slightly green powder. The powder was recrystallized from tetrahydrofuran to give slightly green plates (**1**, 303.1 mg, 49%).

1: ^{1}H NMR ($CDCl_3$) δ 3.84 (s, 6H), 6.92 (d, J= 8.7 Hz, 4H), 7.15 (s, 2H), 7.55 (d, J = 8.7 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 55.60, 114.50 123.10, 127.04, 127.54, 142.79, 159.30; HRMS calcd for $C_{18}H_{16}O_2S$ (M^+) 296.087102, found 296.08710.

Synthesis of 3,4-dibromo-2,5-di(4-methoxyphenyl)thiophene 2. Palladium tetrakis (triphenylphosphine) (287 mg, 0.248 mmol), tetrabromothiophene (2.90 g, 7.25 mmol), 4-methoxyphenylboronic acid (1.10 g, 7.25 mmol) and sodium carbonate (6.15 g, 58.0 mmol) were placed in a 200 ml-Schlenk flask equipped with a septum. The air in the flask was replaced with argon gas. Toluene (80 ml), water (30 ml) and ethanol (10 ml) were added by a cannula through the septum. The septum was removed and a condenser was jointed to the neck under argon atmosphere. The solution was stirred and refluxed (oil bath, 85-90 °C). After 14 h, more 4-methoxyphenylboronic acid (1.10 g , 7.25 mmol) was added to the solution. Further, the solution was refluxed for 26 h. After cooling to room temperature, the aqueous phase was extracted with ethylether (50 ml). The combined organic phases were dried over $MgSO_4$, filtered with silica gel (5 g) and concentrated to obtain yellow solid. The solid was recrystallized from chloroform to give slightly yellow needles (**2**, 1.64 g). The mother liquid was concentrated and the residual solid was chromatographed on silica gel eluting with chloroform-hexane (1:1) to give the second crop of **2** (821 mg). The total yield of **2** is 2.44 g (75%).

2: ^{1}H NMR ($CDCl_3$) δ 3.85 (s, 6H), 6.97 (d, J= 8.8 Hz, 4H), 7.55 (d, J = 8.8 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 55.55, 111.64, 114.22, 125.46, 130.45, 137.52, 160.11.

Synthesis of 3,4-dicyano-2,5-di(4-methoxyphenyl)thiophene 3. Dibromide **2** (454.3 mg, 1.00 mmol) and copper cyanide (198.2 mg, 0.573 mmol) were placed in a 50 ml-Schlenk flask equipped with a septum. The air in the flask was replaced with argon gas.

Dry *N, N*-dimethylformamide (10 ml) was added through a canula. The solution was refluxed for 21 h. After cooling to room temperature, chloroform (40 ml) and aqueous ammonium chloride solution (20 ml) were added and the solution was stirred for 10 min. The organic phase was washed with ammonium chloride solution (20 ml). The solvent was removed by distillation under reduced pressure to give dark solid. The solid was chromatographed on silica gel eluting with chloroform to give pale yellow needles (**3**, 252.5 mg, 73%).

3: ^{1}H NMR ($CDCl_3$) δ 3.88 (s, 6H), 7.02 (d, J = 8.8 Hz, 4H), 7.72 (d, J = 8.8 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 55.76, 106.93, 113.68, 115.15, 122.49, 129.31, 152.62, 161.82; HRMS calcd for $C_{20}H_{14}N_2O_2S$ (M^+) 346.077580, found 346.07758.

Synthesis of 2,5-bis[(4-methoxyphenyl)ethynyl]thiophene 4a. Copper iodide (17.5 mg, 0.0919 mmol), 4-methoxyphenylacetylene (600 mg, 4.55 mmol), trans-bis(triphenylphosphine)palladium dichloride (29.4 mg, 0.0419 mmol) and 2,5-dibromothiophene (0.233 ml, 500 mg, 2.07 mmol) were placed in a 50 ml-Schlenk flask. The air in the flask was replaced with argon gas. Toluene (30 ml) and diisopropylamine (0.870 ml, 628 mg, 6.21 mmol) were added. The solution was stirred at room temperature for 18 h. To the reaction mixture was added 1*N* hydrochloric acid (20 ml) and the solution was stirred for 10 min. The organic phase was washed with 1*N* hydrochloric acid (20 ml) again, dried over $MgSO_4$ and concentrated to give a dark brown oil. The products were separated by column chromatography on silica gel eluting with chloroform-hexane (1:1) to give pale yellow plates (**4a**, 482.7 mg, 68%).

