

Supporting Information (CM0205985)

Effects of Desymmetrization on Thiophene- Based Bent-Rod Mesogens

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X-Ray Diffraction:

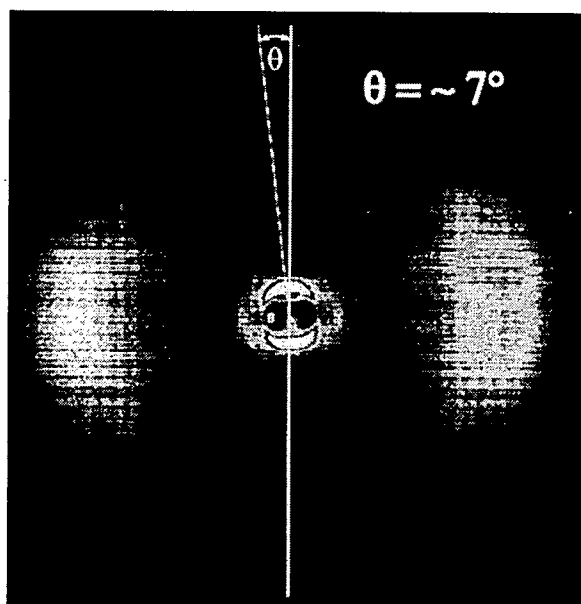


Figure 1. 2-D variable temperature X-ray diffraction of a magnetically aligned sample of the SmC phase of **14** at 85 °C. The inner reflections, corresponding to the layer spacing, are tilted at an angle of approximately 7° with respect to the vertically aligned outer reflections of the liquid aliphatic sidechains. This value corresponds to the tilt angle of the SmC phase.

Experimental Section

General Methods: Dichloromethane, THF and toluene were dried by passing through activated alumina columns. DMF was purchased from Aldrich (sure-seal) and stored over activated molecular sieves before use. (*s*)-(+)-2-Octanol was purchased from Aldrich (>99% purity). All other chemicals were of reagent grade and were used as received, unless otherwise specified. Air and water sensitive reactions employed standard Schlenk techniques under argon atmosphere. NMR spectra were obtained on Varian Mercury-300, Bruker DPX-400 or Varian Inova-500 spectrometers. All chemical shifts are referenced to residual CHCl_3 (7.27 ppm for ^1H , 77.0 ppm for ^{13}C). Multiplicities are indicated as s (singlet), d (doublet), t (triplet), and m (multiplet). High resolution mass spectra were obtained at the MIT Department of Chemistry Instrumentation facility (DCIF) on a Finnigan MAT 8200 or on a Bruker Daltonics Apex II 3T FT-ICR MS. Infrared spectra were recorded on a Perkin-Elmer 1760-X FTIR in KBr pellets. DSC investigations were carried out on a Perkin-Elmer DSC-7. Optical microscopy was carried out on a Leica polarizing microscope in combination with a Linkam LTS350 hotstage. X-ray diffraction studies were carried out on samples in capillary tubes with an INEL diffractometer with a 2 kW Cu K_α X-ray source fitted with an INEL CPS-120 position-sensitive detector and an INEL FURCAP capillary furnace and with a Rigaku RV-300 rotating anode Ni-filtered Cu K_α -radiation source fitted with a Siemens flat camera 2D-Xe-detector (256 x 256 cells) and equipped with an Instec HS 400 hot stage and Instec STC2000 temperature controller. The detectors were calibrated using a silver behenate standard which was produced by Eastman Kodak, and supplied by The Gem Dugout.

2,3,4-Tribromo-5-(4-benzyloxyphenyl)thiophene (4) Tetrabromothiophene (36.78 g, 92.09 mmol) was placed in a 2-necked 2000 mL flask along with 4-benzyloxyphenyl boronic acid (20.38 g, 89.46 mmol), Na₂CO₃ (75.90 g, 716.0 mmol), trans-dichlorobis(triphenylphosphine)palladium (0.50 g, 0.43 mmol), and a stir bar. The flask was evacuated, and argon was introduced. A solvent mixture of toluene (1200 mL), water (250 mL) and ethanol (150 mL) was sparged with argon for 20 minutes, and then added to the reaction flask via cannula. The mixture was heated to reflux with stirring for 46 hours, and water was added (200 mL) followed by extraction of the organics with ether. The extracts were dried over magnesium sulfate. Column chromatography (silica gel, 2:1 hexane/chloroform eluent) yielded **4** (27.31 g, 54.3 mmol, 61%) as a white solid. ¹H NMR (CDCl₃): 5.12 (s, 2H, CH₂O), 7.05 (d, 2H, J = 8.5 Hz, Ar-H), 7.36-7.47 (m, 5H, Ar-H), 7.51 (d, 2H, J = 8.5 Hz). ¹³C NMR (CDCl₃): 70.06, 109.30, 109.81, 114.98, 118.26, 124.79, 127.45, 128.12, 128.64, 130.23, 136.42, 139.86, 159.40. HRMS calcd for C₁₇H₁₁Br₃OS (M+Na)⁺: 522.7973, found (ESI): 522.7964.

