Supporting Information

Design, Synthesis, and Characterization of Ladder-Type Molecules and Polymers. Air-Stable, Solution-Processable *n*-Channel and Ambipolar Semiconductors for Thin-Film Transistors via Experiment and Theory.

Hakan Usta, Chad Risko, Zhiming Wang, Hui Huang, Murat K. Deliomeroglu, Aleksandr Zhukhovitskiy, Antonio Facchetti, and Tobin J. Marks**

Department of Chemistry and the Materials Research Center, Northwestern University, 2145 Sheridan Road, Evanston, Illinois, 60208.

Experimental

Materials and Methods.

All reagents were purchased from commercial sources and used without further purification unless otherwise noted. Anhydrous THF was distilled from Na/benzophenone. Conventional Schlenk techniques were used, and reactions were carried out under N_2 unless otherwise noted. Optical spectra were recorded on a Cary Model 1 UV-Vis spectrophotometer. Fluorescence measurements were recorded on a Photon Technology International model QM-2 fluorimeter. NMR spectra were recorded on a Varian Unity Plus 500 spectrometer (^{1}H, 500 MHz; ^{13}C, 125 MHz). GPC analyses of polymer samples were performed on a Waters Alliance GPCV 2000 (3 columns, Waters Styragel HT 6E, HT 4, HT 2; operation temperature, 150 ^{o}C; mobile phase, 1,2,4-trichlorobenzene or THF at room temperature; flow rate, 1 mL/min) and are reported relative to polystyrene standards purchased from Aldrich. Electrospray mass spectrometry was performed with a Thermo Finnegan model LCQ Advantage mass spectrometer. Electrochemistry was performed on a C3 Cell Stand electrochemical station equipped with BAS Epsilon software (Bioanalytical Systems, Inc., Lafayette, IN).

Synthesis and Characterization.

Synthesis of 1,4-Di-*n*-dodecylbenzene (13). The reagent *n*-dodecylmagnesium bromide (235 mL, 235.0 mmol, 1.0 M in diethyl ether) was added dropwise, over 15 min, to a solution of 1,4-dichlorobenzene (15.00 g, 102.0 mmol) and (dppp)Cl_2Ni (70 mg) in dry ether (70 mL) at 0 °C. The cooling bath was then removed and the reaction mixture allowed to warm to room temperature (~30 min). The mixture was then refluxed for 1 day, cooled to 0 °C, and carefully quenched with water (10 mL), followed by 2 M HCl (70 mL). The aqueous layer was extracted with ether (2×50 mL), the combined organic layer was then washed with water (30 mL), dried over $MgSO_4$, and filtered. The solvent was then removed from the filtrate *in vacuo*, and the crude product was dried at 100 °C under high vacuum (~20 mTorr) for 10 h to remove *n*-octane and *n*-octylbromide. The product was obtained as a white solid (35.00 g, 83 % yield). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 6H), 1.30 (m, 36H), 1.61 (m, 4H), 2.59 (t, 4H), 7.10 (s, 4H) ppm.

Synthesis of 2,5-Dibromo-1,4-di-*n*-dodecylbenzene (14). Bromine (2.5 mL, 44.2 mmol) was added rapidly to a stirring solution of **5** (5.00 g, 12.1 mmol) and iodine (15 mg) in dichloromethane (15 mL) at 0 °C and stirred under rigorous exclusion of light for 2 days at room temperature. Next, 20 % aq. KOH solution (20 mL) was added until the dark color of the solution disappeared. The dichloromethane was then removed under reduced pressure and the precipitate was washed with ethanol. The crude material was purified by recrystallization from ethanol to afford the pure product as a white solid (5.20 g, 75 % yield). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 6H), 1.33 (m, 36H), 1.59 (m, 4H), 2.67 (t, 4H), 7.37 (s, 2H) ppm.

Synthesis of 2,2''-Ethoxycarbonyl-2',5'-didodecyl-[1,1';4',1'']terphenyl (15). The reagent 2,5-dibromo-1,4-di-*n*-dodecylbenzene, (0.7 g, 1.22 mmol), 2-(ethoxycarbonyl)phenylboronic acid pinacol ester (1.01 g, 3.66 mmol) and $Pd(PPh_3)_4$ (150 mg) was dissolved in dry toluene (25 mL) under nitrogen. Deaerated K_2CO_3 solution (2.2 g dissolved in 2.5 mL of water and 5.0 mL of ethanol) and 0.4 mL of Aliquat 336 solution was added under nitrogen and the reaction mixture was refluxed for 1 day. The organic phase was filtered through a plug of Celite and evaporated to dryness to give a semi-solid crude product. The crude product was purified by column chromatography (silica gel, chloroform:hexane (7:3) as eluent), to give the pure product as a colorless oil (0.70 g, 45 % yield). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 6H), 0.97 (t,6H), 1.13-1.45 (m, 40H), 2.37 (m, 4H), 4.08 (q, 4H), 6.95 (d, 2H), 7.30 (t, 2H), 7.42 (q, 2H), 7.53 (q, 2H), 7.97(d, 2H) ppm. ^{13}C NMR ($CDCl_3$): δ 13.8, 14.3, 14.4, 22.9, 29.5, 29.6, 29.6, 29.7, 29.8, 30.9, 30.9, 31.8, 32.2, 32.9, 32.9, 60.8 (d), 127.1 (d), 129.3 (d), 130.2 (d), 131.0 (d), 131.5, 131.6 (d), 136.8 (d), 140.4 (d), 142.8 (d), 168.4 (d) ppm.; Anal. calcd. for ($C_{48}H_{70}O_4$): C, 81.08; H, 9.92, O, 9.00. Found: C, 81.39; H, 9.64, O, 9.30.

Synthesis of 5,11-didodecylindeno[1,2-b]fluorene-6,12-dione (1). The diester **15** (1.0 g, 1.39 mmol) was added to 61 mL of 80 % H_2SO_4 (prepared from 6.1 mL of H_2O and 54.9 mL of concentrated H_2SO_4), and the mixture was heated with stirring at 120 °C for 2 h, during which time the colorless oil turned dark red. The reaction mixture was next poured into ice and filtered to collect pale orange crystals. The crude product was suspended in a stirring sodium hydrogen carbonate solution, then in water, filtered again, and dried at 70 °C under vacuum overnight to give the diketone product as a pale orange solid (0.80 g, 93 % yield). ^{1}H NMR ($CDCl_3$): δ 0.89 (t, 6H), 1.27-1.69 (m, 40H), 3.43 (broad s, 4H), 7.32 (t, 2H), 7.53 (t, 2H), 7.67 (t, 4H). ^{13}C NMR ($CDCl_3$): δ 14.4, 22.9, 27.2, 29.6, 29.8, 29.9, 30.0, 30.1, 30.3, 32.2, 123.6, 124.2, 128.8, 134.9, 135.2, 135.9, 138.4, 143.2, 145.1, 194.6 ppm.; m.p: 123-124 °C; MS(EI) m/z (M^+): calcd for $C_{44}H_{58}O_2$, 618.9; found, 618.4. Anal. calcd. for ($C_{44}H_{58}O_2$): C, 85.38; H, 9.45. Found: C, 85.23; H, 9.46.