4a: ^{1}H NMR ($CDCl_3$) δ 3.82 (s, 6H), 6.87 (d, J = 8.8 Hz, 4H), 7.10 (s, 2H), 7.45 (d, J = 8.8 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 55.53, 81.31, 94.16, 114.28, 114.88, 124.78, 131.56, 133.22, 160.10; HRMS calcd for $C_{22}H_{16}O_2S$ (M^+) 344.087102, found 344.08710.

Synthesis of 3,4-dibromo-2,5-bis[(4-methoxyphenyl)ethynyl]thiophene 5a. Tetrabromothiophene (4.28g, 10.7 mmol), trans-bis(triphenylphosphine)palladium dichloride (153.0 mg, 0.218 mmol) and copper iodide (82.7 mg, 0.434 mmol) were placed in a 200 ml-Schlenk flask equipped with a septum. The air in the flask was replaced with argon gas. Toluene (80 ml) and diisopropylamine (3.75 ml, 2.71 mg, 26.8 mmol) were added. A solution of 4-methoxyphenylacetylene (2.82 g, 21.4 mmol) in toluene (10 ml) was added using a syringe. The solution was stirred at room temperature for 19 h. The solution was washed with 1*N* hydrochloric acid (50 ml), dried over $MgSO_4$ and concentrated. The residual solid was chromatographed on silica gel eluting with hexane-ethyl acetate (4:1) to give yellow crystals (**5a** , 2.71g, 51%).

5a: ^{1}H NMR ($CDCl_3$) δ 3.84 (s, 6H), 6.90 (d, J = 8.8 Hz, 4H), 7.50 (d, J = 8.8 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 55.55, 80.15, 98.99, 114.13, 114.33, 118.51, 121.49, 133.50, 160.55

Synthesis of 3-bromo-4-cyano-2,5-bis[(4-methoxyphenyl)ethynyl]thiophene 6a. Compound **6a** was prepared from dibromide **5a** with the same procedure as that of **3**. The reaction was stopped at an early stage (6 h).

6a: Yield 20%; yellow needles; ^{1}H NMR ($CDCl_3$) δ 3.85 (s, 3H), 3.86 (s, 3H), 6.91 (d, J = 9.0 Hz, 2H), 6.91 (d, J = 9.0 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 55.60, 55.62, 78.41, 78.78, 99.89, 103.40, 113.05, 113.28, 113.62,

114.44, 114.51, 115.81, 116.35, 122.44, 133.23, 133.63, 133.96, 160.85, 161.24; HRMS calcd for $C_{23}H_{14}BrNO_2S$ (M^+) 446.992862, found 446.99286.

Synthesis of 3,4-dicyano-2,5-bis[(4-methoxyphenyl)ethynyl]thiophene 7a.

Compound **7a** was prepared from dibromide **5a** with the same procedure as that of **3**.

7a: Yield 63%; yellow needles; ^{1}H NMR ($CDCl_3$) δ 3.86 (s, 6H), 6.92 (d, J = 8.9 Hz, 4H), 7.54 (d, J = 8.9 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 55.67, 77.63, 104.50, 111.72, 112.52, 113.79, 114.64, 133.81, 134.14, 161.58; HRMS calcd for $C_{24}H_{14}N_2O_2S$ (M^+) 394.077580, found 394.07758.

Synthesis of 2,5-bis[(4-butoxyphenyl)ethynyl]thiophene 4b. Compound **4b** was prepared with the same procedure as that of **4a**. In this case, 4-butoxyphenylacetylene and 2,5-diiodothiophene were used as the starting material instead of 4-methoxyphenylacetylene and 2,5-dibromothiophene.

4b: Yield 95%; yellow needles; ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J = 7.3 Hz, 6H), 1.37 (m, 4H), 1.64 (m, 4H), 3.81 (t, J = 6.5 Hz, 4H), 6.73 (d, J = 8.6 Hz, 4H), 6.98 (s, 2H), 7.32 (d, J = 8.6 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 14.03, 19.38, 31.37, 67.87, 81.20, 94.29, 114.50, 114.70, 124.74, 131.45, 133.11, 159.66; HRMS calcd for $C_{28}H_{28}O_2S$ (M^+) 428.181002, found 428.18100.