3,4-Dibromo-2-(4-benzyloxyphenylethynyl)-5-(4-benzyloxyphenyl)thiophene (5) Compound **4** (8.07 g, 16.04 mmol) was placed in a 1000 mL round-bottom flask with 4-phenylmethoxyphenylacetylene (3.337 g, 16.04 mmol), copper(I)iodide (122 mg, 0.64 mmol), trans-dichlorobis(triphenylphosphine)palladium (450 mg, 0.64 mmol) and a stir bar. The flask was evacuated and argon was introduced, followed by the addition of dry, air-free toluene (300 mL) via cannula, and cooling to 0 °C with an ice bath. Dry diisopropylamine was added via syringe and the reaction was allowed to warm to room temperature and stir overnight. The solution was filtered through silica gel pad with

dichloromethane and dried (MgSO_4). After removal of the solvent in vacuo the remaining solids were purified by column chromatography (silica gel, gradient eluent mixture of hexanes/chloroform) followed by recrystallization from THF/MeOH yielding **5** (8.011 g, 12.71 mmol, 79%) as a yellow crystalline solid. ^1H NMR (CDCl_3): 5.11 (s, 2H, CH_2), 5.13 (s, 2H, CH_2), 6.99 (d, 2H, $J = 8.7$ Hz, Ar-H), 7.06 (d, 2H, $J = 8.7$ Hz, Ar-H), 7.34-7.50 (m, 10H, Ar-H), 7.52 (d, 2H, $J = 9.0$ Hz, Ar-H), 7.58 (d, 2H, $J = 9.0$ Hz, Ar-H). ^{13}C NMR (CDCl_3): 70.03, 70.09, 80.00, 98.18, 110.42, 114.55, 114.97, 114.99, 119.62, 119.86, 125.05, 127.48, 128.14, 128.64, 128.66, 130.32, 133.20, 134.20, 134.31, 136.38, 136.50, 139.01, 159.34, 159.42. HRMS calcd for $\text{C}_{32}\text{H}_{22}\text{Br}_2\text{O}_2\text{S}$ (M^+): 627.9702, found (EI): 627.9711.

3,4-Dicyano-2-(4-benzyloxyphenylethynyl)-5-(4-benzyloxyphenyl)thiophene (6)

Compound **5** (2.303 g, 3.653 mmol) was placed in a 200 mL Schlenk flask with CuCN (1.963 g, 21.92 mmol), copper (I) iodide (1.461 g, 7.672 mmol) and stir bar. The flask was evacuated and argon was introduced, followed by the addition of dry DMF (100 mL) via cannula. The reaction was heated to 130 °C with the exclusion of light and stirred for 8 hours, at which time the reaction was cooled and dichloromethane (200 mL) was added. The solution was washed with a saturated aqueous NH_4Cl followed by water, and the organic layer was dried (MgSO_4). The solvent was removed in vacuo, and the resulting brown solids were purified by column chromatography on silica gel (1:1 hexane/chloroform eluent) which yielded **6** (1.36 g, 2.602 mmol, 71%) as a yellow powder. ^1H NMR (CDCl_3): 5.12 (s, 2H, CH_2), 5.15 (s, 2H, CH_2), 7.00 (d, 2H, $J = 8.7$ Hz, Ar-H), 7.10 (d, 2H, $J = 8.7$ Hz, Ar-H), 7.33-7.48 (m, 10H, Ar-H), 7.54 (d, 2H, $J = 9.0$ Hz, Ar-H), 7.71 (d, 2H, $J = 9.0$ Hz, Ar-H). ^{13}C NMR 69.06, 69.33, 81.01, 98.05, 111.86,

114.50, 119.12, 119.32, 119.41, 121.07, 121.24, 121.32, 121.85, 122.21, 124.46, 128.97, 130.60, 132.93, 132.96, 134.87, 148.66, 151.79, 153.98, 164.63. HRMS calcd for $C_{34}H_{22}N_2O_2S$ (M+Na): 545.1294, found: (ESI) 545.1313.

3,4-Dicyano-2-(4-hydroxyphenylethynyl)-5-(4-hydroxyphenyl)thiophene (7)

Compound **6** (0.687 g, 1.09 mmol) was placed in a 200 mL Schlenk flask with stir bar. The flask was evacuated, and argon was introduced, followed by the addition of dry, air-free dichloromethane (170 mL) via cannula, and cooling to $-10\text{ }^{\circ}\text{C}$ with a NaCl/ice bath. BBr_3 (1M in solution in dichloromethane, 5.5 mL, 5.5 mmol) was added dropwise via syringe, at which point the reaction became an orange suspension. The reaction was stirred for 1 hour at $-10\text{ }^{\circ}\text{C}$, quenched with H_2O (20 mL), and allowed to warm to room temperature. Chloroform (100 mL) was added with a minimal amount of methanol to completely dissolve the solids. The solution was washed with water (3 X 50 mL) and dried over $MgSO_4$, and the resulting material was purified by column chromatography (silica gel, 10:1 $CDCl_3/MeOH$ eluent) yielding **7** (346 mg, 1.01 mmol, 93%) a yellow solid. 1H NMR ($CDCl_3$): 6.69 (d, 2H, $J = 9.0$ Hz, Ar-H), 6.78 (d, 2H, 9.0 Hz), 7.28 (d, 2H, $J = 9.0$ Hz, Ar-H), 7.46 (d, $J = 9.0$ Hz, Ar-H). ^{13}C NMR ($CDCl_3$): 76.42, 103.85, 103.95, 110.92, 111.86, 112.76, 114.21, 115.52, 116.15, 120.40, 128.98, 132.34, 133.52, 154.45, 158.97, 159.91. HRMS calcd for $C_{20}H_{10}N_2O_2S$ (M+Na): 365.0355, found: (ESI) 365.0344.

