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The Interplay of Bent-Shape, Lateral Dipole and Chirality in Thiophene Based Di-, Tri-, and Tetracatenar Liquid Crystals

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Supporting Information

Experimental Section

General Methods. ^{1}H NMR spectra were recorded on a Varian Unity VXR 500, a Bruker DPX-400, and a Varian Unity 300. Chemical shifts are reported in ppm relative to residual $CHCl_3$ (δ = 7.24, ^{1}H). Multiplicities are given as s (singlet), d (doublet), t (triplet) and m (multiplet). MS investigations were run on a Finnigan MAT 8200 equipped with an Ion Tech ion source and a Bruker Daltonics Apex II 3T FT-ICR MS. Optical characterization was performed on a Leica DMRXP polarizing microscope equipped with a Wild Leitz MPS46 Photoautomat along with a Linkam LTS 350 hot stage and a Linkam TP 92 controller. Also attached via a dual beam splitter was a video system (Sony DXC-970MD CCD camera, JVC SRS-970 video recorder, Sony PVM-1353MD color monitor, and a PC with a Scion Image PR-CG7-PCI frame grabber card). Commercially available test cells (E.H.C. Co., LTD and Displaytech, Ltd) were vacuum filled with material and the electro-optic switching was studied by applying a DC voltage and measuring the current response under a polarizing microscope (Tektronix CFG253 function generator, HP 6827A amplifier, Keithley 428 current amplifier, Tektronix TDS 420 oscilloscope, and National Instruments LabView software). Transition temperatures and heats of fusion were determined at scan rates of 5 and 10 °C/min by differential scanning calorimetry using a Perkin-Elmer DSC 7 and Pyris with a Perkin-Elmer Pyris thermal analysis data station. Variable temperature X-ray measurements were performed on an Inel system (CPS 120 detector, XRG 2000 generator, Cu Kα radiation, Minco CT 137 temperature controller (±1 °C) and a home-built heating stage) as well as a Siemens system (flat camera 2D-Xe-detector, 256×256 cells, Instec HS 400 hot stage and STC 200 controller, Rigaku RV-300 rotating anode, Ni-filtered Cu K_α-radiation). Calibration was accomplished by using mica and silicon standards (NBS) as well as silver behenate. Samples were prepared by filling each Lindemann capillary (1.5 mm) with approximately 15 mg of compound. FTIR-spectra were taken with a Nicolet Magna IR 860 and a Nicolet Impact 410. Linear polarization of the incident beam was achieved with a MgSe polarizer. UV-Vis spectra were obtained from a Hewlett-Packard 8452A diode array spectrometer and a Varian Cary 50 spectrophotometer. Dichloromethane and THF were dried by passing through a column of activated alumina and diisopropylamine was

freshly distilled from CaH_2 under an atmosphere of dry argon. All other chemicals and solvents, unless otherwise indicated, were purchased commercially and used as obtained without further purification. Air and water sensitive reactions employed standard Schlenk techniques under argon atmosphere. *N*-BuLi in hexane was titrated *versus* diphenylacetic acid before use. 4,5-dialkoxybenzoic acids, 3,4,5-tridodecyloxybenzoic acid,[1] 1-(benzyloxy)-4-ethynylbenzene,[2] 1-(tetrahydropyranyloxy)-4-ethynylbenzene, and 1,3-bis(4-hydroxyphenylethynyl)benzene (**9a**)[3] were synthesized following literature procedures. The synthesis of 2,5-bis[(4-hydroxyphenyl)ethynyl]-3,4-dicyanothiophene and the hexacatenar 2,5-bis[(4-(3,4,5-tridodecyloxyphenylcarbonyloxy)phenylethynyl]-3,4-dicyanothiophene has been described before but the former diphenolic compound was obtained *via* new routes described herein. The precursor 2,5-diiodo-3,4-dicyano-thiophene was synthesized following the procedure published by Hide *et. al*.[4]

2,5-Bis(4-tetrahydropyranyloxy)phenylethynyl]thiophene (3). A 200ml Schlenk flask was charged with $Pd(PPh_3)_4$ (143mg, 0.124mmol), copper (I) iodide (24mg, 0.124mmol), and a stir bar under argon. In a separate flask, 2,5-dibromothiophene (0.28mL, 2.47mmol), THP-protected hydroxyphenylacetylene (1.00g, 4.94mmol) were dissolved in diisopropylamine (1.7mL, 12.4mmol) and toluene (100mL). The solution was purged with argon for 20 minutes and then added to the reaction (Schlenk) flask *via* a cannula. The yellow solution turned darker after about 15 minutes and was stirred at room temperature for 12 hours. The reaction mixture was washed through a silica gel pad with dichloromethane, and the obtained crude solid was recrystallized from hexane/chloroform to yield **3** as yellow crystals (960mg, 1.98mmol, 80%). ^{1}H NMR ($CDCl_3$, δ): 1.57-1.79 (m, 6H, CH_2CH_2), 1.83-1.89, (m, 4H, CH_2), 1.91-2.09 (m, 2H, CH_2), 3.58-3.63 (m, 2H, CH_2O), 3.83-3.91 (m, 2H, CH_2O), 5.43 (t, 2H, OCHO), 7.04 (d, 4H, J = 9.0 Hz, Ar-H), 7.11 (s, 2H, Ar-H), 7.45 (d, 4H, J = 9.0 Hz). ^{13}C NMR ($CHCl_3$, δ): 18.61, 25.08, 30.18, 62.03, 81.13, 93.97, 96.17, 115.46, 116.40, 124.56, 131.34, 132.86, 157.37. HRMS-EI (*m*/*z*): (M^+) calcd for $C_{30}H_{28}O_4S$ 484.1708, found 484.1701.

2,5-Bis[(4-benzyloxyphenyl)ethynyl]-3,4-dibromothiophene (4). Tetrabromo-thiophene (30.13 g, 75.4 mmol), tris(triphenylphosphine)palladium (5.4 g, 4.7 mmol), and copper iodide (1.78 g, 9.4 mmol) were dissolved in a mixture of toluene (400 mL) and diisopropylamine (27.0 mL, 19.5 g, 193 mmol) under argon. A solution of 4-benzyloxyphenylacetylene (39.12 g, 188 mmol) in toluene (100 mL) was added within 30 min *via* a cannula. The solution was stirred at room temperature for 2 d, quenched with 1 M aqueous HCl (200 mL), and the organic phase was dried over $MgSO_4$. Filtration through silica using toluene as solvent and recrystallization from THF/ethanol yielded pale yellow plates of **4** (42.49 g, 86%). ^{1}H NMR ($CDCl_3$, δ): 5.10 (s, 4H, CH_2), 6.97 (d, *J* = 8.8 Hz, 4H, Ar H), 7.45-7.3, (m, 5H, phenyl), 7.50 (d, *J* = 8.8 Hz, 4H, Ar H). ^{13}C NMR ($CHCl_3$, δ): 70.28, 80.24, 98.94, 114.44, 115.27, 118.27, 118.58, 121.51, 127.70, 128.39, 128.88, 133.55, 136.56, 159.75. HRMS-EI (*m*/*z*): (M^+) calcd for $C_{34}H_{22}O_2SBr_2$ 651.970724, found 651.97072.

2,5- Bis[(4-benzyloxyphenyl)ethynyl]-3,4-dicyanothiophene (5a). **4** (5.00 g, 7.65 mmol), copper iodide (3.05 g, 16 mmol) and copper cyanide (2.74 g, 30.6 mmol) were dissolved in 80 mL DMI (1,3-dimethyl-2-imidazolidinone) (dried over molecular sieve 4Å) and stirred at 125 ºC for 6 h. The reaction mixture was poured into 400 mL of

methanol and a curry colored precipitate was filtered off. This crude product mixture was recrystallized from toluene to remove most of the remaining mono-substituted as well as debrominated side-products. The first precipitates were then further purified by column chromatography on silica using 1,2-dichlorobenzene as eluent to yield **5a** as a yellow solid (1.92 g, 46%). ^{1}H NMR ($CDCl_3$, δ): 5.10 (s, 4H, CH_2), 6.98 (d, J = 8.9 Hz, 4H, Ar H), 7.5-7.3, (m, 5H, phenyl), 7.53 (d, J = 8.9 Hz, 4H, Ar H). ^{13}C NMR ($CHCl_3$, δ): 70.36, 77.70, 104.44, 111.69, 112.78, 113.86, 115.49, 127.71, 128.48, 128.91, 133.78, 134.16, 136.29, 160.73. HRMS-EI (*m*/*z*): (M^+) calcd for $C_{36}H_{22}N_2O_2S$ 546.14020, found 546.14120.

2,5-Bis(4-tetrahydropyranyloxy)phenylethynyl]-3,4-dicyanothiophene (5b). A 200ml Schlenk flask was charged with 2,5-diiodo-3,4-dicyanothiophene (490 mg, 1.27 mmol), $Pd(PPh_3)_4$ (347 mg, 0.30 mmol), copper (I) iodide (114mg, 0.6ommol), a mixture of THF (40 mL) and diisopropylamine (3.0 mL, 38.0 mmol), and a stir bar under argon. In a separate flask, the THP-protected hydroxyphenylacetylene (624 mg, 3.0 mmol) was dissolved in THF (10mL) and added to the reaction (Schlenk) flask *via* a cannula at 0 ºC. The yellow solution was allowed to warm up to room temperature and was stirred at room temperature for 12 hours. The orange reaction mixture was washed through a silica gel pad, first with toluene/hexane 2:1 to remove diacetylene byproducts, and then with DCM to obtain a crude solid as product. Recrystallization from acetone/methanol and ether/hexane yielded **5b** as orange crystals (513 mg, 0.96mmol, 75%). ^{1}H NMR ($CDCl_3$, δ): 1.6-1.8 (m, 6H, CH_2CH_2), 1.90, (m, 4H, CH_2), 2.02 (m, 2H, CH_2), 3.64 (m, 2H, CH_2O), 3.88 (m, 2H, CH_2O), 5.51 (t, 2H, OCHO), 7.09 (d, 4H, J = 8.7 Hz, Ar-H), 7.55 (d, 4H, J = 8.7 Hz). ^{13}C NMR ($CHCl_3$, δ): 18.11, 21.09, 24.66, 29.71, 61.66, 95.77, 103.92, 111.12, 112.64, 113.26, 116.05, 116.29, 124.91, 127.84, 128.65, 133.23, 133.43, 133.54, 137.49, 158.53. MS-EI (*m*/*z*): (M^+) calcd for $C_{32}H_{26}N_2O_4S$ 534, found 534.