Synthesis of 2,2'-(5,11-didodecylindeno[1,2-b]fluorene-6,12-diylidene) dimalononitrile (2). Indenofluorenedione **1** (0.100 g, 0.16 mmol) and malononitrile (0.106 g, 1.60 mmol) were dissolved in dry chlorobenzene (20 mL) under nitrogen, and 0.26 mL of pyridine and 0.17 mL of $TiCl_4$ were added. The resulting mixture was refluxed overnight under nitrogen during which time the color of the solution became dark green. Upon cooling, 20 mL of water was added and the product extracted with chloroform. The organic phase was washed with water, dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified by column chromatography on silica with chloroform as the eluent, affording the dimalononitrile product as a dark green solid (0.063 g, 55 %). ^{1}H NMR ($CDCl_3$): δ 0.87 (t, 6H), 1.27-1.59 (m, 40H), 3.20 (broad s, 2H), 3.60 (broad s, 2H), 7.54 (d, 2H, J = 8.5 Hz), 7.60 (m, 4H), 7.70 (d, 2H, J = 8.5 Hz), 8.41 (d, 2H) ppm. ^{13}C NMR ($CDCl_3$): δ 14.3, 22.9, 23.9, 29.6, 29.9, 30.3, 31.8, 32.1, 40.7, 119.9, 121.2, 123.0, 127.3, 132.6, 132.8, 132.9, 134.2, 134.3, 135.9, 139.4, 140.3, 141.4, 142.5, 150.2, 168.4 ppm; m.p: 134-135 °C; MS(EI) m/z (M^+): calcd for $C_{50}H_{58}N_4$, 715.0; found, 714.6. Anal. calcd. for ($C_{50}H_{58}N_4$): C, 83.99; H, 8.18; N, 7.84. Found: C, 83.69; H, 8.10; N, 7.65; IR (KBr): ν = 2220 cm^{-1} (C≡N). No carbonyl vibrational feature is observed.

Synthesis of 2,8-dibromo-5,11-didodecylindeno[1,2-b]fluorene-6,12-dione (M1). Indenofluorenedione **1** (0.50 g, 0.80 mmol) was dissolved in 45 mL of $CHCl_3$. Next, 20.0 mL of bromine and 0.5 g of $FeCl_3$ as a catalyst was added. The reaction mixture was stirred at room temperature for 1 day under rigorous exclusion of light. Next, 20 % aq. KOH solution (20 mL) was added until the dark color of the solution disappeared. Chloroform was then removed under reduced pressure, and the resulting precipitate was collected by filtration and washed with water. The crude material was purified by column chromatography (silica gel, chloroform:hexane (7:3) as the eluent) giving the pure product as an orange solid (0.53 g, 85 % yield). ^{1}H NMR ($CDCl_3$): δ 0.89 (t, 6H), 1.27-1.59 (m, 40H), 3.29 (broad s, 4H), 7.43 (d, 2H), 7.61 (d, 2H), 7.69 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 14.4, 22.9, 27.2, 29.6, 29.7, 29.8, 29.9, 29.9, 30.2, 32.0, 32.2, 123.1, 124.9, 127.5, 135.7, 136.3, 137.7, 138.6, 141.5, 144.7, 192.9 ppm.; m.p: 122-123 °C; MS(ESI) m/z (M^+): calcd for $C_{44}H_{56}Br_2O_2$, 776.7; found, 775.9. Anal. calcd. for ($C_{44}H_{56}Br_2O_2$): C, 68.04; H, 7.27. Found: C, 67.74; H, 6.92.

Synthesis of 2,2'-(2,8-dibromo-5,11-didodecylindeno[1,2-b]fluorene-6,12-diylidene) dimalononitrile (M2). Dibromotetraphenylenedione, **M1** (0.100 g, 0.128 mmol) and malononitrile (0.085 g, 1.28 mmol) were dissolved in dry chlorobenzene (20 mL) under nitogen, and 0.21 mL of pyridine and 0.14 mL of $TiCl_4$ were added. The resulting mixture was refluxed overnight under nitrogen during which time the color of the solution became dark green. Upon cooling, 20 mL of water was added and the product extracted with chloroform. The organic phase was washed with water, dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified by column chromatography on silica with chloroform as the eluent, affording the dimalononitrile product as a dark green solid (0.060 g, 50 %). ^{1}H NMR ($CDCl_3$): δ 0.87 (t, 6H), 1.27-1.59 (m, 40H), 3.20 (broad s, 2H), 3.60 (broad s, 2H), 7.57 (d, 2H, J = 8.5 Hz), 7.72 (d, 2H, J = 8.5 Hz), 8.43 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$): δ 14.3, 22.9, 23.9, 29.6, 29.9, 30.3, 31.8, 32.1, 40.7, 119.9, 121.2, 123.0, 127.3, 132.6, 132.8, 132.9, 134.2, 134.3, 135.9, 139.4, 140.4, 141.9, 142.9, 151.2, 168.4 ppm; m.p: 136-137 °C; MS(EI) m/z (M^+): calcd for $C_{50}H_{56}Br_2N_4$, 872.8; found, 873.0. Anal. calcd. for ($C_{50}H_{56}Br_2N_4$): C, 68.80; H, 6.47; N, 6.42. Found: C, 68.67; H, 6.48; N, 6.27; IR (KBr): ν = 2220 cm^{-1} (C≡N). No carbonyl vibrational feature is observed.

Synthesis of 2,8-bisthiophene-5,11-didodecylindeno[1,2-b]fluorene-6,12-dione (3). The reagent indenofluorenedione (**M1**) (0.200 g, 0.257 mmol), 2-tributylstannylthiophene (0.231 g, 0.618 mmol), and $Pd(PPh_3)_4$ (20 mg) in anhydrous toluene (8.0 mL) were heated at 110 °C under nitrogen overnight. The reaction mixture was cooled down to RT and evaporated to dryness. The crude product was purified by column chromatography on silica gel with $CHCl_3$/hexanes (7:3) as the eluent to give final product as a purple solid (121 mg, 60.0 % yield). ^{1}H NMR ($CDCl_3$): δ 0.88-1.66 (m, 46H), 3.41 (b s, 4H), 7.05 (d, 2H, J = 3.0 Hz), 7.11(t, 2H), 7.39 (d, 2H, J = 3.0 Hz), 7.62(d, 2H, J = 7.5 Hz), 7.74 (d, 2H, J = 7.5 Hz), 7.88 (s, 2H) ppm. m.p: 205-206 °C; MS(MALDI-TOF) m/z (M^+): calcd. for $C_{52}H_{62}O_2S_2$, 783.2; found, 783.0. Anal. calcd. for $C_{52}H_{62}O_2S_2$: C, 79.75; H, 7.98. Found: C, 79.60; H, 7.82.