3,4-Dicyano-2-[4-(3,4-dihexyloxyphenylcarbonyloxy)phenylethynyl]-5-[4-(3,4-dihexyloxyphenylcarbonyloxy)phenyl]thiophene (8) Compound **7** (100 mg, 0.292 mmol) was placed in a 25 mL Schlenk flask with 3,4-dihexyloxybenzoic acid (207 mg, 0.643 mmol), 4-dimethylaminopyridine (18 mg, 0.146 mmol) and a stir bar. The flask

was evacuated, filled with argon, and 11ml of dichloromethane was added via syringe, forming a yellow suspension. Diisopropylcarbodiimide (183 μ L, 147 mg, 1.17 mmol) was added via syringe, and the solids were rapidly dissolved forming a yellow solution. The reaction was stirred at room temperature for 3 days, after which it was poured into 10 mL of 1N HCl (aqueous), extracted with chloroform, and dried over magnesium sulfate. The solvents were removed in vacuo and the resulting material was purified by column chromatography (silica gel, 2:1 dichloromethane/hexanes) followed by repeated precipitations from THF/methanol, yielding **8** (255 mg, 0.268 mmol, 92%) as a yellow solid. ^1H NMR (CDCl_3): 0.89-0.97 (m, 12H, CH_3), 1.30-1.43 (m, 16H, CH_2CH_2), 1.45-1.61 (m, 8H, CH_2), 1.84-1.92 (m, 8H, CH_2), 4.05-4.15 (m, 8H, CH_2), 6.94-6.97 (m, 2H, Ar-H), 7.30 (d, 2H, $J = 8.5$ Hz, Ar-H), 7.41 (d, 2H, $J = 8.5$ Hz, Ar-H), 7.66-7.69 (m, 4H, Ar-H), 7.83-7.84 (m, 4H, Ar-H). ^{13}C NMR (CDCl_3): 14.01, 22.57, 25.62, 25.66, 28.96, 29.09, 31.52, 31.55, 69.05, 69.31, 69.34, 77.98, 102.91, 106.84, 111.70, 11.85, 112.39, 114.45, 114.48, 116.30, 117.90, 120.70, 120.87, 122.47, 123.34, 124.51, 124.60, 126.71, 129.10, 132.75, 133.41, 148.67, 148.70, 152.65, 153.19, 153.43, 154.06, 154.16, 164.51. HRMS calcd for $\text{C}_{58}\text{H}_{66}\text{N}_2\text{O}_8\text{S}$ ($\text{M}+\text{H}$) $^+$: 951.4618, found (FAB): 951.4634.

3,4-Dicyano-2-[4-(3,4-dioctyloxyphenylcarbonyloxy)phenylethynyl]-5-[4-(3,4-dioctyloxyphenylcarbonyloxy)phenyl]thiophene (9) Preparation same as for **8**. ^1H NMR (CDCl_3): 0.89-0.97 (m, 12H, CH_3), 1.30-1.43 (m, 32H, $(\text{CH}_2)_4$), 1.45-1.61 (m, 8H, CH_2), 1.84-1.92 (m, 8H, CH_2), 4.05-4.15 (m, 8H, CH_2), 6.94-6.97 (m, 2H, Ar-H), 7.30 (d, 2H, $J = 8.5$ Hz, Ar-H), 7.41 (d, 2H, $J = 8.5$ Hz, Ar-H), 7.66-7.69 (m, 4H, Ar-H), 7.83-7.84 (m, 4H, Ar-H). ^{13}C NMR (CDCl_3): 14.09, 22.66, 25.94, 25.98, 29.00, 29.13, 29.23, 29.25, 29.32, 29.34, 31.80, 69.06, 69.31, 69.34, 77.97, 102.90, 106.82, 111.69, 111.85,

112.38, 114.46, 114.50, 116.29, 117.88, 120.69, 120.86, 122.46, 123.32, 124.51, 124.59, 126.69, 129.09, 132.74, 133.40, 148.66, 148.69, 152.65, 153.18, 153.43, 154.06, 154.16, 164.49. HRMS calcd for $C_{66}H_{82}N_2O_8S$ (M+H)⁺: 1063.5870, found (FAB): 1063.5899.