2,5-Bis(4-hydroxyphenylethynyl)thiophene (6) or 2,5-bis(4-hydroxyphenylethynyl)-3,4-dicyanothiophene (8). A stirred suspension of **3** (521mg, 1.075 mmol) or **5b** (588 mg, 1.1 mmol) in THF (21ml), acetic acid (42ml) and water (11mL) was heated to 45 °C, at which point all solids were dissolved, and stirred for 12 hours. Ether was added (100ml) and the mixture was washed with water (5x30ml). The solvents were removed in vacuum yielding an off-white powder that was recrystallized from dichloromethane/hexanes to yield **6** as a white powder (277mg, 0.876 mmol, 82%) or **8** as a yellow powder (337mg, 0.923 mmol, 84%). ^{1}H NMR ($CDCl_3$, δ): 3.52 (s, 2H, OH), 6.73 (d, J = 9.0 Hz, 4H, Ar-H), 7.01 (s, 2H, Ar-H), 7.31 (d, J = 9.0 Hz, 4H, Ar-H). ^{13}C NMR ($CDCl_3$, δ): 80.29, 93.97, 113.28, 115.30, 124.28, 130.95, 132.86, 157.29. HRMS-EI (*m*/*z*): (M^+) calcd for $C_{20}H_{12}O_2S$ 316.0558, found 316.0548.

2,5-Bis(4-hydroxyphenylethynyl)-3,4-dibromothiophene (7) and 2,5-bis(4-hydroxyphenylethynyl)-3,4-dicyanothiophene (8). **4** (2.0 g, 3.6 mmol) or **5a** (2.0 g, 3.1 mmol) were dissolved in dichloromethane (150 mL) and a 0.5 M solution of bromocatecholborane in dichloromethane (30 mL, 15 mmol) were added over 5 min at 0 °C. The solutions were stirred for 2 d at r. t., poured into a mixture of aqueous Na_2CO_3 (0.5 M, 100 mL) and ice, and stirred for 20 min. Aqueous HCl (1.0 M) was added until a pH of 1-2 was reached. The organic layers were separated, washed with unionized water (3 x 150 mL), dried over $MgSO_4$, and finally evaporated in vacuum to give **7** (1.60 g, 94

%) and **8** (1.05 g, 91 %) as dark yellow powders of sufficient purity for the following esterifications. **7** ^{1}H NMR (CD_3OD, δ): 6.83 (d, J = 8.7 Hz, 4H, Ar-H), 7.43 (d, J = 8.7 Hz, 4H, Ar-H). ^{13}C NMR (CD_3OD, δ): 79.98, 100.65, 113.72, 116.87, 118.99, 122.71, 134.55, 160.32. HRMS-EI (*m*/*z*): (M^+) calcd for $C_{22}H_{10}O_2SBr_2$ 471.876824, found 471.87682. **8** ^{1}H NMR (CD_3OD, δ): 6.79 (d, J = 8.5 Hz, 4H, Ar-H), 7.36 (d, J = 8.5 Hz, 4H, Ar-H). ^{13}C NMR (CD_3OD, δ): 77.75, 101.88, 105.78, 112.12, 112.69, 114.43, 117.19, 135.15, 135.23, 161.57. HRMS-EI (*m*/*z*): (M^+) calcd for $C_{22}H_{10}N_2O_2S$ 366.046299, found 366.04630.

Esterification of 2,5-Bis[(4-hydroxyphenyl)ethynyl]-thiophene, 2,5-Bis[(4-hydroxyphenyl)ethynyl]-3,4-dibromothiophene, and 2,5-Bis[(4-hydroxyphenyl)-ethynyl]-3,4-dicyanothiophene. 3 eq. of the appropriate alkoxy substituted benzoic acid were dissolved in dry dichloromethane under argon and an equal molar amount of *N,N'*-diisopropylcarbodiimide was added at 0 ºC. After 2 h of stirring 1 eq. of the 2,5-bis[(4-hydroxyphenyl)ethynyl]thiophene derivative dissolved in dry dichloromethane was added to the mixture at 0 ºC. The mixtures were stirred for another 3 h at 0 ºC and then allowed to warm up to room temperature. The progress of esterification was monitored by following the consumption of the diphenolic starting material and the monoester intermediate by TLC (silica, dichloromethane/ethylacetate 9:1). A complete consumption of the starting materials and intermediates was attained after 1-2 d. The solutions were concentrated in vacuum and chromatographed on silica gel using toluene/heptane mixtures as eluent to give yields of 80-95%. For analytical measurements, a further purification was achieved by filtration of a concentrated THF solution through 2 µm filters and subsequent precipitation by the addition of ethanol.

2,5-Bis[4-(3,4-dihexyloxyphenylcarbonyloxy)phenylethynyl]thiophene (H-TCT-mp6). ^{1}H NMR ($CDCl_3$): 0.87-0.91 (m, 12H, CH_3), 1.27-1.51 (m, 24H, $(CH_2)_3$), 1.84-1.90 (m, 8H, CH_2), 4.06-4.11 (m, 8H, CH_2O), 6.94 (d, 2H, J = 8.6 Hz, Ar-H), 7.18 (s, 2H, Ar-H), 7.23 (d, 4H, J = 8.7 Hz, Ar-H), 7.59 (d, 4H, J = 8.7 Hz, Ar-H), 7.66 (d, 2H, J = 2.0 Hz, Ar-H), 7.82 (dd, 2H, $J1$ = 8.6 Hz, $J2$ = 2.0 Hz, Ar-H). ^{13}C NMR ($CDCl_3$): 14.00, 22.57, 25.60, 25.64, 28.96, 29.07, 31.51, 31.53, 69.02, 69.28, 93.42, 111.83, 114.44, 120.03, 121.13, 122.07,124.42, 124.54, 131.89, 132.66, 148.62,151.25, 153.91, 164.69. HRMS-ESI (*m*/*z*): $(M+Na)^+$ calcd for $C_{58}H_{68}O_8S$ 947.4527, found 947.4560

2,5-Bis[4-(3,4-dioctyloxyphenylcarbonyloxy)phenylethynyl]thiophene (H-TCT-mp8). ^{1}H NMR ($CDCl_3$): 0.87-0.91 (m, 12H, CH_3), 1.27-1.51 (m, 40H, $(CH_2)_5$), 1.84-1.90 (m, 8H, CH_2), 4.06-4.11 (m, 8H, CH_2O), 6.94 (d, 2H, J = 8.6 Hz, Ar-H), 7.18 (s, 2H, Ar-H), 7.23 (d, 4H, J = 8.7 Hz, Ar-H), 7.59 (d, 4H, J = 8.7 Hz, Ar-H), 7.66 (d, 2H, J = 2.0 Hz, Ar-H), 7.82 (dd, 2H, J_1 = 8.6 Hz, J_2 = 2.0 Hz, Ar-H). ^{13}C NMR ($CDCl_3$): 14.09, 22.65, 25.94, 25.98, 29.01, 29.13, 29.23, 29.32, 29.34, 31.79, 69.03, 69.30, 82.31, 93.42, 111.85, 114.48, 120.04, 121.13, 122.07, 124.43, 124.55, 131.89, 132.66, 148.63, 151.26, 153.92, 164.70. HRMS-ESI (*m*/*z*): $(M+Na)^+$ calcd for $C_{66}H_{84}O_8S$ 1059.5779, found 1059.5770.

2,5-Bis[4-(3,4-didecyloxyphenylcarbonyloxy)phenylethynyl]thiophene (H-TCT-mp10). ^{1}H NMR ($CDCl_3$): 0.87-0.91 (m, 12H, CH_3), 1.27-1.53 (m, 56H, $(CH_2)_7$), 1.84-1.91 (m, 8H, CH_2), 4.06-4.11 (m, 8H, CH_2O), 6.94 (d, J = 8.6 Hz, 2H, Ar-H), 7.18 (s, 2H,

Ar-H), 7.23 (d, J = 8.7 Hz, 4H, Ar-H), 7.59 (d, 4H, J = 8.7 Hz, Ar-H), 7.66 (d, J = 2.0 Hz, 2H, Ar-H), 7.82 (dd, J_1 = 8.6 Hz, 2H, J_2 = 2.0 Hz, Ar-H). C_{13} NMR ($CDCl_3$): 14.12, 22.68, 25.95, 25.99, 29.01, 29.13, 29.34, 29.37, 29.39, 29.56, 29.59, 29.61, 31.90, 69.04, 69.30, 82.31, 93.43, 111.85, 114.48, 120.04, 121.14, 122.08, 124.43, 124.56, 131.89, 132.67, 149.64, 151.27, 153.92, 164.69. HRMS-ESI (m/z): $(M+Na)^+$ calcd for $C_{74}H_{100}O_8S$ 1171.7031, found 1171.7005.

2,5-Bis[4-(3,4-didodecyloxyphenylcarbonyloxy)phenylethynyl]thiophene (H-TCT-mp12). ^1H NMR ($CDCl_3$): 0.87-0.91 (m, 12H, CH_3), 1.27-1.51 (m, 72H, $(CH_2)_9$), 1.84-1.90 (m, 8H, CH_2), 4.06-4.11 (m, 8H, CH_2O), 6.94 (d, J = 8.6 Hz, 2H, Ar-H), 7.18 (s, 2H, Ar-H), 7.23 (d, 4H, J = 8.7 Hz, Ar-H), 7.59 (d, 4H, J = 8.7 Hz, Ar-H), 7.66 (d, 2H, J = 2.0 Hz, Ar-H), 7.82 (dd, 2H, J_1 = 8.6 Hz, J_2 = 2.0 Hz, Ar-H). ^{13}C NMR ($CHCl_3$): 14.12, 22.68, 25.95, 26.00, 29.02, 29.13, 29.36, 29.40, 29.60, 29.62, 29.66, 29.69, 31.92, 69.04, 69.31, 82.32, 93.43, 111.86, 114.49, 120.04, 121.14, 122.08, 124.43, 124.56, 131.89, 132.67, 148.64, 151.27, 153.93, 164.70. HRMS-ESI (m/z): $(M+Na)^+$ calcd for $C_{82}H_{116}O_8S$ 1283.8283, found 1283.8227.

2,5-Bis[4-(3,4-ditetradecyloxyphenylcarbonyloxy)phenylethynyl]thiophene (H-TCT-mp14). ^1H NMR ($CDCl_3$): 0.87-0.91 (m, 12H, CH_3O), 1.27-1.51 (m, 88H, $(CH_2)_{11}$), 1.84-1.90 (m, 8H, CH_2), 4.06-4.11 (m, 8H, CH_2O), 6.94 (d, 2H, J = 8.6 Hz, Ar-H), 7.18 (s, 2H, Ar-H), 7.23 (d, 4H, J = 8.7 Hz, Ar-H), 7.59 (d, 4H, J= 8.7 Hz, Ar-H), 7.66 (d, 2H, J = 2.0 Hz, Ar-H), 7.82 (dd, 2H, J_1 = 8.6 Hz, J_2 = 2.0 Hz, Ar-H). C^{13} NMR ($CDCl_3$): 14.13, 22.69, 25.96, 26.00, 29.02, 29.14, 29.37, 29.41, 29.63, 29.66, 29.71, 31.93, 69.05, 69.32, 82.32, 93.43, 111.87, 114.50, 120.05, 121.15, 122.09, 124.44, 124.56, 131.89, 132.68, 148.65, 151.28, 153.94, 164.71. HRMS-ESI (m/z): $(M+Na)^+$ cacld for $C_{90}H_{132}O_8S$ 1395.9535, found 1395.9562.