Synthesis of 2,2'-(2,8- bisthiophene -5,11-didodecylindeno[1,2-b]fluorene-6,12-diylidene) dimalononitrile (4). The reagent indenofluorenedione (**M2**) (0.224 g, 0.257 mmol), 2-tributylstannylthiophene (0.231 g, 0.618 mmol), and $Pd(PPh_3)_4$ (20 mg) in anhydrous toluene (8.0 mL) were heated at 110 °C under nitrogen overnight. The reaction mixture was cooled down to RT and evaporated to dryness. The crude product was purified by column chromatography on silica gel with $CHCl_3$/hexanes (7:3) as the eluent to give final product as a purple solid (136 mg, 60.0 % yield). ^{1}H NMR ($CDCl_3$): δ 0.88-1.66 (m, 46H), 3.40 (b s, 4H), 7.10 (t, 2H), 7.29 (d, 2H, J = 3.0 Hz), 7.33 (d, 2H, J = 3.0 Hz), 7.62(d, 2H, J = 7.5 Hz), 7.74 (d, 2H, J = 7.5 Hz), 8.30 (s, 2H) ppm. m.p: 225-226 °C; MS(MALDI-TOF) m/z (M^+): calcd. for $C_{58}H_{62}N_4S_2$, 879.3; found, 879.0. Anal. calcd. for $C_{58}H_{62}N_4S_2$: C, 79.23; H, 7.11. Found: C, 79.10; H, 7.20.

Synthesis of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-9,9-didodecylfluorene (16). *t*-BuLi (43.9 ml, 74.7 mmol, 1.7 M in pentane) was added over 30 min. to a stirring solution of 2,7-dibromo-9,9-didodecylfluorene (12.02 g, 18.2 mmol) in dry THF (90.0 mL) under nitrogen at -78 °C. The reaction mixture was stirred for another 30 min. at -78 °C, and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (22.2 mL, 108.6 mmol) was added dropwise to the resulting mixture and stirred overnight at room temperature. The solution was then quenched with water, the THF was evaporated, and the product was extracted with 200 mL ether. The organic phase was washed with water, dried over $MgSO_4$, filtered, and the filtrate evaporated to dryness to give the title compound as a white solid (12.36 g, 90 % yield). ^{1}H NMR ($CDCl_3$): δ 0.55 (t, 4H), 0.88 (m, 6H), 1.01 (m, 6H), 1.15-1.28 (m, 14H), 1.4 (s, 24 H), 2.01(t, 4H), 7.72 (2H, d, *J* =7.5 Hz), 7.75 (2H, s), 7.82 (2H, d, *J* =7.5 Hz) ppm.

Synthesis of Dimethyl 6,6'-(9,9-didodecylfluorene-2,7-diyl)bis(3-bromobenzoate) (17). A mixture of **16** (3.120 g, 4.14 mmol), methyl 2-iodo-benzoate (2.547 g, 9.52 mmol), and Aliquat 336 (0.800 g) was degassed 3 times with N_2 before 30.0 mL of dry toluene was added. Tetrakis(triphenylphosphine)palladium (0.50 g) and 1M aqueous sodium carbonate solution (1.80 g in 17 mL of water) which was already deaerated for 2 h was added under N_2. The mixture was stirred vigorously and heated at reflux for 3 days. The mixture was then allowed to cool to room temperature, and the organic phase was passed through a plug of Celite to remove palladium black, and the filtrates concentrated to dryness *in vacuo*. The product was purified by column chromatography (silica gel) with ethyl acetate: hexane (1:9) as the eluent, affording the pure product as a colorless oil (3.13 g, 96 % yield). ^{1}H NMR ($CDCl_3$): δ 0.83 (t, 6H), 1.10 (s, 24H), 1.95 (m, 4H), 3.61 (s, 6H), 7.22 (s, 2H), 7.28 (d, 2H, *J* = 7.5 Hz), 7.33 (d, 2H, *J* = 7.5 Hz), 7.67 (d, 2H, *J* = 7.5 Hz), 7.74 (m, 4H, *J* = 7.5 Hz), 7.97 (d, 2H, *J* = 7.5 Hz) ppm.

Synthesis of 6,6'-didodecylbisindenofluorene-12,15-dione (5). Diester **17** (0.288 g, 0.367 mmol) was added to 13 mL of 80 % H_2SO_4 (prepared from 1.3 mL of H_2O and 11.7 mL of concentrated H_2SO_4) and the mixture was heated with stirring at 165 °C for 3 h, during which time the white solid turned dark red. The reaction mixture was next poured into ice and filtered to the collect dark colored crystals. The collected product was then extracted into dichloromethane and was washed with sodium hydrogen carbonate solution and dried over

$MgSO_4$. After filtration and solvent evaporation, the crude product was purified by column chromatography on silica with chloroform: hexane (7:3) as the eluent, affording the product diketone as a yellow solid (0.181 g, 70 % yield). ^{1}H NMR ($CDCl_3$): δ 0.66 (br s, 6H), 0.85-1.24 (m, 40H), 2.08 (t, 4H), 7.45 (s, 2H), 7.47 (d, 2H, J = 8.0 Hz), 7.64 (d, 2H, J = 8.0 Hz), 7.74 (m, 4H, J = 7.5 Hz), 7.80 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$): δ 14.3, 22.8, 24.1, 29.4, 30.2, 31.9, 40.5, 56.6, 115.2, 116.6, 121.9, 123.1, 127.8, 134.0, 136.8, 137.3, 141.7, 143.4, 144.0, 159.0, 191.9 ppm; m.p: 138-139 °C; MS(EI) m/z (M^+): calcd for $C_{51}H_{62}O_2$, 707.0; found, 707.3. Anal. calcd. for ($C_{51}H_{62}O_2$): C, 86.64; H, 8.84. Found: C, 86.44; H, 8.70. IR (KBr): ν = 1722cm^{-1} (C=O).

Synthesis of 2,2'-(6,6'-didodecylbisindenofluorene-12,15-diylidene) dimalononitrile (6). Tetraphenylenedione, **5** (0.424 g, 0.60 mmol) and malononitrile (0.570 g, 8.66 mmol) were dissolved in dry DMSO (14 mL) and 0.5 mL of piperidine was added. The resulting mixture was stirred at 110 °C for 5 h during which time the color of the solution became dark red. Upon cooling, the product precipitated from the solution as brown solid which was collected by filtration, washed with isopropanol, and dried in vacuo. The crude product was purified by column chromatography on silica with chloroform as the eluent, affording the dimalononitrile product as a purple solid (0.337 g, 70 % yield). ^{1}H NMR ($CDCl_3$): δ 0.64 (br s, 6H), 0.85-1.27 (m, 40H), 2.12 (t, 4H), 7.46 (s, 2H), 7.50 (d, 2H, J = 8.0 Hz), 7.67 (t, 2H, J = 8.0 Hz),), 7.87 (t, 2H, J = 8.0 Hz), 8.52 (d, 2H, J = 8.0 Hz), 8.83 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$): δ 14.2, 22.4, 24.1, 29.6, 30.1, 30.2, 31.7, 40.3, 56.7, 113.2, 112.2, 115.5, 117.9, 122.1, 123.2, 130.0, 133.9, 136.7, 137.5, 140.2, 141.0, 141.9, 157.9, 159.7 ppm; MS(EI) m/z (M^+): calcd for $C_{57}H_{62}N_4$, 803.1; found, 803.3; m.p: 251-252 °C; Anal. calcd. for ($C_{57}H_{62}N_4$): C, 85.24; H, 7.78; N, 6.98. Found: C, 85.49; H, 7.80; N, 6.88. IR (KBr): ν = 2220 cm^{-1} (C≡N). No carbonyl vibrational feature is observed.