3,4-Dicyano-2-[4-(3,4-didecyloxyphenylcarbonyloxy)phenylethynyl]-5-[4-(3,4-didecyloxyphenylcarbonyloxy)phenyl]thiophene (10) Preparation same as for **8**. ¹H NMR (CDCl₃): 0.85-0.94 (m, 12H, CH₃), 1.22-1.41 (m, 48H, (CH₂)₆), 1.43-1.58 (m, 8H, CH₂), 1.81-1.92 (m, 8H, CH₂), 4.05-4.14 (m, 8H, CH₂), 6.92-6.97 (m, 2H, Ar-H), 7.27 (d, 2H, J = 8.5 Hz, Ar-H), 7.37 (d, 2H, J = 8.5 Hz, Ar-H), 7.63-7.65 (m, 4H, Ar-H), 7.78-7.82 (m, 4H, Ar-H). ¹³C NMR (CDCl₃): 14.08, 22.65, 25.91, 25.96, 28.97, 29.11, 29.31, 29.34, 29.36, 29.53, 29.56, 29.57, 31.86, 69.00, 69.27, 69.30, 77.94, 102.85, 106.75, 111.65, 111.81, 112.34, 114.43, 114.45, 116.27, 117.83, 120.66, 120.82, 122.41, 123.27, 124.46, 124.57, 126.63, 129.03, 132.65, 133.35, 148.63, 148.67, 152.61, 153.11, 153.40, 154.02, 154.12, 164.42. HRMS calcd for $C_{74}H_{98}N_2O_8S$ (M+H)⁺: 1175.7122, found (FAB): 1175.7159.

3,4-Dicyano-2-[4-(3,4-didodecyloxyphenylcarbonyloxy)phenylethynyl]-5-[4-(3,4-didodecyloxyphenylcarbonyloxy)phenyl]thiophene (11) Preparation same as for **8**. ¹H NMR (CDCl₃): 0.84-0.90 (m, 12H, CH₃), 1.21-1.39 (m, 64H, (CH₂)₈), 1.43-1.52 (m, 8H, CH₂), 1.82-1.90 (m, 8H, CH₂), 4.04-4.12 (m, 8H, CH₂), 6.91-6.94 (m, 2H, Ar-H), 7.28 (d, 2H, J = 8.5 Hz, Ar-H), 7.38 (d, 2H, J = 8.5 Hz, Ar-H), 7.63-7.67 (m, 4H, Ar-H), 7.79-7.82 (m, 4H, Ar-H). ¹³C NMR (CDCl₃): 14.12, 22.68, 25.95, 25.99, 29.00, 29.13, 29.35, 29.40, 29.61, 29.65, 29.68, 31.91, 69.04, 69.31, 69.34, 77.97, 102.90, 106.82, 111.69, 111.85, 112.38, 114.50, 114.50, 116.29, 117.88, 120.69, 120.86, 122.46, 123.33, 124.51, 124.59, 126.69, 129.09, 132.74, 133.40, 148.67, 148.70, 152.65, 153.18, 153.43,

154.06, 154.16, 164.49. HRMS calcd for $C_{82}H_{114}N_2O_8S$ ($M+H$)⁺: 1287.8374, found (FAB): 1287.8353.

Symmetric Compounds:

3,4-Dicyano-2,5-bis[4-(hexyloxy)phenylethynyl]thiophene (13) Placed **12** (52 mg, 0.142 mmol) in a 25 mL Schlenk flask with PPh_3 (82 mg, 0.312 mmol) and a stir bar. The flask was evacuated and filled with argon several times. Dry, air-free THF (5 mL) was added via syringe. Diethylazodicarboxylate (49 μ L, 0.312 mmol) was added via syringe, at which point the solution became an intense red color. After stirring for 48 hours the original yellow color had returned to the solution. Organics were washed with water, dried ($MgSO_4$) and removed in vacuo, yielding a dark yellow solid which was purified by column chromatography (silica gel, 1:1 hexane/dichloromethane eluent) followed by multiple precipitations from dichloromethane/methanol, yielding 55 mg (0.104 mmol, 73%) of **13** as a yellow solid. 1H NMR ($CDCl_3$): 0.88-0.93 (t, 6H, CH_3), 1.28-1.40 (m, 8H, $(CH_2)_2$), 1.40-1.55 (m, 4H, CH_2), 1.78-1.84 (m, 4H, CH_2), 4.00 (t, 4H, $J = 6.5$ Hz, CH_2O), 6.91 (d, 4H, $J = 8.5$ Hz, Ar-H), 7.52 (d, 4H, $J = 8.5$ Hz, Ar-H). ^{13}C NMR ($CDCl_3$): 14.03, 22.57, 25.64, 25.64, 29.04, 31.52, 68.25, 77.38, 104.44, 111.53, 111.99, 113.50, 114.87, 133.90, 161.00. HRMS calcd for $C_{34}H_{34}N_2O_2S$ ($M+Na$)⁺: 557.2233, found (ESI): 557.2223.