2,5-Bis[(4-(3,4-dibutyloxyphenylcarbonyloxy)phenylethynyl]-3,4-dibromo-thiophene (Br-TCT-mp4). ^1H NMR ($CDCl_3$, δ): 1.00 (t, 6H, J = 7.3 Hz, CH_3), 1.01 (t, 6H, J = 7.3 Hz, CH_3), 1.54 (m, 8H, CH_2), 1.86 (m, 8H, CH_2), 4.09 (t, J = 6.8 Hz, 4H, OCH_2), 4.11 (t, J = 6.8 Hz, 4H, OCH_2), 6.95 (d, J = 8.5 Hz, 2H, Ar H), 7.24 (d, J = 8.6 Hz, 4H, Ar H), 7.64 (d, 4H, J = 8.6 Hz, Ar H), 7.66 (d, 2H, J = 2.1 Hz, Ar H), 7.83 (dd, J = 8.5, 2.1 Hz, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 14.30, 14.32, 19.60, 19.62, 31.44, 31.57, 69.15, 69.39, 81.43, 98.46, 112.19, 114.78, 119.55, 119.74, 121.43, 121.72, 122.29, 122.65, 124.88, 133.40, 149.03, 152.17, 154.35, 165.09. HRMS-MALDI (m/z): $[M+Na]^+$ calcd for $C_{50}H_{50}O_8SBr_2Na$ 991.1485, found 991.1499.

2,5-Bis[(4-(3,4-dihexyloxyphenylcarbonyloxy)phenylethynyl]-3,4-dibromo-thiophene (Br-TCT-mp6). ^1H NMR ($CDCl_3$, δ): 0.92 (t, 6H, J = 7.1 Hz, CH_3), 0.93 (t, 6H, J = 7.1 Hz, CH_3), 1.37 (m, 16H, CH_2), 1.51 (m, 8H, CH_2), 1.86 (m, 8H, CH_2), 4.09 (t, J = 6.7 Hz, 4H, OCH_2), 4.10 (t, J = 6.7 Hz, 4H, OCH_2), 6.95 (d, J = 8.5 Hz, 2H, Ar H), 7.24 (d, J = 8.6 Hz, 4H, Ar H), 7.64 (d, 4H, J = 8.6 Hz, Ar H), 7.66 (d, 2H, J = 2.0 Hz, Ar H), 7.83 (dd, J = 8.5, 2.0 Hz, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 14.47, 23.03, 26.05, 26.08, 29.38, 29.49, 31.96, 31.98, 69.43, 69.67, 81.43, 98.46, 112.16, 114.73, 119.55, 119.74, 121.42, 121.72, 122.29, 122.65, 124.87, 133.40, 149.01, 152.17, 154.33, 165.09. HRMS-MALDI (m/z): $[M+Na]^+$ calcd for $C_{58}H_{66}O_8SBr_2Na$ 1103.2737, found 1103.2728.

2,5-Bis[(4-(3,4-dioctyloxyphenylcarbonyloxy)phenylethynyl]-3,4-dibromo-thiophene (Br-TCT-mp8). ^{1}H NMR ($CDCl_3$, δ): 0.88 (t, 6H, J = 7.1 Hz, CH_3), 0.89 (t, 6H, J = 7.1 Hz, CH_3), 1.2-1.7 (m, 40H, CH_2), 1.8-2.0 (m, 8H, CH_2), 4.07 (t, J = 6.7 Hz, 4H, OCH_2), 4.09 (t, J = 6.7 Hz, 4H, OCH_2), 6.94 (d, J = 8.5 Hz, 2H, Ar H), 7.25 (d, J = 8.4 Hz, 4H, Ar H), 7.63 (d, 4H, J = 8.4 Hz, Ar H), 7.66 (d, 2H, J = 1.9 Hz, Ar H), 7.82 (dd, J = 8.5, 1.9 Hz, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 14.33, 22.89, 26.18, 26.22, 29.24, 29.37, 29.47, 29.48, 29.55, 29.58, 32.02, 32.03, 69.27, 69.55, 81.23, 98.27, 112.08, 114.72, 119.34, 119.54, 121.28, 121.53, 122.42, 124.68, 133.18, 148.87, 152.00, 154.20, 164.84. HRMS-FAB (*m*/*z*): $[M+H]^+$ calcd for $C_{66}H_{82}O_8SBr_2$ 1193.417539, found 1193.41871.

2,5-Bis[(4-(3,4-didecyloxyphenylcarbonyloxy)phenylethynyl]-3,4-dibromothiophene (Br-TCT-mp10). ^{1}H NMR ($CDCl_3$, δ): 0.90 (t, J = 6.4 Hz, 12H, CH_3), 1.2-1.4 (m, 60H, CH_2), 1.5 (m, 8H, CH_2), 1.85 (m, 8H, CH_2), 4.06 (t, J = 6.5 Hz, 4H, OCH_2), 4.08 (t, J = 6.5 Hz, 4H, OCH_2), 6.90 (d, J = 8.7 Hz, 2H, Ar H), 7.24 (d, J = 8.5 Hz, 4H, Ar H), 7.63 (d, J = 2.0 Hz, 2H, Ar H), 7.66 (d, J = 8.5 Hz, 4H, Ar H), 7.80 (dd, J = 8.7, 2.0 Hz, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 14.14, 22.69, 25.96, 26.00, 29.02, 29.15, 29.36, 29.58, 29.61, 31.92, 69.06, 69.33, 81.20, 98.38, 111.86, 114.47, 119.33, 119.60, 121.27, 121.32, 122.23, 124.47, 132.98, 148.66, 153.98, 154.05, 164.24. HRMS-MALDI (*m*/*z*): $[M+Na]^+$ calcd for $C_{74}H_{98}O_8SBr_2Na$, 1327.5241, found 1327.5216.

2,5-Bis[(4-(3,4-didodecyloxyphenylcarbonyloxy)phenylethynyl]-3,4-dibromothiophene (Br-TCT-mp12). ^{1}H NMR ($CDCl_3$, δ): 0.89 (t, J = 6.6 Hz, 12H, CH_3), 1.2-1.5 (m, 68H, CH_2), 1.5-1.6 (m, 8H, CH_2), 1.75-1.95 (m, 8H, CH_2), 4.07 (t, J = 6.5 Hz, 4H, OCH_2), 4.08 (t, J = 6.4 Hz, 4H, OCH_2), 6.94 (d, J = 8.8 Hz, 2H, Ar H), 7.23 (d, J = 8.6 Hz, 4H, Ar H), 7.62 (d, J = 2.0 Hz, 2H, Ar H), 7.67 (d, J = 8.6 Hz, 4H, Ar H), 7.81 (dd, J = 8.8, 2.0 Hz, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 14.31, 22.90, 26.21, 26.25, 29.31, 29.44, 29.58, 29.60, 29.63, 29.83, 29.85, 29.88, 32.15, 69.37, 69.69, 81.26, 98.33, 112.33, 115.06, 119.36, 119.58, 121.44, 121.59, 122.41, 124.72, 133.17, 149.03, 152.09, 154.35, 164.79. HRMS-MALDI (*m*/*z*): $[M+Na]^+$ calcd for $C_{82}H_{114}O_8SBr_2Na$, 1439.6493, found 1439.6443.

2,5-Bis[(4-(3,4-dibutyloxyphenylcarbonyloxy)phenylethynyl]-3,4-dicyanothiophene (NC-TCT-mp4). ^{1}H NMR ($CDCl_3$, δ): 1.00 (t, J = 7.3 Hz, 12H, CH_3), 1.53 (tq, J = 7.3, 7.3 Hz, 8H, CH_2), 1.8-2.0 (m, 8H, CH_2), 4.08 (t, J = 6.4 Hz, 4H, OCH_2), 4.10 (t, J = 6.4 Hz, 4H, OCH_2), 6.94 (d, J = 8.7 Hz, 2H, Ar H), 7.29 (d, J = 8.7 Hz, 4H, Ar H), 7.66 (d, J = 2.0 Hz, 2H, Ar H), 7.67 (d, J = 8.7 Hz, 4H, Ar H), 7.81 (dd, J = 8.7, 2.0 Hz, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 14.05, 14.07,19.38, 19.40, 31.23, 31.37, 68.96, 69.23, 78.25, 103.39, 111.41, 112.06, 114.69, 117.85, 121.03, 122.70, 124.73, 133.62, 133.71, 148.87, 152.99, 154.29, 164.65. HRMS-FAB (*m*/*z*): $[M+H]^+$ calcd for $C_{52}H_{50}N_2O_8S$, 863.336614, found 863.33579.

Table 1. Crystal data and structure refinement for **NC-TCT-mp4**.

Identification code	071047t	
Empirical formula	C_{52} H_{50} N_2 O_8 S	
Formula weight	863.00	
Temperature	183(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 25.072(7) Å	α= 90°.
	b = 17.476(5) Å	β= 101.412(4)°.
	c = 10.492(3) Å	γ = 90°.
Volume	4506(2) $Å^3$	
Z	4	
Density (calculated)	1.272 Mg/m^3	
Absorption coefficient	0.130 mm^{-1}	
F(000)	1824	
Crystal size	.3 x .3 x .4 mm^3	
Theta range for data collection	2.31 to 21.99°.	
Index ranges	-25<=h<=26, -18<=k<=10, -11<=l<=10	
Reflections collected	7972	
Independent reflections	2755 [R(int) = 0.0349]	
Completeness to theta = 21.99°	99.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	2755 / 0 / 288	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0643, wR2 = 0.1752	
R indices (all data)	R1 = 0.0725, wR2 = 0.1809	
Extinction coefficient	0.0002(3)	
Largest diff. peak and hole	0.634 and -0.495 e.Å^{-3}	

2,5-Bis[(4-(3,4-dipentyloxyphenylcarbonyloxy)phenylethynyl]-3,4-dicyanothiophene (NC-TCT-mp5). ^{1}H NMR ($CDCl_3$, δ): 0.91 (t, *J* = 7.2 Hz, 12H, CH_3), 1.5 (m, 16H, CH_2), 1.8 (m, 8H, CH_2), 4.05 (t, *J* = 6.4 Hz, 4H, OCH_2), 4.08 (t, *J* = 6.4 Hz, 4H, OCH_2), 6.93 (d, *J* = 8.8 Hz, 2H, Ar H), 7.27 (d, *J* = 8.7 Hz, 4H, Ar H), 7.66 (d, *J* = 2.0 Hz, 2H, Ar H), 7.67 (d, *J* = 8.7 Hz, 4H, Ar H), 7.79 (dd, *J* = 8.8, 2.0 Hz, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 14.05, 22.45, 28.14, 28.18, 28.70, 28.82, 69.06, 69.32, 78.07, 103.21, 111.24, 111.84, 114.44, 114.53, 117.68, 120.85, 122.53, 122.70, 124.54, 133.45, 133.54, 148.68, 152.82, 154.08, 164.51. HRMS-FAB (*m*/*z*): $[M+H]^+$ calcd for $C_{56}H_{58}N_2O_8S$ 919.399214, found 919.4021.