Synthesis of 2,10-dibromo-6,6'-didodecylbisindenofluorene-12,15-dione (M3). To a solution of **5** (0.271 g, 0.383 mmol) in $CHCl_3$/HOAc (5:1) (V_t = 24.0 mL) was added bromine (Br_2; 123.0 mg, 0.766 mmol) in one portion. The mixture was stirred at room temperature for 10 h and water (50 mL) was then added. The mixture was next extracted with chloroform (3×50 mL). The combined organic phase was washed with water (50 mL), KOH solution, and dried over $MgSO_4$. After filtration, the chloroform was removed, and the product was purified by silica gel column chromatography using chloroform as the eluent to give an orange solid (0.265 g, 80 % yield). ^{1}H NMR ($CDCl_3$): δ 0.65 (br s, 6H), 0.85-1.25 (m, 40H), 2.09 (t, 4H), 7.45 (s, 2H), 7.51 (d, 2H, J = 8.0 Hz), 7.67 (d, 2H, J = 8.0 Hz), 7.73 (s, 2H) ppm, 7.83 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$): δ 14.3, 22.8, 24.1, 29.4, 30.2, 31.9, 40.5, 56.6, 115.2, 116.6, 121.9, 123.1, 127.8, 134.0, 136.8, 137.3, 142.7, 142.4, 144.0, 161.0, 190.9 ppm; m.p: 136-137 °C; MS(ESI) m/z (M^+): calcd for $C_{51}H_{60}Br_2O_2$, 864.8; found, 864.6. Anal. calcd. for ($C_{51}H_{60}Br_2O_2$): C, 70.83; H, 6.99. Found: C, 70.74; H, 6.92.

Synthesis of 2,2'-(2,10-Dibromo-6,6'-didodecylbisindenofluorene-12,15-diylidene) dimalononitrile (M4). Dibromotetraphenylenedione, **M3** (0.520 g, 0.60 mmol) and malononitrile (0.570 g, 8.66 mmol) were dissolved in dry DMSO (14 mL) and 0.5 mL of piperidine was added. The resulting mixture was stirred at 110 °C for 5 h during which time the color of the solution became dark red. Upon cooling, the product precipitated from the solution as brown solid which was collected by filtration, washed with isopropanol, and dried in vacuo. The crude product was purified by column chromatography on silica with chloroform as the eluent, affording the dimalononitrile product as a purple solid (0.37 g, 65 % yield). ^{1}H NMR ($CDCl_3$): δ 0.67 (br s, 6H), 0.85-1.27 (m, 40H), 2.08 (t, 4H), 7.50 (s, 2H), 7.51 (d, 2H, J = 8.0 Hz), 7.67 (d, 2H, J = 8.0 Hz), 8.52 (s, 2H), 8.83 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$): δ 14.2, 22.4, 24.1, 29.6, 30.1, 30.2, 31.7, 40.3, 56.7, 113.2, 113.2, 115.5, 118.9, 122.1, 123.2, 130.0, 133.9, 136.7, 137.5, 141.2, 141.4, 141.9, 158.9, 159.7 ppm; MS(EI) m/z (M^+): calcd for $C_{57}H_{60}Br_2N_4$, 960.9; found, 960.3; m.p: 252-253 °C; Anal. calcd. for ($C_{57}H_{60}Br_2N_4$): C, 71.25; H, 6.29; N, 5.83. Found: C, 71.49; H, 6.42; N, 5.59. IR (KBr): ν = 2222 cm^{-1} (C≡N). No carbonyl vibrational feature is observed.

Synthesis of 2,10-dithiophene-6,6'-didodecylbisindenofluorene-12,15-dione (7). The reagent Dibromotetraphenylenedione **M3** (0.464g, 0.531 mmol), 2-tributylstannylthiophene (0.476 g, 1.275 mmol), and $Pd(PPh_3)_4$ (50 mg) in anhydrous toluene (20.0 mL) were heated at 110 °C under nitrogen overnight. The reaction mixture was cooled down to RT and evaporated to dryness. The crude product was purified by column chromatography on silica gel with $CHCl_3$/hexanes (7:3) as the eluent to give final product as a yellow solid (0.302 g, 65% yield). ^{1}H NMR ($CDCl_3$): δ 0.88-1.66 (m, 46H), 2.13 (t, 4H), 7.15 (t, 2H), 7.36 (d, 2H, J = 4.5 Hz), 7.44 (d, 2H, J = 3.0 Hz), 7.50 (s, 2H), 7.61 (d, 2H, J = 7.5 Hz), 7.78(d, 2H, J = 7.5 Hz), 7.97 (s, 2H), 8.03 (s, 2H) ppm. m.p: 180-181 °C; MS(MALDI-TOF) m/z (M^+): calcd. for $C_{59}H_{66}O_2S_2$, 871.3; found, 871.9. Anal. calcd. for $C_{59}H_{66}O_2S_2$: C, 81.33; H, 7.64. Found: C, 81.15; H, 7.76.

Synthesis of 2,2'-(2,10-Dithiophene-6,6'-didodecylbisindenofluorene-12,15-diylidene) dimalononitrile (8). The reagent dibromotetraphenylenedimalononitrile **M4** (180 mg, 0.187 mmol), 2-tributylstannylthiophene (168 mg, 0.449 mmol), and $Pd(PPh_3)_4$ (15 mg) in anhydrous toluene (8.0 mL) were heated at 110 °C under nitrogen overnight. The reaction mixture was cooled down to RT and evaporated to dryness. The crude product was purified by column chromatography on silica gel with $CHCl_3$/hexanes (7:3) as the eluent to give final product as a yellow solid (0.114 g, 70 % yield). ^{1}H NMR ($CDCl_3$): δ 0.88-1.66 (m, 46H), 2.10 (t, 4H), 7.13 (t,2H) 7.35 (d, 2H, J = 4.5 Hz), 7.44 (d, 2H, J = 3.5 Hz), 7.51 (s, 2H), 7.75(d, 2H, J = 8.0 Hz), 8.69 (s, 2H), 8.78 (s, 2H) ppm. m.p: 280-281 °C; MS(MALDI-TOF) m/z (M^+): calcd. for $C_{65}H_{66}N_4S_2$, 967.4; found, 967.8. Anal. calcd. for $C_{65}H_{66}N_4S_2$: C, 80.70; H, 6.88. Found: C, 80.50; H, 6.90.