Synthesis of 2,5-bis[(4-butoxyphenyl)ethynyl]-3,4-dibromothiophene 5b.

Compound **5b** was prepared from 4-butoxyphenylacetylene and tetrabromothiophene with the same procedure as that of **5a**.

5b: Yield 50%; yellow needles; ^{1}H NMR ($CDCl_3$) δ 0.98 (t, J = 7.3 Hz, 6H), 1.4-1.6 (m, 4H), 1.7-1.85 (m, 4H), 3.98 (t, J = 6.5 Hz, 4H), 6.87 (d, J = 8.7 Hz, 4H), 7.48 (d, J = 8.7

Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 14.07, 19.42, 31.39, 68.02, 80.08, 99.11, 113.86, 114.85, 118.44, 121.51, 133.49, 160.20.

Synthesis of 2,5-bis[(4-butoxyphenyl)ethynyl]-3-bromo-4-cyanothiophene 6b.

Compound **6b** was prepared from dibromide **5b** with the same procedure as that of **6a**.

6b: Yield 20%; yellow needles; ^{1}H NMR ($CDCl_3$) δ 0.98 (t, J = 7.3 Hz, 6H), 1.50 (m, 4H), 1.7-1.85 (m, 4H), 3.99 (t, J = 6.4 Hz, 2H), 3.99 (t, J = 6.4 Hz, 2H), 6.89 (d, J = 8.6 Hz, 2H), 6.89 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.6 Hz, 2H), 7.51 (d, J = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ14.06, 19.40, 31.36, 68.08, 78.37, 78.72, 100.02, 103.56, 112.74, 113.32, 114.80, 115.06, 115.12, 115.72, 116.26, 122.42, 133.25, 133.62, 133.94, 160.47, 160.87; HRMS calcd for $C_{29}H_{26}BrNO_2S$ (M^+) 531.086762, found 531.08676.

Synthesis of 2,5-Bis[(4-butoxyphenyl)ethynyl]-3,4-dicyanothiophene 7b.

Compound **7b** was prepared from dibromide **5b** with the same procedure as that of **3**.

7b: Yield 25%; yellow needles; ^{1}H ($CDCl_3$) δ 0.98 (t, J = 7.3 Hz, 6H), 1.49 (m, 4H), 1.78 (m, 4H), 3.99 (t, J = 6.5 Hz, 4H), 6.90 (d, J = 8.8 Hz, 4H), 7.51 (d, J = 8.8 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 14.02, 19.37, 31.30, 68.12, 77.60, 104.63, 111.71, 112.15, 113.63, 115.05, 133.76, 134.06, 161.19; HRMS calcd for $C_{30}H_{26}N_2O_2S$ (M^+) 478.171500, found 478.17150.

Synthesis of 2,5-Bis[(4-hydroxyphenyl)ethynyl]-3,4-dicyanothiophene 7a'.

Dicyanide **7a** (105.7 mg, 0.268 mmol) was placed in a 200 ml-Schlenk flask. The air was replaced with argon gas. Dichloromethane (50 ml) was added through a canula. The solution was cooled to -10 °C in a salt-ice bath. A solution of boron tribromide in dichloromethane (2.7 ml, 1M solution) was added dropwise, and orange precipitate

appeared. After the addition was completed, the salt-ice bath was removed and the solution was stirred at room temperature for 24 h. Water (20 ml) was added to quench the reaction. The aqueous phase was extracted with 30 ml of chloroform-methanol (2:1) solution (five 30 ml-portions) and then with chloroform (five 30 ml-portions). The combined organic phases were dried over $MgSO_4$ and concentrated in vacuo. The product was purified by column chromatography on silica gel eluting with chloroform-methanol (19:1) to obtain yellow solid (**7a'**, 75.4 mg, 77%).