2,5-Bis[(4-(3,4-dihexyloxyphenylcarbonyloxy)phenylethynyl]-3,4-dicyanothiophene (NC-TCT-mp6). ^{1}H NMR ($CDCl_3$, δ): 0.91 (t, *J* = 6.8 Hz, 12H, CH_3), 1.25-1.45 (m, 16H, CH_2), 1.45-1.65 (m, 8H, CH_2), 1.75-1.95 (m, 8H, CH_2), 4.07 (t, *J* = 6.5 Hz, 4H, OCH_2), 4.09 (t, *J* = 6.5 Hz, 4H, OCH_2), 6.93 (d, *J* = 8.7 Hz, 2H, Ar H), 7.29 (d, *J* = 8.6 Hz, 4H, Ar H), 7.64 (d, *J* = 1.9 Hz, 2H, Ar H), 7.66 (d, *J* = 8.6 Hz, 4H, Ar H), 7.81 (dd, *J* = 8.7, 1.9 Hz, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 14.18, 22.74, 22.75, 25.79, 25.82, 29.14, 29.26, 31.69, 31.71, 69.19, 69.46, 78.22, 103.35, 111.36, 111.99, 114.59, 114.64, 117.78, 120.98, 122.64, 124.67, 133.55, 133.66, 148.82, 152.96, 154.23, 164.58. HRMS-FAB (*m*/*z*): $[M+H]^+$ calcd for $C_{60}H_{66}N_2O_8S$ 975.461814, found 975.46332.

2,5-Bis[(4-(3,4-diheptyloxyphenylcarbonyloxy)phenylethynyl]-3,4-dicyanothiophene (NC-TCT-mp7). ^{1}H NMR ($CDCl_3$, δ): 0.90 (t, *J* = 6.7 Hz, 12H, CH_3), 1.25-1.45 (m, 24H, CH_2), 1.45-1.65 (m, 8H, CH_2), 1.75-1.9 (m, 8H, CH_2), 4.07 (t, *J* = 6.6 Hz, 4H, OCH_2), 4.09 (t, *J* = 6.6 Hz, 4H, OCH_2), 6.93 (d, *J* = 8.7 Hz, 2H, Ar H), 7.29 (d, *J* = 8.5 Hz, 4H, Ar H), 7.64 (d, *J* = 1.9 Hz, 2H, Ar H), 7.66 (d, *J* = 8.5 Hz, 4H, Ar H), 7.81 (dd, *J* = 8.7, 1.9 Hz, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 14.11, 22.61, 25.92, 25.96, 29.05, 29.07, 29.15, 31.80, 69.06, 69.33, 78.07, 103.21, 111.24, 111.85, 114.46, 114.53, 117.69, 120.85, 122.53, 124.54, 133.45, 133.55, 148.69, 152.82, 154.09, 164.51. HRMS-FAB (*m*/*z*): $[M+H]^+$ calcd for $C_{64}H_{74}N_2O_8S$ 1031.524415, found 1031.5210.

2,5-Bis[(4-(3,4-dioctyloxyphenylcarbonyloxy)phenylethynyl]-3,4-dicyanothiophene (NC-TCT-mp8). ^{1}H NMR ($CDCl_3$, δ): 0.89 (t, *J* = 6.9 Hz, 12H, CH_3), 1.3-1.45 (m, 32H,

CH_2), 1.45-1.55 (m, 8H, CH_2), 1.8-2.0 (m, 8H, CH_2), 4.07 (t, J = 6.5 Hz, 4H, OCH_2), 4.09 (t, J = 6.5 Hz, 4H, OCH_2), 6.94 (d, J = 8.6 Hz, 2H, Ar H), 7.29 (d, J = 8.7 Hz, 4H, Ar H), 7.65 (d, J = 1.9 Hz, 2H, Ar H), 7.67 (d, J = 8.7 Hz, 4H, Ar H), 7.81 (dd, J = 8.6, 1.9 Hz, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 14.30, 22.85, 26.15, 26.18, 29.21, 29.34, 29.43, 29.45, 29.52, 29.54, 31.99, 32.00, 69.24, 69.52, 78.24, 103.38, 111.39, 112.05, 114.68, 117.82, 121.02, 122.68, 123.87, 124.71, 133.59, 133.69, 148.87, 152.99, 154.28, 164.62. HRMS-FAB (*m*/*z*): $[M+H]^+$ calcd for $C_{68}H_{82}N_2O_8S$, 1087.587015, found 1087.58867.

2,5-Bis[(4-(3,4-dinonyloxyphenylcarbonyloxy)phenylethynyl]-3,4-dicyanothiophene (NC-TCT-mp9). ^{1}H NMR ($CDCl_3$, δ): 0.88 (t, J = 6.8 Hz, 12H, CH_3), 1.3-1.45 (m, 40H, CH_2), 1.45-1.55 (m, 8H, CH_2), 1.8-1.9 (m, 8H, CH_2), 4.07 (t, J = 6.4 Hz, 4H, OCH_2), 4.09 (t, J = 6.4 Hz, 4H, OCH_2), 6.94 (d, J = 8.4 Hz, 2H, Ar H), 7.29 (d, J = 8.7 Hz, 4H, Ar H), 7.65 (d, J = 2.0 Hz, 2H, Ar H), 7.67 (d, J = 8.7 Hz, 4H, Ar H), 7.81 (dd, J = 8.4, 2.0 Hz, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 14.13, 22.69, 25.96, 26.00, 29.02, 29.15, 29.28, 29.39, 29.41, 29.57, 31.90, 69.07, 69.34, 78.07, 103.21, 111.24, 111.86, 114.47, 114.53, 117.69, 120.85, 122.53, 124.55, 133.45, 133.55, 148.69, 152.82, 154.09, 164.51. HRMS-FAB (*m*/*z*): $[M+H]^+$ calcd for $C_{72}H_{90}N_2O_8S$ 1143.649615, found 1143.6531.

2,5-Bis[(4-(3,4-didecyloxyphenylcarbonyloxy)phenylethynyl]-3,4-dicyanothiophene (NC-TCT-mp10). ^{1}H NMR ($CDCl_3$, δ): 0.88 (t, J = 6.9 Hz, 12H, CH_3), 1.2-1.45 (m, 48H, CH_2), 1.45-1.6 (m, 8H, CH_2), 1.8-1.95 (m, 8H, CH_2), 4.07 (t, J = 6.5 Hz, 4H, OCH_2), 4.09 (t, J = 6.5 Hz, 4H, OCH_2), 6.94 (d, J = 8.4 Hz, 2H, Ar H), 7.29 (d, J = 8.6 Hz, 4H, Ar H), 7.65 (d, J = 1.9 Hz, 2H, Ar H), 7.67 (d, J = 8.6 Hz, 4H, Ar H), 7.81 (dd, J = 8.4, 1.9 Hz, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 14.32, 22.89, 26.15, 26.19, 29.21, 29.34, 29.55, 29.57, 29.60, 29.76, 29.77, 29.80, 29.82, 32.11, 69.25, 69.53, 78.25, 103.39, 111.40, 112.05, 114.67, 114.70, 117.85, 121.03, 122.69, 124.72, 133.61, 133.71, 148.87, 153.00, 154.28, 164.66. HRMS-FAB (*m*/*z*): $[M+H]^+$ calcd for $C_{76}H_{98}N_2O_8S$, 1199.712215, found 1199.71502.

2,5-Bis[(4-(3,4-diundecyloxyphenylcarbonyloxy)phenylethynyl]-3,4-dicyanothiophene (NC-TCT-mp11). ^{1}H NMR ($CDCl_3$, δ): 0.88 (t, J = 6.9 Hz, 12H, CH_3), 1.2-1.45 (m, 56H, CH_2), 1.45-1.6 (m, 8H, CH_2), 1.8-1.95 (m, 8H, CH_2), 4.08 (t, J = 6.6 Hz, 4H, OCH_2), 4.10 (t, J = 6.6 Hz, 4H, OCH_2), 6.94 (d, J = 8.4 Hz, 2H, Ar H), 7.29 (d, J = 8.6 Hz, 4H, Ar H), 7.65 (d, J = 2.0 Hz, 2H, Ar H), 7.67 (d, J = 8.6 Hz, 4H, Ar H), 7.81 (dd, J = 8.4, 2.0 Hz, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 14.14, 22.70, 26.00, 29.11, 29.15, 29.21, 29.37, 29.63, 31.93, 69.24, 69.58, 78.07, 103.41, 111.37, 112.05, 114.61, 114.64, 117.75, 121.03, 122.54, 124.55, 133.55, 148.69, 153.09, 154.16, 164.56. MS-FAB (*m*/*z*): $[M+H]^+$ calcd for $C_{80}H_{106}N_2O_8S$ 1225, found 1225.

2,5-Bis[(4-(3,4-didodecyloxyphenylcarbonyloxy)phenylethynyl]-3,4-dicyanothiophene (NC-TCT-mp12). ^{1}H NMR ($CDCl_3$, δ): 0.88 (t, J = 6.6 Hz, 12H, CH_3), 1.2-1.5 (m, 68H, CH_2), 1.5-1.6 (m, 8H, CH_2), 1.75-1.95 (m, 8H, CH_2), 4.07 (t, J = 6.5 Hz, 4H, OCH_2), 4.09 (t, J = 6.3 Hz, 4H, OCH_2), 6.94 (d, J = 8.7 Hz, 2H, Ar H), 7.29 (d, J = 8.6 Hz, 4H, Ar H), 7.65 (d, J = 2.0 Hz, 2H, Ar H), 7.67 (d, J = 8.6 Hz, 4H, Ar H), 7.81 (dd, J = 8.7, 2.0 Hz, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 14.32, 22.89, 26.16, 26.20, 29.22, 29.35, 29.56, 29.60, 29.82, 29.86, 29.90, 32.12, 69.25, 69.53, 78.25, 103.39,

111.39, 112.06, 114.70, 117.84, 121.04, 122.69, 123.90, 124.72, 133.60, 133.70, 148.89, 153.01, 154.29, 164.63. MS-FAB (*m*/*z*): $[M+H]^+$ calcd for $C_{84}H_{114}N_2O_8S$ 1313, found 1313.