Synthesis of 4,4''-dibromo-2,2''-Methoxycarbonyl-[1,1';4',1'']terphenyl (18). A mixture of 1,4-benzenediboronic acid bis(pinacol) ester (4.40 g, 13.33 mmol), methyl 2-iodo-5-bromobenzoate (9.95 g, 29.18 mmol), and Aliquat 336 (1.60 mL) was degassed 3 times with N_2 before 90.0 mL of dry toluene was added. Tetrakis(triphenylphosphine)palladium (1.50 g, 1.30 mmol) and 1M aqueous sodium carbonate solution (5.73 g in 54.0 mL of water) which was already deaerated for 2 h were then added under N_2. The mixture was stirred vigorously and heated at reflux for 2 days. The mixture was then allowed to cool to room temperature, the organic phase was passed through a plug of Celite to remove palladium black, and the filtrate was concentrated to dryness *in vacuo*. The product was purified by column chromatography (silica gel) with chloroform as the eluent, affording the pure product as a white solid (6.00 g, 89% yield). ^{1}H NMR ($CDCl_3$): δ 3.72 (s, 6H), 7.32(d, 2H, J = 8.0 Hz), 7.33 (s, 4H), 7.69(d, 2H, J = 8.0 Hz), 8.01 (s, 2H) ppm.

Synthesis of 2,8-dibromo-indeno[1,2-b]fluorene-6,12-dione (19). The diester **18** (0.50 g, 0.99 mmol) was added to 50.0 mL of 80 % H_2SO_4 (prepared from 10.0 mL of H_2O and 40.0 mL of concentrated (99.99 %) H_2SO_4), and the mixture was heated with stirring at 120 °C for 10 h, during which time the white solid turned dark red. The reaction mixture was next poured into ice and filtered to the collect the red crystals. The collected product was then washed with sodium hydrogen carbonate solution and water. The product was collected by filtration (0.40 g, 92%). The crude product was used for the next step without any further purification. m.p: > 300 °C.

MS(MALDI-TOF) m/z (M^+): calcd for $C_{20}H_8O_2Br_2$, 440.1; found, 440.7. Anal. calcd. for $C_{20}H_8O_2Br_2$: C, 54.58; H, 1.83 Found: C, 54.12; H, 1.72.

Synthesis of 2,8-di-3-dodecylthiophene-indeno[1,2-b]fluorene-6,12-dione (9). The reagent 2-tributylstannyl-3-dodecylthiophene (**22**) (0.320 g, 0.591 mmol), **19** (0.120 g, 0.273 mmol), and $Pd(PPh_3)_2Cl_2$ (30.0 mg, 0.043 mmol) in anhydrous DMF (12.0 mL) were heated at 125 °C under nitrogen overnight. The reaction mixture was cooled down to RT and evaporated to dryness. The crude product was purified by column chromatography on silica gel with $CHCl_3$/hexanes (7:3) as the eluent to give final product as a purple solid (70.0 mg, 35% yield). ^1H NMR ($CDCl_3$): δ 0.88-1.66 (m, 46H), 2.70 (t, 4H), 7.02 (d, 2H, J = 4.5 Hz), 7.29 (d, 2H, J = 4.5 Hz), 7.59 (d, 2H, J = 7.5 Hz), 7.61(d, 2H, J = 7.5 Hz), 7.74 (s, 2H), 7.81 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$): δ 14.4, 22.96, 29.0, 29.6, 29.7, 29.8, 29.9, 30.0, 31.2, 32.2, 116.3, 121.0, 124.7, 125.5, 130.1, 134.6, 136.1, 136.4, 136.8, 139.8, 140.0, 142.3, 145.9, 192.8 ppm.; m.p: 152-153 °C; MS(MALDI-TOF) m/z (M^+): calcd. for $C_{52}H_{62}O_2S_2$, 783.2; found, 783.0. Anal. calcd. for $C_{52}H_{62}O_2S_2$: C, 79.75; H, 7.98. Found: C, 79.50; H, 7.89.

Synthesis of 2,8-di-3-dodecylthiophene-indeno[1,2-b]fluorene-6,12-dimalononitrile (10). A mixture of **9** (50.0 mg, 0.064 mmol) and malononitrile (60.0 mg, 0.91 mmol) was dissolved in dry chlorobenzene (5.0 mL) under nitrogen, and pyridine (0.100 mL, 1.24 mmol) and $TiCl_4$ (0.070 mL, 0.64 mmol) were added. The resulting mixture was stirred at 110 °C for 5 h under nitrogen during which time the color of the solution became dark green. Upon cooling, 20.0 mL of water was added and the product extracted with chloroform. The organic phase was washed with water, dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was then purified by column chromatography on silica gel with chloroform as the eluent, affording the dimalononitrile product as a dark green solid (22.5 mg, 40%). ^1H NMR ($CDCl_3$): δ 0.88-1.67 (m, 46H), 2.74 (t, 4H), 7.05 (d, 2H, J = 4.0 Hz), 7.33 (d, 2H, J = 4.0 Hz), 7.66 (d, 2H, J = 7.5 Hz), 7.71 (d, 2H, J = 7.5 Hz), 8.52 (s, 2H), 8.60 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$): δ 14.4, 22.9, 29.2, 29.6, 29.7, 29.8, 29.9, 31.1, 32.2, 112.9, 113.3, 118.4, 121.5, 125.1, 127.8, 130.3, 134.7, 134.7, 135.8, 136.1, 137.3, 139.6, 139.7, 140.5, 143.4, 159.8 ppm.; m.p: 232-233 °C; MS(EI) m/z (M^+): calcd for $C_{58}H_{62}S_2N_4$, 879.3; found, 879.5. Anal. calcd. for $C_{58}H_{62}S_2N_4$: C, 79.23; H, 7.11; N, 6.37. Found: C, 79.07; H, 7.15; N, 6.35; IR (KBr): ν = 2225 cm^{-1} (C≡N). No carbonyl peak is observed.

Synthesis of 2,8-di-5-bromo-3-dodecylthiophene-indeno[1,2-b]fluorene-6,12-dione (M5). To a solution of **9** (0.30 g, 0.383 mmol) in $CHCl_3$/HOAc (5:1) (V_t = 24.0 mL) was added bromine (Br_2; 123.0 mg, 0.766 mmol) in one portion. The mixture was stirred at room temperature for 10 h and water (50 mL) was then added. The mixture was next extracted with chloroform (3×50 mL). The combined organic phase was washed with water (50 mL), KOH solution, and dried over $MgSO_4$. After filtration, the chloroform was removed, and the product was purified by silica gel column chromatography using chloroform as the eluent to give a purple solid (0.340 g, 95% yield). ^{1}H NMR ($CDCl_3$): δ 0.87-1.61 (m, 46H), 2.70 (t, 4H), 6.96 (s, 2H), 7.56 (d, 2H, J = 7.5 Hz), 7.61(d, 2H, J = 7.5 Hz), 7.69 (s, 2H), 7.84 (s, 2H) ppm. MS(EI) m/z (M^+): calcd for $C_{52}H_{60}Br_2O_2S_2$, 941.0; found, 941.1. Anal. calcd. for ($C_{52}H_{60}Br_2O_2S_2$): C, 66.37; H, 6.43. Found: C, 66.34; H, 6.43.

Note that the syntheses of the compounds 23 and 25 follow similar procedures to those employed for 24 and 26, respectively.