3,4-Dicyano-2,5-bis[4-(octyloxy)phenylethynyl]thiophene (14) Preparation same as for **13**. 1H NMR ($CDCl_3$): 0.88-0.93 (t, 6H, CH_3), 1.28-1.40 (m, 16H, $(CH_2)_4$), 1.40-1.55 (m, 4H, CH_2), 1.78-1.84 (m, 4H, CH_2), 4.00 (t, 4H, $J = 6.5$ Hz, CH_2O), 6.91 (d, 4H, $J = 8.5$ Hz, Ar-H), 7.52 (d, 4H, $J = 8.5$ Hz, Ar-H). ^{13}C NMR ($CDCl_3$): 14.10, 22.65, 25.97, 29.08, 29.21, 29.31, 31.79, 68.25, 77.38, 104.44, 111.53, 111.99, 113.49, 114.87, 133.61,

133.91, 161.00. HRMS calcd for $C_{38}H_{42}N_2O_2S$ ($M+Na$)⁺: 613.2859, found (ESI): 613.2895.

3,4-Dicyano-2,5-bis[4-(decyloxy)phenylethynyl]thiophene (15) Preparation same as for 13. ¹H NMR (CDCl₃): 0.88-0.93 (t, 6H, CH₃), 1.28-1.40 (m, 24H, (CH₂)₆), 1.40-1.55 (m, 4H, CH₂), 1.78-1.84 (m, 4H, CH₂), 4.00 (t, 4H, J = 6.5 Hz, CH₂O), 6.91 (d, 4H, J = 8.5 Hz, Ar-H), 7.52 (d, 4H, J = 8.5 Hz, Ar-H). ¹³C NMR (CDCl₃): 14.11, 22.67, 25.95, 29.06, 29.30, 29.34, 29.53, 31.87, 68.24, 77.38, 104.44, 111.52, 111.97, 113.46, 114.86, 133.59, 133.89, 160.99. HRMS calcd for $C_{42}H_{50}N_2O_2S$ ($M+Na$)⁺: 669.3485, found (ESI): 669.3464.

3,4-Dicyano-2,5-bis[4-(dodecyloxy)phenylethynyl]thiophene (16) Preparation same as for 13. ¹H NMR (CDCl₃): 0.88-0.93 (t, 6H, CH₃), 1.28-1.40 (m, 32H, (CH₂)₈), 1.40-1.55 (m, 4H, CH₂), 1.78-1.84 (m, 4H, CH₂), 4.00 (t, 4H, J = 6.5 Hz, CH₂O), 6.91 (d, 4H, J = 8.5 Hz, Ar-H), 7.52 (d, 4H, J = 8.5 Hz, Ar-H). ¹³C NMR (CDCl₃): 14.12, 22.67, 25.95, 29.07, 29.34, 29.54, 29.57, 29.62, 29.64, 31.90, 68.23, 77.38, 104.43, 111.50, 111.96, 113.46, 114.86, 133.57, 133.87, 160.98. HRMS calcd for $C_{46}H_{58}N_2O_2S$ ($M+Na$)⁺: 725.4111, found (ESI): 725.4103.

3,4-Dicyano-2,5-bis[4-(1-methylheptyloxy)phenylethynyl]thiophene (17)
Preparation same as for 13. ¹H NMR (CDCl₃): 0.88-0.93 (t, 6H, CH₃), 1.28-1.54 (m, 22H), 1.56-1.63 (m, 2H), 1.64-1.82 (m, 2H), 4.39-4.49 (m, 2H), 6.88 (d, 4H, J = 8.7 Hz, Ar-H), 7.50 (d, 4H, J = 8.5 Hz, Ar-H). ¹³C NMR (CDCl₃): 14.14, 19.63, 22.63, 25.44, 29.25, 31.78, 74.06, 77.42, 104.43, 111.43, 111.58, 113.30, 115.73, 133.45, 133.80, 160.00. HRMS calcd for $C_{38}H_{42}N_2O_2S$ ($M+Na$)⁺: 613.2859, found (ESI): 613.2823.

Unsymmetric Compounds:

3,4-Dicyano-2-(4-hexyloxyphenylethynyl)-5-(4-hexyloxyphenyl)thiophene (18)

Compound **7** (50 mg, 0.146 mmol) was placed in a 25 mL Schlenk flask with PPh₃ (84 mg, 0.321 mmol) and a stir bar. The flask was evacuated and argon was introduced. THF (5 mL), *n*-Hexanol (40 μ L, 0.312 mmol), and diethylazodicarboxylate (51 μ L, 0.312 mmol) were added via syringe, respectively, and the reaction was stirred at room temperature for 48 hours. The solution became a deep red color upon the addition of DEAD, and faded to yellow over the course of the reaction. The poured into water and the organics were extracted with chloroform. The extracts were dried over magnesium sulfate and purified by column chromatography (silica gel, 1:1 hexane/dichlormethane eluent) followed by precipitation from dichloromethane/methanol yielding **18** (52 mg, 0.101 mmol, 71%) as a yellow solid. ¹H NMR (CDCl₃): 0.89-0.94 (m, 6 H, CH₃), 1.29-1.40 (m, 8H, (CH₂)₂), 1.40-1.55 (m, 4H, CH₂), 1.78-1.84 (m, 4H, CH₂), 3.99-4.03 (m, 4H, CH₂O), 6.90 (d, 2H, J = 9.0 Hz, Ar-H), 6.99 (d, 2H, J = 9.0 Hz, Ar-H), 7.51 (d., 2H, J = 9.0 Hz, Ar-H), 7.69 (d, 2H, J = 9.0 Hz, Ar-H). ¹³C NMR (CDCl₃): 14.01, 22.55, 25.61, 29.00, 29.03, 31.50, 31.51, 68.20, 68.35, 76.74, 103.78, 105.01, 112.05, 112.27, 112.93, 114.79, 115.24, 115.44, 121.65, 129.15, 132.32, 133.71, 153.86, 160.76, 161.53. HRMS calcd for C₃₂H₃₄N₂O₂S (M+Na)⁺: 533.2233, found (ESI): 533.2218.