2,5-Bis[(4-(3,4-di(2-methylbutyloxy)phenylcarbonyloxy)phenylethynyl]-3,4-dicyanothiophene (NC-TCT-mp4*(S)). ^1H NMR ($CDCl_3$, δ): 0.98 (t, *J* = 7.4 Hz, 6H, CH_3), 0.99 (t, *J* = 7.4 Hz, 6H, CH_3), 1.06 (d, *J* = 6.7 Hz, 6H, CH_3), 1.07 (d, *J* = 6.7 Hz, 6H, CH_3), 1.33 (m, 4H, CH_2), 1.63 (m, 4H, CH_2), 1.97 (m, 4H, CH), 3.98 (m, 4H, OCH_2), 3.89 (t, 4H, OCH_2), 6.94 (d, *J* = 8.8 Hz, 2H, Ar H), 7.30 (d, *J* = 8.7 Hz, 4H, Ar H), 7.64 (d, *J* = 2.0 Hz, 2H, Ar H), 7.68 (d, *J* = 8.7 Hz, 4H, Ar H), 7.82 (dd, *J* = 8.8, 2.0 Hz, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 11.79, 11.82, 16.94, 16.99, 26.56, 35.10, 35.21, 74.06, 74.37, 78.48, 103.63, 111.67, 112.16, 114.72, 114.90, 118.08, 121.12, 122.96, 124.90, 133.88, 133.96, 149.34, 153.22, 154.75, 164.97. HRMS-MALDI (*m*/*z*): $[M+Na]^+$ calcd for $C_{56}H_{58}N_2O_8SNa$ 941.3806, found 941.3818.

2,5-Bis[(4-(3,4-di((S)-3,7-dimethyloctyloxy)phenylcarbonyloxy)phenylethynyl]-thiophene (H-TCT-mp10*(S)). ^1H NMR ($CDCl_3$, δ): 0.87 (d, *J* = 5.9 Hz, 12H, CH_3), 0.88 (d, *J* = 5.9 Hz, 12H, CH_3), 0.98 (d, *J* = 6.0 Hz, 6H, CH_3), 0.99 (d, *J* = 6.0 Hz, 6H, CH_3), 1.16 (m, 8H, CH_2), 1.28 (m, 8H, CH_2), 1.33 (m, 8H, CH_2), 1.53 (m, 4H, CH), 1.68 (m, 8H, CH_2), 1.93 (m, 4H, CH), 4.10 (t, *J* = 6.5 Hz, 4H, OCH_2), 4.12 (t, *J* = 6.5 Hz, 4H, OCH_2), 6.90 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.18 (s, 2H, thiophene-H), 7.23 (d, *J* = 8.7 Hz, 4H, Ar-H), 7.54 (d, 4H, *J* = 8.7 Hz, Ar-H), 7.63 (d, *J* = 2.0 Hz, 2H, Ar-H), 7.80 (dd, J_1 = 8.6 Hz, 2H, J_2 = 2.0 Hz, Ar-H). MS-MALDI (*m*/*z*): $[M+H]^+$ calcd for $C_{74}H_{100}O_8S$ 1151, found 1151.

2,5-Bis[(4-(3,4-di(3,7-dimethyloctyloxy)phenylcarbonyloxy)phenylethynyl]-3,4-dibromothiophene (Br-TCT-mp10*(S)). ^1H NMR ($CDCl_3$, δ): 0.87 (d, *J* = 6.6 Hz, 12H, CH_3), 0.88 (d, *J* = 6.6 Hz, 12H, CH_3), 0.97 (d, *J* = 6.2 Hz, 6H, CH_3), 0.98 (d, *J* = 6.2 Hz, 6H, CH_3), 1.16 (m, 8H, CH_2), 1.28 (m, 8H, CH_2), 1.33 (m, 8H, CH_2), 1.53 (m, 4H, CH), 1.68 (m, 8H, CH_2), 1.93 (m, 4H, CH), 4.12 (t, *J* = 6.5 Hz, 4H, OCH_2), 4.13 (t, *J* = 6.5 Hz, 4H, OCH_2), 6.90 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.23 (d, *J* = 8.7 Hz, 4H, Ar-H), 7.54 (d, 4H, *J* = 8.7 Hz, Ar-H), 7.63 (d, *J* = 2.0 Hz, 2H, Ar-H), 7.80 (dd, J_1 = 8.6 Hz, 2H, J_2 = 2.0 Hz, Ar-H). ^{13}C NMR ($CDCl_3$, δ): 20.13, 20.15, 23.04, 23.14, 25.15, 28.41, 30.33, 36.31, 36.46, 37.72, 39.63, 67.82, 68.00, 81.44, 98.47, 112.08, 114.58, 119.56, 119.75, 121.41, 121.72, 122.29, 122.66, 124.85, 131.04, 133.40, 149.03, 152.18, 154.30, 165.10. HRMS-MALDI (*m*/*z*): $[M+Na]^+$ calcd for $C_{74}H_{98}O_8SBr_2Na$, 1327.5241, found 1327.5216.

2,5-Bis[(4-(3,4-di(3,7-dimethyloctyloxy)phenylcarbonyloxy)phenylethynyl]-3,4-dicyanothiophene (NC-TCT-mp10*rac, (R), and (S)). ^1H NMR ($CDCl_3$, δ): 0.87 (d, *J* = 5.9 Hz, 12H, CH_3), 0.88 (d, *J* = 5.9 Hz, 12H, CH_3), 0.98 (d, *J* = 6.0 Hz, 6H, CH_3), 0.99 (t, *J* = 6.0 Hz, 6H, CH_3), 1.16 (m, 8H, CH_2), 1.28 (m, 8H, CH_2), 1.33 (m, 8H, CH_2), 1.53 (m, 4H, CH), 1.68 (m, 8H, CH_2), 1.93 (m, 4H, CH), 4.10 (t, *J* = 6.5 Hz, 4H, OCH_2), 4.12 (t, *J* = 6.5 Hz, 4H, OCH_2), 6.95 (d, *J* = 8.4 Hz, 2H, Ar H), 7.31 (d, *J* = 8.6 Hz, 4H, Ar H), 7.64 (d, *J* = 1.9 Hz, 2H, Ar H), 7.66 (d, *J* = 8.6 Hz, 4H, Ar H), 7.82 (dd, *J* = 8.4, 1.9 Hz, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 19.63, 19.65, 22.54, 22.64, 24.65, 27.91, 29.86, 35.83, 35.99, 37.25, 39.15, 67.39, 67.59, 78.00, 103.13, 111.16, 111.68, 114.22, 114.46, 117.62,

120.76, 122.46, 124.44, 133.38, 133.47, 148.62, 152.75, 153.98, 164.45. MALDI (*m*/*z*): $[M+Na]^+$ calcd for $C_{76}H_{98}N_2O_8SNa$, 1221.6936, found 1221.6970.

2,5-Bis[(4-(4-((S)-2-methylbutyloxy)phenylcarbonyloxy)phenylethynyl]-3,4-dicyanothiophene (NC-DCT-p4*(S)). ^{1}H NMR ($CDCl_3$, δ): 0.97 (t, *J* = 7.4 Hz, 6H, CH_3), 1.05 (d, *J* = 6.7 Hz, 6H, CH_3), 1.31 (m, 2H, CH_2), 1.59 (m, 2H, CH_2), 1.91 (m, 2H, CH), 3.85 (dd, *J* = 15.4, 6.0 Hz, 2H, OCH_2), 3.89 (t, *J* = 15.4, 6.6 Hz, 2H, OCH_2), 6.98 (d, *J* = 8.8 Hz, 4H, Ar H), 7.29 (d, *J* = 8.6 Hz, 4H, Ar H), 7.67 (d, *J* = 8.6 Hz, 4H, Ar H), 8.13 (d, *J* = 8.8 Hz, 4H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 11.51, 16.67, 26.23, 34.80, 73.27, 78.24, 103.40, 111.41, 114.17, 114.42, 114.66, 115.03, 117.81, 120.97, 122.52, 122.83, 132.54, 132.57, 133.62, 133.78, 152.95, 164.14, 164.53. MS-MALDI (*m*/*z*): $[M+H]^+$ calcd for $C_{46}H_{38}N_2O_6S$ 746, found 746.

Table 2. Crystal data and structure refinement for **NC-DCT-p4*(S)**.

Identification code	98194
Empirical formula	C46 H38 N2 O6 S
Formula weight	746.84
Temperature	183(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)
Unit cell dimensions	a = 20.907(4) Å, α= 90° b = 6.4942(13) Å, β= 101.97(3)° c = 29.052(6) Å, γ = 90°
Volume	3858.7(13) Å^3
Z	4
Density (calculated)	1.286 Mg/m^3
Absorption coefficient	0.137 mm^{-1}
F(000)	1568
Crystal size	0.3 x 0.4 x 0.5 mm^3
Theta range for data collection	1.34 to 23.27°.
Index ranges	-22<=h<=18, -6<=k<=6, -23<=l<=31

Reflections collected	14769
Independent reflections	9221 [R(int) = 0.1396]
Completeness to theta = 23.27°	99.5 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9221 / 39 / 922
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.1089, wR2 = 0.2528
R indices (all data)	R1 = 0.2018, wR2 = 0.3429
Absolute structure parameter	0.2(4)
Extinction coefficient	0.0014(6)
Largest diff. peak and hole	0.421 and -0.416 e.$Å^{-3}$

2,5-Bis[(4-(4-((S)-3,7-dimethyloctyloxy)phenylcarbonyloxy)phenylethynyl]-3,4-dicyanothiophene (NC-DCT-p10*(S)). ^{1}H NMR ($CDCl_3$, δ): 0.89 (d, *J* = 6.8 Hz, 6H, CH_3), 0.97 (d, *J* = 6.5 Hz, 3H, CH_3), 1.00 (t, *J* = 7.4 Hz, 3H, CH_3), 1.01 (t, *J* = 7.4 Hz, 3H, CH_3), 1.18 (m, 2H, CH_2), 1.28 (m, 2H, CH_2), 1.35 (m, 2H, CH_2), 1.55 (m, 4H, CH_2, 1H, CH), 1.64 (m, 2H, CH_2), 1.86 (m, 4H, CH_2, 1H, CH), 4.10 (m, 6H, OCH_2), 6.99 (d, *J* = 8.9 Hz, 4H, Ar H), 7.30 (d, *J* = 8.6 Hz, 4H, Ar H), 7.68 (d, *J* = 8.6 Hz, 4H, Ar H), 8.16 (d, *J* = 8.9 Hz, 4H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 20.04, 23.01, 23.12, 25.06, 28.38, 30.20, 36.37, 37.65, 39.61, 67.12, 78.47, 103.98, 111.65, 114.82, 114.93, 118.08, 121.27, 122.91, 132.81, 133.95, 153.19, 164.20, 164.79. MS-MALDI (*m*/*z*): $[M+H]^+$ calcd for $C_{56}H_{58}N_2O_6S$ 888, found 888.