Synthesis of 2, 8-di-5-bromo-3-dodecylthiophene-indeno[1,2-b]fluorene-6,12-dimalononitrile (M6). A mixture of **M5** (230.0 mg, 0.245 mmol) and malononitrile (230.0 mg, 3.48 mmol) was dissolved in dry chlorobenzene (20.0 mL) under nitrogen, and pyridine (0.40 mL, 4.94 mmol) and $TiCl_4$ (0.30 mL, 2.73 mmol) were added. The resulting mixture was stirred at 110 °C for 5 h under nitrogen during which time the color of the solution became dark green. Upon cooling, 20.0 mL of water was added and the product was extracted with chloroform. The organic phase was washed with water, dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified by column chromatography on silicagel with chloroform as the eluent, affording the product as a dark green solid (120.0 mg, 48% yield). ^{1}H NMR ($CDCl_3$): δ 0.89-1.62 (m, 46H), 2.66 (t, 4H), 7.00 (s, 2H), 7.59 (d, 2H, J = 7.5 Hz), 7.71 (d, 2H, J = 7.5 Hz), 8.47 (s, 2H), 8.62 (s, 2H) ppm. MS(EI) m/z (M^+): calcd for $C_{58}H_{60}Br_2S_2N_4$, 1037.1; found, 1037.4. Anal. calcd. for $C_{58}H_{60}Br_2S_2N_4$: C, 67.17; H, 5.83; N, 5.40. Found: C, 66.76; H, 5.82; N, 5.18; IR (KBr): ν = 2225 cm^{-1} (C≡N). No carbonyl peak is observed.

Synthesis of 2-bromo-3-dodecylthiophene (21). To a solution of 3-dodecylthiophene (5.00 g, 19.8 mmol) in $CHCl_3$/HOAc (1:1) (V_t = 20.0 mL) at 0 °C was added NBS (3.52 g, 19.8 mmol) in portions over a period of 45 min. The reaction mixture was stirred for 1 h at 0 °C, and overnight at room temperature. The reaction mixture was then poured into water (50.0 mL) and extracted with chloroform (3×50.0 mL). The combined organic phase was washed with water

(50.0 mL), NaOH solution, and dried over $MgSO_4$. After filtration through Celite, the chloroform was removed *in vacuo*, and the product was obtained as a colorless oil (6.05 g, 93% yield). ^{1}H NMR ($CDCl_3$): δ 0.84-1.54 (m, 23H), 2.53 (t, 2H), 6.76 (d, 1H, J = 4.5 Hz), 7.15 (d, 1H, J = 4.5 Hz).

Synthesis of 2-tributylstannyl-3-dodecylthiophene (22). To magnesium turnings (0.160 g, 6.6 mmol) in anhydrous THF (8.0 mL), heated to maintain a mild reflux, was added dropwise 2-bromo-3-dodecylthiophene (**21**; 2.00 g, 6.0 mmol). The reaction mixture was refluxed for 2 h before being transferred to a solution of tributyltin chloride (1.80 mL, 6.41 mmol) in 10.0 mL of anhydrous THF at –78 °C. The mixture was allowed to warm to room temperature and stirred overnight before being poured into water. The aqueous layer was extracted with hexanes, and the combined organic phase was washed with brine and dried over magnesium sulfate. After filtration, the solvent was removed in vacuo to yield the product as a yellow liquid (3.10 g, 95% yield). ^{1}H NMR ($CDCl_3$): δ 0.90-1.63 (m, 50H), 2.62 (t, 2H), 7.12 (d, 1H, J = 4.5 Hz), 7.55 (d, 1H, J = 4.5 Hz).

Synthesis of 4,4'-didodecyl-2,2'-bithiophene (24). *n*-BuLi (7.04 mL, 2.5 M in hexanes) was added dropwise to a stirring solution of 3-dodecylthiophene (4.000 g, 15.8 mmol) and N,N,N',N'-tetramethylethylenediamine (2.75 mL, 17.6 mmol) in 80.0 mL of dry ether at -78 °C. The solution was then warmed to room temperature and refluxed for 1 h. After cooling down to -78 °C, $CuCl_2$ (2.640 g, 19.6 mmol) was added in one portion. The reaction mixture was stirred overnight, during which time the temperature rose to room temperature. The reaction mixture was quenched with water and extracted with chloroform, washed with water, dried over $MgSO_4$, filtered, and the filtrate was evaporated to dryness. The crude product was purified by column chromatography on silica gel with hexanes as the eluent to yield a mixture of 4,4'- and 3,3'-didodecylthiophene (~15 % of the mixture by ^{1}H NMR). Recrystallization from an acetone:ethanol (1:1) mixture gave the pure product as a white solid (2.200 g, 55% yield). ^{1}H NMR ($CDCl_3$): δ 0.91 (t, 6H), 1.33 (m, 36H), 1.66 (q, 4H), 2.60 (t, 4H), 6.80 (s, 2H), 7.01 (s, 2H) ppm.

Synthesis of 4,4'-didocecyl-5,5'-trimethylstannyl-2,2'-bithiophene (26). To a solution of **24** (1.00 g, 2.0 mmol) in 30.0 mL of THF was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (2.0 mL, 5.0 mmol) at –78 °C. The solution was stirred at –78 °C for 30 min and at room temperature for another 1 h. The solution was then cooled to –78 °C, and a 1.0 M solution of trimethyltin chloride in THF (6.0 mL, 6.0 mmol) was added in one portion. The solution was warmed to room temperature and 30.0 mL of water and 30.0 mL of ethyl acetate were added. The organic layer was washed twice with 30 mL of water and dried over magnesium sulfate. After filtration, the solvent was removed from the filtrate *in vacuo* to yield the product as a yellow oil (0.60 g, 72% yield). ^{1}H NMR ($CDCl_3$, d): 0.40 (s, 18H), 0.95 (t, 6H), 1.33 (br, 36H), 1.60 (q, 4H), 2.61 (t, 4H), 7.18 (s, 2H).

Synthesis of 4,4'-didocecyl-5-bromo-2,2'-bithiophene (27). To a solution of 4,4'-didodecyl-2,2'-bithiophene (**24**) (0.100 g, 0.199 mmol) in $CHCl_3$/HOAc (1:1) (V_t = 2.0 mL) at 0 °C was added NBS (35.7 mg, 0.199 mmol) in portions over a period of 45 min. The reaction mixture was stirred for 1 h at 0 °C, and overnight at room temperature. The reaction mixture was then poured into water (50.0 mL) and extracted with chloroform (3×50.0 mL). The combined organic phase was washed with water (50.0 mL), NaOH solution, and dried over $MgSO_4$. After filtration through Celite, the chloroform was removed *in vacuo*, and the product was obtained as a colorless oil after column chromatography using hexanes as the eluent (98.0 mg, 85% yield). ^{1}H NMR ($CDCl_3$): δ 0.84-1.54 (m, 46H), 2.57 (m, 4H), 6.81 (s, 1H), 6.84 (s, 1H), 6.94 (s, 1H).