Synthesis of 2,5-Bis[[4-[(*S*)-2-butoxypropanoyloxy]phenyl]ethynyl]-3,4-dicyano-thiophene 8a. In a 50 ml-Schlenk flask, 4-dimethyaminopyridine (10.2 mg, 0.0835 mmol) was placed. The air in the flask is replaced with argon gas. A solution of **7a'** (95.6 mg, 0.261 mmol) in tetrahydrofuran (3 ml) and a solution of (*S*)-2-butoxypropanoic acid (93.4 mg, 0.584 mmol) in tetrahydrofuran (3 ml) were added using a syringe. Then a solution of *N, N'*-dicyclohexylcarbodiimide (124 mg, 0.601 mmol) in tetrahydrofuran (2 ml) was added using a syringe. The solution was stirred at room temperature for 23 h. To the reaction mixture were added 1*N* hydrochloric acid (10 ml) and ethyl acetate (10 ml) and the solution was stirred for 10 min. The aqueous phase was extracted with ethyl acetate (10 ml). The combined organic phases were dried over $MgSO_4$ and concentrated. The oily solid was chromatographed on silica gel eluting with chloroform-ethyl acetate (9:1) to give yellow solid (**8a**, 35.9 mg, 21%).

8a: ^{1}H ($CDCl_3$) δ 0.95 (t, J = 7.3 Hz, 6H), 1.43 (m, 4H), 1.57 (d, J = 6.8 Hz, 6H), 1.6-1.75 (m, 4H), 3.50 (dt, J = 8.9, 6.5 Hz, 2H), 3.69 (dt, J = 8.9, 6.5 Hz, 2H), 4.20 (q, J = 6.8 Hz, 2H), 7.20 (d, J = 8.6 Hz, 4H), 7.64 (d, J = 8.6 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 14.70, 18.88, 19.45, 31.98, 75.09, 75.13, 78.32, 103.11, 111.37, 114.80, 118.21, 121.89,

122.10, 122.40, 122.60, 133.58, 133.69, 133.83, 152.24, 171.73; HRMS calcd for $C_{36}H_{34}N_2O_6S$ (M^+) 622.213759, found 622.21376.

Synthesis of 2,5-bis[[4-[(*S*)-2-butoxypropanoyloxy]phenyl]ethynyl]-3,4-dicyano-thiophene 8b. Compound **8b** was prepared from **7a'** and (*S*)-2-decoxypropanoic acid with the same procedure as that of **8a**.

8b: Yield 30%; yellow solid; ^{1}H ($CDCl_3$) δ 0.88 (t, J = 7.3 Hz, 6H), 1.2-1.5 (m, 28H), 1.58 (d, J = 6.6 Hz, 6H), 1.5-1.85 (m, 4H), 3.48 (m, 2H), 3.68 (m, 2H), 4.21 (q, J = 6.6 Hz, 2H), 7.20 (d, J = 8.3 Hz, 4H), 7.64 (d, J = 8.3 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 14.30, 18.84, 22.85, 26.21, 29.48, 29.59, 29.72, 29.74, 29.92, 32.05, 70.98, 75.07, 78.28, 103.08, 111.31, 114.75, 118.15, 122.20, 122.41, 133.53, 133.64, 133.70, 152.23, 171.64; HRMS calcd for $C_{48}H_{58}N_2O_6S$ (M^+) 790.401560, found 790.40156.

X ray crystallography of 7a.

The yellow crystals of **7a** were obtained by crystallization from $CHCl_3$.

Diffraction data for **7a** was collected on a Siemens Platform/CCD automated diffractometer, equipped with graphite-monochromated MoKα (λ = 0.71073). The structure of **7a** was solved by direct methods.[*1] Hydrogen atoms were fixed on calculated positions, and full-matrix least squares refinement (SHELXL-93)[*2] was based on F^2. The data for compound **7a** were corrected for absorption analytically.[*2]

(*1) Sheldrick, G. M. SHELX-76. *Program for crystal structure determination*; University of Cambridge: Cambridge, England, 1976.

(*2) Sheldrick, G. M. SHELXL-93; University of Göttingen, Germany, 1993.

Crystal data for 7a: $C_{24}H_{14}N_2O_2S$, M = 394.43, space group $P2_1/n$, a = 11.5757(2) Å, b = 10.03300(10) Å, c = 17.3438(4) Å, β = 100.4580(10)°, Z = 4, V = 1980.83(6) Å^3, Dc =

1.323 Mg/m^3. $R = 0.0519$, $Rw = 0.1124$ for 2824 independent, observed reflections [$I > 2\sigma(I)$] with $1.96 < \theta < 23.29$. $GOF = 1.147$.