2,5-Bis[(4-(4-decyloxyphenylcarbonyloxy)phenylethynyl]-3,4-dicyanothiophene (NC-DCT-p10). ^{1}H NMR ($CDCl_3$, δ): 0.89 (t, *J* = 6.9 Hz, 6H, CH_3), 1.1-1.6 (m, 28H, CH_2), 1.83 (tt, *J* = 6.9, 6.3 Hz, 4H, CH_2), 4.04 (t, *J* = 6.3 Hz, 4H, OCH_2), 6.98 (d, *J* = 8.5 Hz, 4H, Ar H), 7.29 (d, *J* = 8.4 Hz, 4H, Ar H), 7.67 (d, *J* = 1.9 Hz, 4H, Ar H), 8.14 (d, *J* = 8.5 Hz, 4H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 14.34, 22.90, 26.18, 29.28, 29.53, 29.57, 29.77, 30.51, 32.11, 68.59, 78.27, 103.43, 111.44, 114.60, 117.86, 121.05, 122.70, 125.73, 132.60, 133.60, 133.66, 133.74, 152.98, 164.02, 164.57. HRMS-MALDI (*m*/*z*): $[M+Na]^+$ calcd for $C_{56}H_{58}N_2O_6SNa$ 909.3908, found 909.3948.

2,5-Bis[(4-(4-dodecyloxyphenylcarbonyloxy)phenylethynyl]-3,4-dicyanothiophene (NC-DCT-p12). ^{1}H NMR ($CDCl_3$, δ): 0.90 (t, *J* = 6.8 Hz, 6H, CH_3), 1.1-1.6 (m, 36H, CH_2), 1.83 (tt, *J* = 6.8, 6.3 Hz, 4H, CH_2), 4.09 (t, *J* = 6.3 Hz, 4H, OCH_2), 7.01 (d, *J* = 8.5 Hz, 4H, Ar H), 7.34 (d, *J* = 8.4 Hz, 4H, Ar H), 7.71 (d, *J* = 1.9 Hz, 4H, ArH), 8.19 (d, *J* =

8.5 Hz, 4H, Ar H). HRMS-MALDI (*m*/*z*): $[M+Na]^+$ calcd for $C_{60}H_{66}N_2O_6SNa$ 965.4534, found 965.4546.

2-[(4-(3,4-di(3,7-dimethyloctyloxy)phenylcarbonyloxy)phenylethynyl]-5-[(4-(3,4-dihexyloxyphenylcarbonyloxy)phenylethynyl]-3,4-dicyanothiophene (NC-TCT-mp6,mp10*(R)). ^{1}H NMR ($CDCl_3$, δ): 0.87 (d, *J* = 6.8 Hz, 6H, CH_3), 0.88 (d, *J* = 6.8 Hz, 6H, CH_3), 0.92 (m, 6H, CH_3), 0.97 (d, *J* = 6.5 Hz, 3H, CH_3), 0.98 (d, *J* = 6.5 Hz, 3H, CH_3), 1.17 (m, 6H, CH_2), 1.36 (m, 14H, CH_2), 1.51 (m, 4H, CH_2, 2H, CH), 1.66 (m, 4H, CH_2), 1.86 (m, 4H, CH_2, 2H, CH), 4.08 (m, 6H, OCH_2), 6.94 (d, *J* = 8.5 Hz, 1H, Ar H), 6.95 (d, *J* = 8.5 Hz, 1H, Ar H), 7.66 (m, 2H, Ar H), 7.69 (d, *J* = 8.6 Hz, 4H, Ar H), 7.82 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, δ): 14.02, 19.71, 22.59, 22.69, 24.72, 25.61, 25.65, 27.97, 28.94, 29.06, 29.88, 31.54, 35.86, 36.02, 37.29, 39.19, 67.41, 67.59, 69.02, 69.26, 78.05, 103.18, 111.24, 111.67, 111.75, 114.17, 114.32, 114.47, 117.66, 120.77, 122.52, 124.51, 133.44, 133.53, 148.62, 152.77, 154.02, 164.52. MS-MALDI (*m*/*z*): $[M+Na]^+$ calcd for $C_{67}H_{80}N_2O_8SNa$ 1095.5528, found 1109.5525.

2-[(4-(4-(3,7-dimethyloctyloxy)phenylcarbonyloxy)phenylethynyl]-5-[(4-(3,4-dihexyloxyphenylcarbonyloxy)phenylethynyl]-3,4-dicyanothiophene (NC-TrCT-mp6,p10*(S)). ^{1}H NMR ($CDCl_3$, δ): 0.89 (d, *J* = 6.8 Hz, 6H, CH_3), 0.92 (m, 6H, CH_3), 0.97 (d, *J* = 6.5 Hz, 3H, CH_3), 1.07 (m, 2H, CH_2), 1.36 (m, 10H, CH_2), 1.51 (m, 4H, CH_2, 1H, CH), 1.64 (m, 2H, CH_2), 1.86 (m, 4H, CH_2, 1H, CH), 4.08 (m, 6H, OCH_2), 6.94 (d, *J* = 8.5 Hz, 1H, Ar H), 6.99 (d, *J* = 8.8 Hz, 2H, Ar H), 7.31 (d, *J* = 8.6 Hz, 4H, Ar H), 7.65 (d, *J* = 1.8 Hz, 1H, Ar H), 7.68 (d, *J* = 8.6 Hz, 4H, Ar H), 7.82 (dd, *J* = 8.5 Hz, 1.8 Hz, 1H, Ar H), 8.14 (d, *J* = 8.8 Hz, 4H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 14.45, 20.04, 23.02, 23.13, 25.07, 26.04, 26.08, 28.39, 29.37, 29.49, 30.19, 31.95, 31.97, 36.37, 37.65, 39.61, 67.11, 69.45, 69.69, 78.48, 103.61, 111.67, 112.18, 114.75, 114.81, 114.90, 118.08, 121.24, 122.92, 122.94, 124.94, 132.81, 133.86, 133.96, 149.05, 153.20, 154.45, 164.19, 164.79, 164.93. HRMS-MALDI (*m*/*z*): $[M+NA]^+$ calcd for $C_{58}H_{62}N_2O_7SNa$ 953.4174, found 953.4174.

2-[(4-(4-(3,7-dimethyloctyloxy)phenylcarbonyloxy)phenylethynyl]-5-[(4-(3,4-dibutyloxyphenylcarbonyloxy)phenylethynyl]-3,4-dicyanothiophene (NC-TrCT-mp4,p10*(S)). ^{1}H NMR ($CDCl_3$, δ): 0.89 (d, *J* = 6.8 Hz, 6H, CH_3), 0.98 (d, *J* = 6.5 Hz, 3H, CH_3), 1.10 (t, *J* = 7.4 Hz, 3H, CH_3), 1.11 (t, *J* = 7.4 Hz, 3H, CH_3), 1.19 (m, 2H, CH_2), 1.35 (m, 2H, CH_2), 1.53 (m, 4H, CH_2, 1H, CH), 1.64 (m, 2H, CH_2), 1.86 (m, 4H, CH_2, 1H, CH), 4.09 (m, 6H, OCH_2), 6.94 (d, *J* = 8.5 Hz, 1H, Ar H), 6.99 (d, *J* = 8.8 Hz, 2H, Ar H), 7.30 (d, *J* = 8.6 Hz, 2H, Ar H), 7.31 (d, *J* = 8.6 Hz, 2H, Ar H), 7.65 (d, *J* = 1.8 Hz, 1H, Ar H), 7.68 (d, *J* = 8.6 Hz, 4H, Ar H), 7.82 (dd, *J* = 8.5 Hz, 1.8 Hz, 1H, Ar H), 8.14 (d, *J* = 8.8 Hz, 4H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 14.27, 19.62, 20.04, 23.12, 25.06, 28.39, 30.19, 31.58, 36.37, 37.65, 39.61, 69.18, 69.37, 78.48, 103.61, 111.67, 112.18, 114.75, 114.82, 114.93, 118.08, 121.24, 122.91, 122.94, 124.94, 132.81, 133.86, 133.95, 149.05, 153.20, 154.45, 164.19, 164.79, 164.93. MS-MALDI (*m*/*z*): $[M+H]^+$ calcd for $C_{54}H_{54}N_2O_7S$ 876, found 876.

2-[(4-(3,4,5-tridodecyloxyphenylcarbonyloxy)phenylethynyl]-5-[(4-(4-octyloxyphenylcarbonyloxy)phenylethynyl]-3,4-dicyanothiophene (NC-TCT-mpm12,p8) ^{1}H NMR ($CDCl_3$, δ): 0.89 (m, 12H, CH_3), 1.26-1.40 (m, 56H, CH_2), 1.45-

1.55 (m, 8H, CH_2), 1.78 (m, 2H, CH_2), 1.86 (m, 6H, CH_2), 4.07 (m, 8H, OCH_2), 7.00 (d, *J* = 7.0 Hz, 2H, ArH), 7.29 (d, *J* = 8.7 Hz, 2H, Ar H), 7.31 (d, *J* = 8.7 Hz, 2H, Ar H), 7.66 (d, *J* = 8.7 Hz, 2H, ArH), 7.68 (d, *J* = 8.7 Hz, 2H, ArH), 8.14 (d, *J* = 7.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, δ): 15.06, 23.58, 23.62, 26.99, 29.98, 30.15, 30.17, 30.24, 30.29, 30.49, 30.56, 30.58, 30.62, 30.66, 32.72, 32.84, 69.28, 70.14, 74.52, 78.96, 109.39, 112.16, 115.29, 115.41, 118.56, 121.72, 123.43, 133.32, 134.30, 134.46, 134.49, 144.09, 153.91, 164.72, 165.21. MS-MALDI (*m*/*z*): $[M+Na]^+$ calcd for $C_{80}H_{106}N_2O_8SNa$ 1277.7562, found 1277.7517.

2,4-Bis(4-phenylmethoxyphenylethynyl)-1,3-dibromobenzene. 1,5-diiodo-2,4-dibromobenzene (1.50g, 7.21mmol), 4-(phenylmethoxy)phenylacetylene (1.76g, 3.61mmol), copper (I) iodide (28mg, 0.144mmol), and $Pd(PPh_3)Cl_2$ (51mg, 0.072mmol) were placed in a 250mL Schlenk flask with stir bar. The flask was evacuated, argon was introduced and dry, air-free toluene (125mL) and diisopropylamine (2.0 ml, 14.4mmol) were added sequentially *via* a syringe. The reaction was stirred at room temperature for 12 hours and quickly became orange, then brown. 25 mL of 1N HCl (aqueous) were added, the mixture was extracted with Et_2O (200ml), dried ($MgSO_4$), and filtered through a silica gel pad. The solvents were removed in vacuo and the remaining yellow solid was purified by column chromatography (silica gel, 3:2 hexane/dichloromethane eluent) and crystallized from hexane/chloroform yielding the product (1.85g, 2.85mmol, 79%) as a white solid. ^{1}H NMR ($CDCl_3$): 5.078 (s, 4H, OCH_2Ar), 6.98 (d, 4H, J = 8.9 Hz, Ar-H), 7.32-7.44 (m, 10H, Ar-H), 7.52 (d, 4H, J = 8.9 Hz, Ar-H), 7.69 (s, 1H, Ar-H), 7.87 (s, 1H, Ar-H). ^{13}C NMR ($CDCl_3$): 70.01, 85.67, 95.37, 114.76, 114.98, 124.63, 124.99, 127.46, 128.12, 128.63, 133.27, 135.54, 136.02, 136.40, 159.29. HRMS-FAB (*m*/*z*): (M^+) calcd for $C_{36}H_{24}Br_2O_2$ 646.0143, found 646.0133.