Synthesis of 4,4'-didocecyl-5-trimethylstannyl-2,2'-bithiophene (28). To a solution of **27** (100 mg, 0.172 mmol) in 4.0 mL of THF was added dropwise a 2.5 M solution of *n*-butyllithium in hexane (0.076 mL, 0.189 mmol) at –78 °C. The solution was stirred at –78 °C for 1 h. 1.0 M solution of trimethyltin chloride in THF (0.20 mL, 0.20 mmol) was then added in one portion. The solution was warmed to room temperature and 10.0 mL of water and 10.0 mL of diethylether were added. The organic layer was washed twice with 20 mL of water and dried over magnesium sulfate. After filtration, the solvent was removed from the filtrate *in vacuo* to yield the product as a yellow oil (0.103 g, 90% yield). ^{1}H NMR ($CDCl_3$): δ 0.84-1.64 (m, 46H), 2.58 (m, 4H), 6.77 (s, 1H), 6.99 (s, 1H), 7.13 (s, 1H).

Synthesis of 2,8-di-4,4'-didodecyl-2,2'-bithiophene-indeno[1,2-b]fluorene-6,12-dione (11). The reagent 5-trimethylstannyl-4,4'-didodecyl-2,2'-bithiophene (**28**) (0.457 g, 0.686 mmol), **19** (0.140 g, 0.312 mmol), and $Pd(PPh_3)_2Cl_2$ (45.0 mg, 0.064 mmol) in anhydrous DMF (25.0 mL) were heated at 125 °C under nitrogen overnight. The reaction mixture was cooled down to RT and evaporated to dryness. The crude product was purified by column chromatography on silica gel with $CHCl_3$/hexanes (4:6) as the eluent to give final product as a green solid (100.0 mg, 25% yield). ^{1}H NMR ($CDCl_3$): δ 0.88-1.66 (m, 92H), 2.60 (t, 4H), 2.67(t, 4H), 6.83 (s, 2H), 7.03

(s, 2H), 7.05 (d, 2H), 7.61(q, 4H), 7.77 (s, 2H), 7.83 (s, 2H) ppm. m.p: 96-97 °C; MS(MALDI-TOF) m/z (M^+): calcd. for $C_{84}H_{114}O_2S_4$, 1284.1; found, 1284.0. Anal. calcd. for $C_{84}H_{114}O_2S_4$: C, 78.57; H,8.95. Found: C, 78.20; H, 8.60.

Synthesis of 2,8-di-4,4'-didodecyl-2,2'-bithiophene-indeno[1,2-b]fluorene-6,12-dimalononitrile (12). A mixture of **11** (40.0 mg, 0.031 mmol) and malononitrile (35.0 mg, 0.53 mmol) was dissolved in dry chlorobenzene (3.0 mL) under nitrogen, and pyridine (0.06 mL) and $TiCl_4$ (0.04 mL, 0.64 mmol) were added. The resulting mixture was stirred at 110 °C for 5 h under nitrogen during which time the color of the solution became dark green. Upon cooling, 20.0 mL of water was added and the product extracted with chloroform. The organic phase was washed with water, dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was then purified by column chromatography on silica gel with chloroform as the eluent, affording the dimalononitrile product as a dark green solid (25 mg, 58%). ^{1}H NMR ($CDCl_3$): δ 0.88-1.66 (m, 92H), 2.58 (t, 4H), 2.71(t, 4H), 6.83 (s, 2H), 7.05 (s, 2H), 7.06 (d, 2H), 7.63 (d, 2H, J = 8.0 Hz), 7.68(d, 2H, J = 8.0 Hz), 8.51 (s, 2H), 8.56 (s, 2H) ppm. m.p: 96-97 °C; MS(MALDI-TOF) m/z (M^+): calcd. for $C_{90}H_{114}N_4S_4$, 1380.1; found, 1380.0. Anal. calcd. for $C_{90}H_{114}N_4S_4$: C, 78.32; H,8.33. Found: C, 78.55; H, 8.49.

Synthesis indenofluorenedicyanovinylene homopolymer (P2). $Ni(COD)_2$ (211 mg, 0.746 mmol), 2,2'-bipyridyl (116.5 mg, 0.746 mmol), and 1,5-cyclooctadiene (COD, 0.091 mL, 0.746 mmol) were mixed in dry DMF (5 mL) and dry toluene (1.6 mL) in a glove box. The purple solution was heated to 80°C for 30 minutes. Dibromo-functionalized indenofluorenedicyanovinylene M2 (271 mg, 0.311 mmol) in 6 mL of dry toluene was added. The solution was stirred under argon for 1 day, and bromobenzene (1.0 mL) was added. The reaction mixture was poured in methanol and filtered. The resulting solids were subjected to Soxhlet extraction for 2 days in acetone, dissolved in THF, precipitated in methanol (3 times), and filtered to give the tetraphenylenedimalononitrile homopolymer as a yellow solid (125 mg, 46 %). ^{1}H NMR ($CDCl_3$): δ 0.78-1.67 (m, 46H), 3.70 (br s, 4H), 7.45 (br s, 2H), 7.72 (br s, 2H), 8.45 (br s, 2H) ppm. Anal. calcd.: C, 84.22; H, 7.92; Found: C, 84.52; H, 7.50. GPC (HT in TCB): M_n = 9,137 g mol^{-1}, M_w = 13,250 g mol^{-1}, and D = 1.45 (against PS standard).

Synthesis indenofluorenedionebithiophene copolymer (P3). 2,5-Bis(tributylstannyl)thiophene (0.095 g, 0.128mmol), 2,8-Dibromo-5,11-didodecylindeno[1,2-b]fluorene-6,12-dione **M1** (0.100 g, 0.128 mmol) and $Pd(PPh_3)_4$ (10 mg) in anhydrous toluene

(5 mL) were heated at 110 °C with stirring under nitrogen for two days. The reaction mixture was allowed to cool to room temperature, and was poured into methanol (300 mL). The resulting solids were subjected to Soxhlet extraction for two days in acetone, then dissolved in chlorobenzene by Soxhlet extraction, precipitated in methanol (2 times), and filtered to give the tetraphenylenedimalononitrile copolymer as a black solid (78.0 mg, 40 %). ^{1}H NMR ($CDCl_3$): δ 0.78-1.67 (m, 46H), 3.40(b, 4H), 7.39 (br m, 4H), 7.45 (br s, 2H), 7.63 (br s, 2H), 7.88 (br s, 2H) ppm. Anal. calcd.: C, 79.95; H, 7.74; Found: C, 79.65; H, 7.50. GPC (HT in TCB): M_n = 9400 g mol^{-1}, M_w = 11,200 g mol^{-1}, and D = 1.20 (against PS standard).

Synthesis indenofluorenedicyanovinylenebithiophene copolymer (P4). 2,5-Bis(tributylstannyl)thiophene (0.095 g, 0.128mmol), 2,8-Dibromo-5,11-didodecylindeno[1,2-b]fluorene-6,12-dicyanovinylene **M2** (0.112 g, 0.128 mmol) and $Pd(PPh_3)_4$ (10 mg) in anhydrous toluene (5 mL) were heated at 110 °C with stirring under nitrogen for two days. The reaction mixture was allowed to cool to room temperature, and was poured into methanol (300 mL). The resulting solids were subjected to Soxhlet extraction for two days in acetone, then dissolved in chlorobenzene by Soxhlet extraction, precipitated in methanol (2 times), and filtered to give the tetraphenylenedimalononitrile copolymer as a black solid (55.0 mg, 42 %). ^{1}H NMR ($CDCl_3$): δ 0.78-1.65 (m, 46H), 3.42(b, 4H), 7.40 (br m, 4H), 7.60 (br s, 2H), 7.70 (br s, 2H), 8.20 (br s, 2H) ppm. Anal. calcd.: C, 79.40; H, 6.90; Found: C, 79.68; H, 6.50. GPC (HT in TCB): M_n = 9467 g mol^{-1}, M_w = 14,200 g mol^{-1}, and D = 1.50 (against PS standard).