3,4-Dicyano-2-(4-octyloxyphenylethynyl)-5-(4-octyloxyphenyl)thiophene (19)

Preparation same as for **18**. ¹H NMR (CDCl₃): 0.89-0.94 (m, 6 H, CH₃), 1.29-1.40 (m, 16H, (CH₂)₄), 1.40-1.55 (m, 4H, CH₂), 1.78-1.84 (m, 4H, CH₂), 3.99-4.03 (m, 4H, CH₂O), 6.90 (d, 2H, J = 9.0 Hz, Ar-H), 6.99 (d, 2H, J = 9.0 Hz, Ar-H), 7.51 (d., 2H, J = 9.0 Hz, Ar-H), 7.69 (d, 2H, J = 9.0 Hz, Ar-H). ¹³C NMR (CDCl₃): 14.09, 22.64, 25.95, 29.03, 29.08, 29.20, 29.29, 29.31, 31.78, 68.21, 68.36, 76.74, 103.78, 105.04, 109.41,

112.06, 112.28, 112.94, 114.80, 115.25, 115.45, 121.67, 129.17, 132.33, 133.72, 153.88, 160.77, 161.54. HRMS calcd for $C_{36}H_{42}N_2O_2S$ ($M+Na$)⁺: 589.2859, found (ESI): 589.2856.

3,4-Dicyano-2-(4-decyloxyphenylethynyl)-5-(4-decyloxyphenyl)thiophene (20)

Preparation same as for 18. ¹H NMR (CDCl₃): 0.89-0.94 (m, 6 H, CH₃), 1.29-1.40 (m, 24H, (CH₂)₆), 1.40-1.55 (m, 4H, CH₂), 1.78-1.84 (m, 4H, CH₂), 3.99-4.03 (m, 4H, CH₂O), 6.90 (d, 2H, J = 9.0 Hz, Ar-H), 6.99 (d, 2H, J = 9.0 Hz, Ar-H), 7.51 (d, 2H, J = 9.0 Hz, Ar-H), 7.69 (d, 2H, J = 9.0 Hz, Ar-H). ¹³C NMR (CDCl₃): 14.12, 22.67, 25.96, 29.05, 29.09, 29.31, 29.34, 29.55, 31.88, 68.23, 68.38, 76.74, 103.80, 105.09, 112.07, 112.30, 112.95, 114.83, 115.28, 115.49, 121.70, 129.20, 132.37, 133.74, 153.92, 160.80, 161.56. HRMS calcd for $C_{40}H_{50}N_2O_2S$ ($M+Na$)⁺: 645.3485, found (ESI): 645.3499.

3,4-Dicyano-2-(4-dodecyloxyphenylethynyl)-5-(4-dodecyloxyphenyl)thiophene (21)

Preparation same as for 18. ¹H NMR (CDCl₃): 0.89-0.94 (m, 6 H, CH₃), 1.29-1.40 (m, 32H, (CH₂)₆), 1.40-1.55 (m, 4H, CH₂), 1.78-1.84 (m, 4H, CH₂), 3.99-4.03 (m, 4H, CH₂O), 6.90 (d, 2H, J = 8.9 Hz, Ar-H), 6.99 (d, 2H, J = 8.9 Hz, Ar-H), 7.51 (d, 2H, J = 8.9 Hz, Ar-H), 7.69 (d, 2H, J = 8.9 Hz, Ar-H). ¹³C NMR (CDCl₃): 14.13, 22.68, 25.96, 29.04, 29.08, 29.34, 29.55, 29.58, 29.63, 29.65, 31.91, 68.22, 68.37, 103.79, 105.07, 112.07, 112.28, 112.95, 114.81, 115.47, 121.68, 129.19, 132.36, 133.73, 153.91, 160.78, 161.54. HRMS calcd for $C_{44}H_{58}N_2O_2S$ ($M+Na$)⁺: 701.4111, found (ESI): 701.4131.