2,4-Bis(4-phenylmethoxyphenylethynyl)-1,3-dicyanobenzene. 2,4-Bis(4-phenylmethoxyphenylethynyl)-1,3-dibromobenzene (1.00 g, 1.54 mmol), copper (I) cyanide (345 mg, 3.86 mmol), and a stir bar were placed in a 50ml Schlenk tube. The flask was evacuated, argon was introduced and dry DMF (20 ml) was added via a syringe. The mixture was stirred at 145 °C for 12 hours then cooled to room temperature, and 100ml of 1N NH_4Cl (aqueous) were added. The mixture was extracted with Et_2O and $CHCl_3$, the combined extracts dried over $MgSO_4$, and the solvents removed in vacuum. A small amount of brown solution of product in residual DMF was obtained, which was purified by column chromatography (silica gel, 1.5:1 DCM/hexane eluent) yielding the product (630 mg, 1.17 mmol, 76%) as a yellow crystalline solid which was used without further purification. ^{1}H NMR ($CDCl_3$): 5.12 (s, 4H, OCH_2Ar), 7.01 (d, 4 H, J = 8.4 Hz, Ar-H), 7.38-7.48 (m, 10H, Ar-H), 7.57 (d, 4H, J = 8.4 Hz, Ar-H) 7.56 (s, 1H, Ar-H), 7.85 (s, 1H, Ar-H). 13C NMR ($CDCl_3$): 70.08, 83.94, 101.60, 113.13, 113.45, 115.11, 115.78, 127.39, 128.12, 128.57, 131.28, 134.00, 134.16, 136.04, 160.16. HRMS-EI (*m*/*z*): (M^+) calcd for $C_{38}H_{24}N_2O_2$ 540.1838, found: 540.1825.

2,4-Bis(4-hydroxyphenylethynyl)-1,3-dibromobenzene (9b) 2,4-Bis(4-phenylmethoxyphenylethynyl)-1,3-dibromobenzene (750mg, 1.16mmol) was placed in a 100ml Schlenk flask with a stir bar which was then evacuated and filled with argon. Dry, air-free CH_2Cl_2 (50 ml) was added and the yellow solution was cooled to 0 °C after which BBr_3 (2.5 ml, 1M solution in CH_2Cl_2, 2.54mmol) was added dropwise via syringe.

The solution became orange in color and was stirred at 0 °C for 30 minutes at which time 10ml of 1N HCl (aqueous) was added. The solids were extracted with $CHCl_3$, dried over $MgSO_4$ and the solvents were removed in vacuo. The remaining orange solids were purified by silica gel chromatography using 20:1/CH_2Cl_2:THF as the eluent followed by precipitation from THF/CH_2Cl_2 by the addition of hexanes yielding the product (319mg, 0.681mmol, 59%) as a yellow solid which was used without further purification. ^{1}H NMR ($CDCl_3$): 6.80 (d, 4H, J = 8.50 Hz, Ar-H), 7.42 (d, 4H, J = 8.50 Hz, Ar-H), 7.65 (s, 1H, Ar-H), 7.83 (s, 1H, Ar-H). 13C NMR ($CDCl_3$): 85.14, 95.69, 115.53, 124.36, 125.07, 133.35, 135.46, 135.90, 149.06. HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{22}H_{12}Br_2O_2$ 488.9096, found: 488.9089.

2,4-Bis(4-hydroxyphenylethynyl)-1,3-dicyanobenzene (9c). 2,4-Bis(4-phenylmethoxyphenylethynyl)-1,3-dicyanobenzene (400 mg, 0.740 mmol) was placed in a 250 ml Schlenk flask with a stir bar. The flasks was evacuated, argon was introduced and dry, air-free dichloromethane (175 mL) was added via cannula. The mixture was cooled to –78 °C with a dry-ice/acetone bath and BBr_3 (1M in DCM, 8.9 ml, 8.9 mmol) was added drop-wise via syringe. The orange suspension was allowed to warm to room temperature. Solvents and excess BBr_3 were removed under vacuum into a cooled trap. The residue was cooled to 0 °C and first H_2O (100 ml), then EtOH (100 ml) were added. Extraction of the mixture at room temperature with Et_2O (200 mL), drying of the organic phase over $MgSO_4$, and evaporation of the solvents in vacuum yielded an orange solid which were purified by chromatography (silica gel, 2% EtOAc in DCM) yielding **9c** (206mg, 57.2mmol, 77%) as a slightly orange solid. ^{1}H NMR ($CDCl_3$): 6.81 (d, 4H, J = 9.0 Hz, Ar-H), 7.48 (d, 4H, J = 9.0 Hz, Ar-H), 7.85 (s, 1H, Ar-H), 8.24 (s, 1H, Ar-H). ^{13}C NMR ($CDCl_3$): 84.57, 102.41, 104.59, 112.66, 114.62, 116.90, 132.11, 135.03, 135.07, 138.11, 161.11. HRMS-EI (*m*/*z*): $[M^+]$ calcd for $C_{24}H_{12}N_2O_2$ 360.0893, found: 360.0884.

Synthesis of 1,3- and 1,4-Bis[4-(3,4-dihexyloxyphenylcarbonyloxy) phenylethynyl]benzene derivatives

9a, **9b**, or **9c** (0.167 mmol) were placed in a 25ml Schlenk flask with 3,4-(dioctyloxy)benzoic acid (0.445 mmol), DMAP (10mg, 0.083mmol), and a stir bar. Argon atmosphere was introduced and dry, air-free dichloromethane (10ml) was added *via* a syringe, followed by diisopropylcarbodiimide (104 µl, 0.67 mmol) *via* a microsyringe. The mixture was stirred at room tempemperature for 4 days, 4ml of 1N HCl (aqueous) were added, and the mixture was extracted with $CHCl_3$. The combined organic extracts were dried over $MgSO_4$, and evaporated in vacuum. The remaining solids were purified by column chromatography (silica gel, DCM/hexane eluent) followed by recrystallization from DCM/MeOH yielding the products as a white or yellow solid in 60-70%).

1,3-Bis[4-(3,4-dihexyloxyphenylcarbonyloxy)phenylethynyl]benzene (H-mTCP-mp6): ^{1}H NMR ($CDCl_3$, δ): 0.90 (t, *J* = 6.8 Hz, 6H, CH_3), 0.91 (t, *J* = 6.8 Hz, 6H, CH_3), 1.25-1.40 (m, 16H, CH_2), 1.55 (m, 8H, CH_2), 1.91 (m, 8H, CH_2), 4.07 (t, *J* = 6.5 Hz, 4H, OCH_2), 4.09 (t, *J* = 6.5 Hz, 4H, OCH_2), 6.94 (d, *J* = 8.8 Hz, 2H, Ar H), 7.22 (d, *J* = 8.5

Hz, 4H, Ar H), 7.36 (t, J = 8.0 Hz, 1H, Ar H), 7.51 (dd, J = 8.0, 1.6 Hz, 2H, Ar H), 7.60 (d, J = 8.5 Hz, 4H, Ar H), 7.67 (d, J = 2.0 Hz, 2H, Ar H), 7.74 (t, J = 1.6 Hz, 1H, Ar H), 7.82 (dd, J = 8.8, 2.0 Hz, 2H, Ar H). ^{13}C NMR ($CDCl_3$, δ): 14.44, 23.01, 26.04, 26.08, 29.39, 29.51, 31.95, 31.97, 69.45, 69.71, 88.96, 89.73, 112.25, 114.86, 120.91, 121.61, 122.44, 123.94, 124.84, 128.92, 131.73, 133.25, 134.9, 149.05, 151.52, 154.31, 165.18. HRMS-MALDI (m/z): $[M+Na]^+$ calcd for $C_{60}H_{70}O_8Na$ 941.4963, found 941.4988.

1,3-Bis[4-(3,4-didecyloxyphenylcarbonyloxy)phenylethynyl]benzene (H-mTCP-mp10): ^{1}H NMR ($CDCl_3$, δ): 0.90 (t, J = 6.8 Hz, 6H, CH_3), 0.91 (t, J = 6.8 Hz, 6H, CH_3), 1.25-1.45 (m, 32H, CH_2), 1.55 (m, 8H, CH_2), 1.91 (m, 8H, CH_2), 4.07 (t, J = 6.5 Hz, 4H, OCH_2), 4.09 (t, J = 6.5 Hz, 4H, OCH_2), 6.94 (d, J = 8.8 Hz, 2H, Ar H), 7.22 (d, J = 8.5 Hz, 4H, Ar H), 7.36 (t, J = 8.0 Hz, 1H, Ar H), 7.51 (dd, J = 8.0, 1.6 Hz, 2H, Ar H), 7.60 (d, J = 8.5 Hz, 4H, Ar H), 7.67 (d, J = 2.0 Hz, 2H, Ar H), 7.74 (t, J = 1.6 Hz, 1H, Ar H), 7.82 (dd, J = 8.8, 2.0 Hz, 2H, Ar H). HRMS-MALDI (m/z): $[M+Na]^+$ calcd for $C_{76}H_{102}O_8Na$ 1165.7467, found 1165.7475.

2,4-Bis[4-(3,4-dihexyloxyphenylcarbonyloxy)phenylethynyl]-1,3-dibromobenzene (Br-mTCP-mp6) ^{1}H NMR ($CDCl_3$): 0.92 (m, 12H, CH_3), 1.36-1.38 (m, 16H, $(CH_2)_2$), 1.49-1.53 (m, 8H, CH_2), 1.85-1.88 (m, 8H, CH_2), 4.07-4.10 (m, 8H, CH_2O), 6.94 (d, 2H, J = 8.6 Hz, Ar-H), 7.25 (d, 4H, J = 8.7 Hz, Ar-H), 7.64 (d, 4H, J = 8.7 Hz, Ar-H), 7.67 (d, 2H, J = 2.0 Hz, Ar-H), 7.74 (s, 1H, Ar-H), 7.83 (dd, 2H, J_1 = 8.6 Hz, J_2 = 2.0 Hz, Ar-H), 7.90 (s, 1H, Ar-H). ^{13}C NMR ($CDCl_3$, δ): 14.02, 22.58, 22.59, 25.62, 25.66, 28.96, 29.08, 31.53, 31.55, 69.03, 69.29, 86.61, 94.64, 111.81, 114.42, 119.88, 121.10, 122.14, 124.43, 124.70, 125.30, 132.95, 135.73, 136.43, 148.62, 151.54, 153.92, 164.68. HRMS-FAB (m/z): $[M+H]^+$ calcd for $C_{60}H_{68}Br_2O_8$ 1075.3359, found 1075.3332.