3,4-Difluoro-2,5-bis(4-tetrahydropyranyloxy)phenylethynyl]thiophene (22)

2,5-Dibromo-3,4-difluorothiophene (400 mg, 1.44 mmol) was placed in a 100 mL Schlenk flask with 4-(tetrahydropyranyloxy)phenylacetylene (591 mg, 2.92 mmol), Pd(PPh₃)₄ (83 mg, 0.072 mmol), copper(I)iodide (14 mg, 0.072 mmol) and a stir bar. The flask was

repeatedly evacuated and filled with argon. In a separate flask a mixture of 1.0 mL DIPA (7.2 mmol) in 50 mL toluene were degassed by sparging with argon for 20 min, after which it was added to the reaction flask via cannula. The solution was stirred at room temperature for 12 hours after which the solvents were removed in vacuo, and the remaining solids were purified by silica gel chromatography (3:2 hexane:dichloromethane eluent) yielding **22** (417 mg, 0.801 mmol, 56%) as a yellow crystalline powder. ^1H NMR (CDCl_3 , δ): 1.60-1.78 (m, 6H, CH_2CH_2), 1.85-1.90 (m, 4H, CH_2), 1.99-2.04 (m, 2H, CH_2), 3.61-3.65 (m, 2H, CH_2O), 3.85-3.91 (m, 2H, CH_2O), 5.47 (t, 2H, OCHO), 7.05 (d, 4H, $J = 8.7$ Hz, Ar-H), 7.46 (d, 4H, $J = 8.7$ Hz, Ar-H). ^{13}C NMR (CHCl_3 , δ): 18.57, 25.06, 30.15, 62.02, 75.98, 96.14, 98.77, 103.42, 114.64, 116.44, 133.08, 145.71 (dd, $J_1 = 268.2$ Hz, $J_2 = 19.6$ Hz), 157.82. ^{19}F NMR (CDCl_3 , δ vs. CFCl_3): 45.56 (s). MS-EI (m/z): (M^+) calcd for $\text{C}_{30}\text{H}_{26}\text{F}_2\text{O}_4\text{S}$: 520.1514, found: 520.1510.

3,4-Difluoro-2,5-bis(4-hydroxyphenylethynyl)thiophene (23) 3,4-Difluoro-2,5-Bis(4-tetrahydropyranyloxy)phenylethynyl]thiophene **22** (323 mg, 0.620 mmol) was placed in a 100 mL round-bottom flask to which THF (12 mL), glacial acetic acid (25 mL) and H_2O (7 mL) were added. The suspension was heated to 45 °C and stirred for 5 h, at which point the resulting yellow solution was allowed to cool to room temperature. Diethyl ether (100 mL) was added and the organics were washed with water (5 x 50 mL), dried over MgSO_4 and concentrated in vacuo yielding 192 mg (0.545 mmol, 88%) of **23** as a slightly yellow powder. ^1H NMR (CDCl_3 , δ): 3.72 (s, 2H, Ar-OH), 6.73 (d, 4H, $J = 8.7$ Hz, Ar-H), 7.30 (d, 4H, $J = 8.7$ Hz, Ar-H). ^{13}C NMR (CHCl_3 , δ): 75.26, 98.96, 103.31 (d, $J = 11.5$ Hz), 112.57, 115.49, 133.21, 144.43 (dd, $J_1 = 267.8$ Hz, $J_2 = 19.0$ Hz),

157.96. ^{19}F NMR (CDCl_3 , δ vs. CFCl_3): 43.42 (s). MS-EI (m/z): (M^+) calcd for $\text{C}_{20}\text{H}_{10}\text{F}_2\text{O}_2\text{S}$: 352.0364, found: 352.0349.

3,4-Difluoro-2,5-bis[4-(octyloxy)phenylethynyl]thiophene (24) 3,4-Difluoro-2,5-Bis(4-hydroxyphenylethynyl)thiophene **23** (40 mg, 0.114 mmol) was placed in a 25 mL Schlenk tube with PPh_3 (66 mg, 0.250 mmol) and a stir bar. The flask was evacuated and filled with argon, and 10 mL of dry, air-free THF was added via syringe. Dry *n*-octanol (40 μL , 0.250 mmol) and diethylazodicarboxylate (40 μL , 0.250 mmol) were added sequentially via microsyringe. The mixture was stirred at room temperature for 48 h, diluted with 25 mL CH_2Cl_2 , washed with H_2O and dried over MgSO_4 . The crude product was purified by silica gel chromatography (3:1 hexane/ CH_2Cl_2 eluent) followed by precipitation from CH_2Cl_2 with MeOH yielding **24** (50 mg, 0.087 mmol, 76%) as a yellow powder. ^1H NMR (CDCl_3 , δ): 0.87-0.97 (m, 6H, $-\text{CH}_3$), 1.29-1.42 (m, 16H, $(\text{CH}_2)_4$), 1.43-1.58 (m, 4H, CH_2), 1.78-1.85 (m, 4H, CH_2), 3.96-4.02 (m, 4H, OCH_2), 6.88 (d, 4H, $J = 8.7$ Hz, Ar-H), 7.46 (d, 4H, $J = 8.7$, Ar-H). ^{13}C NMR (CDCl_3 , δ): 14.11, 22.65, 25.99, 29.13, 29.22, 29.33, 31.79, 68.12, 75.87, 98.86, 103.42, 113.58, 114.61, 133.18, 145.67 (dd, $J_1 = 267.8$ Hz, $J_2 = 19.0$ Hz), 159.94. ^{19}F NMR (CDCl_3 , δ vs. CFCl_3): 44.20 (s). MS-EI (m/z): (M^+) calcd for $\text{C}_{36}\text{H}_{42}\text{F}_2\text{O}_2\text{S}$: 576.2868, found: 576.2878.

3,4-Difluoro-2,5-bis[4-(dodecyloxy)phenylethynyl]thiophene (25) Preparation same as for **24**. ^1H NMR (CDCl_3 , δ): 0.87-0.97 (m, 6H, $-\text{CH}_3$), 1.29-1.42 (m, 32H, $(\text{CH}_2)_8$), 1.43-1.58 (m, 4H, CH_2), 1.78-1.85 (m, 4H, CH_2), 3.96-4.02 (m, 4H, OCH_2), 6.88 (d, 4H, $J = 8.7$ Hz, Ar-H), 7.46 (d, 4H, $J = 8.7$, Ar-H). ^{13}C NMR (CDCl_3 , δ): 14.13, 22.69, 25.98, 29.12, 29.35, 29.36, 29.56, 29.58, 29.63, 29.65, 31.91, 68.11, 75.87, 98.86, 103.38 (d, $J = 5.7$ Hz), 113.57, 114.60, 133.18, 145.67 (dd, $J_1 = 268.3$ Hz, $J_2 = 19.0$ Hz), 159.94.

^{19}F NMR (CDCl_3 , δ vs. CFCl_3): 45.43 (s). MS-EI (m/z): (M^+) calcd for $\text{C}_{44}\text{H}_{58}\text{F}_2\text{O}_2\text{S}$: 688.4120, found: 688.4140.

3,4-Difluoro-2,5-bis[4-(hexadecyloxy)phenylethynyl]thiophene (26) Preparation same as for **24**. ^1H NMR (CDCl_3 , δ): 0.87-0.97 (m, 6H, $-\text{CH}_3$), 1.29-1.42 (m, 48H, $(\text{CH}_2)_{12}$), 1.43-1.58 (m, 4H, CH_2), 1.78-1.85 (m, 4H, CH_2), 3.96-4.02 (m, 4H, OCH_2), 6.88 (d, 4H, $J = 8.7$ Hz, Ar-H), 7.46 (d, 4H, $J = 8.7$, Ar-H). ^{13}C NMR (CDCl_3 , δ): 14.13, 22.69, 25.98, 29.13, 29.37, 29.56, 29.58, 29.66, 29.67, 29.69, 31.92, 68.12, 75.87, 98.86, 103.41, 113.58, 114.62, 133.19, 145.68 (dd, $J_1 = 267.7$ Hz, $J_2 = 19.0$ Hz), 159.94. ^{19}F NMR (CDCl_3 , δ vs. CFCl_3): 45.42 (s). MS-EI (m/z): (M^+) calcd for $\text{C}_{52}\text{H}_{74}\text{F}_2\text{O}_2\text{S}$: 800.5372, found: 800.5358.

3,4-Difluoro-2,5-bis[(4-(3,4-dioctyloxyphenylcarbonyloxy)phenylethynyl]thiophene (27) 3,4-Difluoro-2,5-Bis(4-hydroxyphenylethynyl)thiophene **23** (40 mg, 0.114 mmol) was placed in a 25 mL Schlenk tube with 3,4-dihexyloxybenzoic acid (95 mg, 0.250 mmol), DMAP (7 mg, 0.057 mmol) and a stir bar. The flask was evacuated and filled with argon. Dry dichloromethane (10 mL) was added via cannula and diisopropylcarbodiimide (71 μL , 0.454 mmol) was added via microsyringe. The reaction was stirred for 48 h at room temperature after which it was diluted with 25 mL CH_2Cl_2 , washed with H_2O and dried over MgSO_4 . The crude product was then purified by column chromatography (3:2 hexane/ CH_2Cl_2 eluent) and precipitated from CH_2Cl_2 with MeOH. ^1H NMR (CDCl_3 , δ): 0.88-0.95 (m, 12H, CH_3), 1.26-1.44 (m, 32H, $(\text{CH}_2)_8$), 1.45-1.57 (m, 8H, CH_2), 1.82-1.95 (m, 8H, CH_2), 4.03-4.15 (m, 4H, CH_2), 6.95 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.25 (d, 4H, $J = 8.7$ Hz, Ar-H), 7.61 (d, 4H, $J = 8.7$ Hz, Ar-H), 7.66 (d, 2H, $J = 2.1$ Hz, Ar-H), 7.82 (dd, 4H, $J_1 = 8.4$ Hz, $J_2 = 2.1$ Hz, Ar-H). ^{13}C NMR (CDCl_3 ,

δ): 14.11, 22.67, 25.95, 25.99, 29.01, 29.13, 29.25, 29.26, 29.33, 29.35, 31.80, 31.81, 69.04, 69.31, 98.13, 111.84, 114.46, 119.25, 121.04, 122.19, 124.45, 126.46, 132.87, 148.64, 151.74, 153.97, 164.64. ^{19}F NMR (CDCl_3 , δ vs. CFCl_3): 43.67 (s). MS-EI (m/z): (M+H) calcd for $\text{C}_{36}\text{H}_{42}\text{F}_2\text{O}_2\text{S}$: 1073.5771, found: 1073.5730.