2,4-Bis[4-(3,4-dioctyloxyphenylcarbonyloxy)phenylethynyl]-1,3-dibromobenzene (Br-mTCP-mp8) ^{1}H NMR ($CDCl_3$): 0.92 (m, 12H, CH_3), 1.36-1.38 (m, 32H, $(CH_2)_4$), 1.49-1.53 (m, 8H, CH_2), 1.85-1.88 (m, 8H, CH_2), 4.07-4.10 (m, 8H, CH_2O), 6.94 (d, 2H, J = 8.6 Hz, Ar-H), 7.25 (d, 4H, J = 8.7 Hz, Ar-H), 7.64 (d, 4H, J = 8.7 Hz, Ar-H), 7.67 (d, 2H, J = 2.0 Hz, Ar-H), 7.74 (s, 1H, Ar-H), 7.83 (dd, 2H, J_1 = 8.6 Hz, J_2 = 2.0 Hz, Ar-H), 7.90 (s, 1H, Ar-H). ^{13}C NMR ($CDCl_3$, δ): 14.11, 22.67, 25.95, 25.98, 29.01, 29.13, 29.25, 29.26, 29.33, 29.35, 31.79, 31.80, 69.03, 69.30, 86.61, 94.64, 111.82, 114.45, 119.88, 121.10, 122.14, 124.44, 124.70, 125.30, 132.94, 135.73, 136.43, 148.62, 151.54, 153.92, 164.68. MS-FAB (m/z): $[M+H]^+$ calcd for $C_{68}H_{85}Br_2O_8$ 1188.4689, found 1188.4650.

2,4-Bis[4-(3,4-didecyloxyphenylcarbonyloxy)phenylethynyl]-1,3-dibromobenzene (Br-mTCP-mp10) ^{1}H NMR ($CDCl_3$): 0.92 (m, 12H, CH_3), 1.36-1.38 (m, 48H, $(CH_2)_6$), 1.49-1.53 (m, 8H, CH_2), 1.85-1.88 (m, 8H, CH_2), 4.07-4.10 (m, 8H, CH_2O), 6.94 (d, 2H, J = 8.6 Hz, Ar-H), 7.25 (d, 4H, J = 8.7 Hz, Ar-H), 7.64 (d, 4H, J = 8.7 Hz, Ar-H), 7.67 (d, 2H, J = 2.0 Hz, Ar-H), 7.74 (s, 1H, Ar-H), 7.83 (dd, 2H, J_1 = 8.6 Hz, J_2 = 2.0 Hz, J_2 = 8.6 Hz, Ar-H), 7.90 (s, 1H, Ar-H). ^{13}C NMR ($CDCl_3$, δ): 14.12, 22.68, 25.95, 25.98, 29.01, 29.13, 29.34, 29.37, 29.39, 29.56, 29.60, 29.61, 31.90, 69.03, 69.29, 86.61, 94.63, 111.82, 114.44, 119.87, 121.09, 122.14, 124.43, 124.69, 125.29, 132.94, 135.72, 136.42,

148.62, 151.53, 153.92, 164.67. HRMS-FAB (*m*/*z*): $[M+H]^+$ calcd for $C_{76}H_{100}Br_2O_8$ 1299.5863, found 1299.5822.

2,4-Bis[4-(3,4-didodecyloxyphenylcarbonyloxy)phenylethynyl]-1,3-dibromo-benzene (Br-mTCP-mp12) ^{1}H NMR ($CDCl_3$): 0.92 (m, 12H, CH_3), 1.36-1.38 (m, 64H, $(CH_2)_8$), 1.49-1.53 (m, 8H, CH_2), 1.85-1.88 (m, 8H, CH_2), 4.07-4.10 (m, 8H, CH_2O), 6.94 (d, 2H, *J* = 8.6 Hz, Ar-H), 7.25 (d, 4H, *J* = 8.7 Hz, Ar-H), 7.64 (d, 4H, *J* = 8.7 Hz, Ar-H), 7.67 (d, 2H, *J* = 2.0 Hz, Ar-H), 7.74 (s, 1H, Ar-H), 7.83 (dd, 2H, J_1 = 8.6 Hz, J_2 = 2.0 Hz, Ar-H), 7.90 (s, 1H, Ar-H). ^{13}C NMR ($CDCl_3$, δ): 14.12, 22.69, 25.95, 25.99, 29.01, 29.13, 29.36, 29.40, 29.61, 29.62, 29.66, 29.69, 31.92, 69.03, 69.30, 86.61, 94.64, 111.82, 114.45, 119.87, 121.10, 122.14, 124.43, 124.69, 125.29, 132.94, 135.73, 136.42, 148.62, 151.54, 153.92, 164.67. HRMS-FAB (*m*/*z*): $[M+H]^+$ calcd for $C_{84}H_{116}Br_2O_8$ 1411.7115, found 1411.7067.

2,4-Bis[4-(3,4-dioctyloxyphenylcarbonyloxy)phenylethynyl]-1,3-dicyanobenzene (NC-mTCP-mp8) ^{1}H NMR ($CDCl_3$): 0.92 (m, 12H, CH_3), 1.36-1.38 (m, 32H, $(CH_2)_4$), 1.49-1.53 (m, 8H, CH_2), 1.85-1.88 (m, 8H, CH_2), 4.07-4.15 (m, 8H, CH_2O), 6.95 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.29 (d, 4H, *J* = 8.7 Hz, Ar-H), 7.66 (d, 2H, *J* = 2.1 Hz, Ar-H), 7.71 (d, 4H, *J* = 8.7 Hz, Ar-H), 7.83 (dd, 2H, J_1 = 8.4 Hz, J_2 = 2.1 Hz, Ar-H), 7.88 (s, 1H, Ar-H) 7.96 (s, 1H, Ar-H). ^{13}C NMR ($CDCl_3$, δ): 14.07, 22.63, 25.92, 25.96, 28.98, 29.11, 29.22, 29.31, 29.30, 29.32, 31.76, 69.03, 69.31, 84.42, 100.53, 111.84, 114.41, 114.47, 115.58, 118.31, 120.90, 122.40, 124.49, 131.02, 133.66, 134.93, 136.22, 148.64, 152.56, 154.02, 164.53. HRMS-FAB (*m*/*z*): $[M]^+$ calcd for $C_{70}H_{84}N_2O_8$ 1081.6228, found 1081.6256.

2,4-Bis[4-(3,4-didodecyloxyphenylcarbonyloxy)phenylethynyl]-1,3-dicyanobenzene (NC-mTCP-mp12): ^{1}H NMR ($CDCl_3$): 0.87-0.91 (m, 12H, CH_3O), 1.27-1.51 (m, 72 H, $(CH_2)_9$), 1.84-1.90 (m, 8H, CH_2), 4.06-4.11 (m, 8H, CH_2O), 6.87 (d, 2H, J = 8.4 Hz, Ar-H), 7.21 (d, 4H, J = 9.0 Hz, Ar-H), 7.58 (d, 2H, J = 1.2 Hz, Ar-H), 7.63 (d, 4H, J = 9.0 Hz), 7.74 (dd, 2H, J_1 = 8.4 Hz, J_2 = 1.5 Hz, Ar-H), 7.79 (s, 1H, Ar-H), 7.87 (s, 1H, Ar-H). ^{13}C NMR ($CDCl_3$):14.07, 22.64, 25.92, 25.95, 28.97, 29.10, 29.32, 29.36, 29.57, 29.61, 29.65, 31.87, 68.98, 69.26, 84.43, 100.48, 111.80, 114.38, 114.44, 115.54, 118.26, 120.88, 122.36, 124.45, 130.93, 133.62, 134.84, 136.16, 148.63, 152.54, 154.00, 164.44.. HRMS calcd for $C_{86}H_{116}N_2O_8$ (M+H) 1305.8810, found (FAB): 1305.8754.

1,4-Bis[4-(3,4-dipentyloxyphenylcarbonyloxy)phenylethynyl]-benzene (H-pTCP-mp6): ^{1}H NMR ($CDCl_3$, δ): 0.91 (t, *J* = 6.2 Hz, 6H, CH_3), 0.92 (t, *J* = 6.2 Hz, 6H, CH_3), 1.25-1.40 (m, 16H, CH_2), 1.55 (m, 8H, CH_2), 1.91 (m, 8H, CH_2), 4.07 (t, *J* = 6.7 Hz, 4H, OCH_2), 4.09 (t, *J* = 6.7 Hz, 4H, OCH_2), 6.94 (d, *J* = 8.6 Hz, 2H, Ar H), 7.22 (d, *J* = 8.7 Hz, 4H, Ar H), 7.53 (s, 4H, Ar H), 7.60 (d, *J* = 8.7 Hz, 4H, Ar H), 7.66 (d, *J* = 2.0 Hz, 2H, Ar H), 7.82 (dd, *J* = 8.6, 2.0 Hz, 2H, Ar H). HRMS-MALDI (*m*/*z*): $[M+Na]^+$ calcd for $C_{60}H_{70}O_8Na$ 941.4963, found 941.4988.

1,4-Bis[4-(3,4-didecyloxyphenylcarbonyloxy)phenylethynyl]-benzene (H-pTCP-mp10): ^{1}H NMR ($CDCl_3$, δ): 0.91 (t, *J* = 6.2 Hz, 6H, CH_3), 0.92 (t, *J* = 6.2 Hz, 6H, CH_3), 1.25-1.45 (m, 32H, CH_2), 1.55 (m, 8H, CH_2), 1.91 (m, 8H, CH_2), 4.07 (t, *J* = 6.7 Hz, 4H, OCH_2), 4.09 (t, *J* = 6.7 Hz, 4H, OCH_2), 6.94 (d, *J* = 8.6 Hz, 2H, Ar H), 7.22 (d, *J* = 8.7 Hz, 4H, Ar H), 7.53 (s, 4H, Ar H), 7.60 (d, *J* = 8.7 Hz, 4H, Ar H), 7.66 (d, *J* = 2.0 Hz,

2H, Ar H), 7.82 (dd, J = 8.6, 2.0 Hz, 2H, Ar H). HRMS-MALDI (m/z): $[M+H]^+$ calcd for $C_{76}H_{102}O_8$ 1143.7647, found 1143.7654.

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