Synthesis of tetraphenylenedimalononitrile homopolymer (P6). $Ni(COD)_2$ (211 mg, 0.746 mmol), 2,2'-bipyridyl (116.5 mg, 0.746 mmol), and 1,5-cyclooctadiene (COD, 0.091 mL, 0.746 mmol) were mixed in dry DMF (5 mL) and dry toluene (1.6 mL) in a glove box. The purple solution was heated to 80°C for 30 minutes. Dibromotetraphenylenedimalononitrile M4 (300 mg, 0.311 mmol) in 6 mL of dry toluene was added. The solution was stirred under argon for 1 day, and bromobenzene (1.0 mL) was added. The reaction mixture was poured in methanol and filtered. The resulting solids were subjected to Soxhlet extraction for 2 days in acetone, dissolved in THF, precipitated in methanol (3 times), and filtered to give the tetraphenylenedimalononitrile homopolymer as a dark solid (125 mg, 50 %). ^{1}H NMR ($CDCl_3$): δ 0.75-1.24 (br m, 46H), 2.12 (br s, 4H), 7.50 (br m, 4H), 7.67 (br s, 2H), 8.55 (br s, 2H), 8.79 (br s, 2H) ppm. Anal. calcd.: C, 85.45; H, 7.55; N, 7.00. Found: C, 83.85; H, 7.63; N, 6.77. GPC (HT in TCB): Mn = 8,037 g mol^{-1}, Mw = 12,455 g mol^{-1}, and D = 1.55 (against PS standard).

Synthesis of tetraphenylenedionebithiophene copolymer (P7). 2,5-Bis(tributylstannyl)bithiophene (0.143 g, 0.193 mmol), dibromotetraphenylenedione **(**M3) (0.145 g, 0.193 mmol), and $Pd(PPh_3)_4$ (25 mg) in anhydrous toluene (10 mL) were heated at 110 °C with stirring under nitrogen for two days. The reaction mixture was allowed to cool to room temperature, and was poured into methanol (300 mL). The resulting solids were subjected to Soxhlet extraction for two days in acetone, then dissolved in chlorobenzene by Soxhlet extraction,, precipitated in methanol (2 times), and filtered to give the tetraphenylenedimalononitrile copolymer as a black solid (100 mg, 35 %). ^{1}H NMR ($CDCl_3$): δ 0.70-1.65 (br m, 46H), 2.67 (br, 4H), 7.00 (br, 4H), 7.45 (br, 2H), 7.65 (br, 4H), 7.82 (br, 4H) ppm. Anal. calcd.: C, 81.51; H, 7.43; Found: C, 81.20; H, 7.10. GPC (HT in TCB): M_n = 6200 g mol^{-1}, M_w = 9,400 g mol^{-1}, and D = 1.52 (against PS standard).

Synthesis of tetraphenylenedimalononitrilebithiophene copolymer (P8). 2,5-Bis(tributylstannyl)bithiophene (0.45 mmol, 0.33 g), dibromotetraphenylenedimalononitrile (M4) (0.45 mmol, 0.43 g), and $Pd(PPh_3)_2Cl_2$ (40 mg) in anhydrous toluene (10 mL) were heated at 80 °C with stirring under nitrogen for two days. The reaction mixture was allowed to cool to room temperature, and was poured into methanol (300 mL). The resulting solids were subjected to Soxhlet extraction for two days in acetone, then dissolved in chloroform, precipitated in methanol (3 times), and filtered to give the tetraphenylenedimalononitrile copolymer as a black solid (210 mg, 50 %). ^{1}H NMR ($CDCl_3$): δ 0.74-1.23 (br m, 46H), 2.12 (br s, 4H), 7.15 (br, 4H), 7.48 (br m, 4H), 7.67 (br s, 2H), 8.51 (br s, 2H), 8.72 (br s, 2H) ppm. Anal. calcd.: C, 80.87; H, 6.67; N, 5.80. Found: C, 81.35; H, 6.70; N, 5.60**.** GPC (HT in TCB): M_n = 8,100 g mol^{-1}, M_w = 10,500 g mol^{-1}, and D = 1.30 (against PS standard).

Synthesis of 2,8-di-4,3'-didodecyl-2,2'-bithiophene-indeno[1,2-b]fluorene-6,12-dione copolymer (P12). A 20 mL microwave glass vial was charged with a stirrer bar, 2,8-di-5-bromo-3-dodecylthiophene-indeno[1,2-b]fluorene-6,12-dione (M5) (91.0 mg, 0.096 mmol), 4,4'-didocecyl-5,5'-trimethylstannyl-2,2'-bithiophene (26; 80.0 mg, 0.096 mmol), tris(dibenzylideneacetone)dipalladium(0) (2.0 mg, 0.002 mmol), tri-(o-tolylphosphine) (2.5 mg, 0.008 mmol) and chlorobenzene (2.0 mL). The glass vial was purged with nitrogen, securely sealed, and heated in a microwave reactor. A temperature ramp was used such that the vial was heated with stirring at 140 °C for 120 seconds, then at 160 °C for 120 sec, and finally at 180 °C for 900 seconds.The power was 300 W during the reaction. After cooling to 50 °C, the crude product was precipitated with methanol. The precipitate was collected by filtration, dissolved in THF, filtered through a 0.45 μm filter, and precipitated with methanol again. This dissolution/precipitation procedure was repeated three more times. The final collected polymer was subjected to Soxhlet extraction (with acetone and methanol) and dried overnight at 100 °C to give 65.0 mg product as a dark-colored solid (55 % yield). ^{1}H NMR ($CDCl_3$): δ 0.89-1.60 (br m, 92H), 2.55 (br, 4H), 2.62 (br, 4H), 7.05 (br, 2H), 7.40 (br, 2H), 7.60 (br, 4H), 7.75 (br, 4H) ppm. Anal. calcd.: C, 78.69; H, 8.81; Found: C, 78.77; H, 8.47. GPC (HT in TCB) M_w = 18,300 g/mol , M_n = 7,320 g/mol, PDI = 2.50 (against PS standard).

Synthesis of 2,8-di-4,3'-didodecyl-2,2'-bithiophene-indeno[1,2-b]fluorene-6,12-dimalononitrile copolymer (P13). A 20 mL microwave glass vial was charged with a stirrer bar, 2,8-di-5-bromo-3-dodecylthiophene-indeno[1,2-b]fluorene-6,12-dimalononitrile (M6) (100.0 mg, 0.096 mmol), 4,4'-didocecyl-5,5'-trimethylstannyl-2,2'-bithiophene (26; 80.0 mg, 0.096 mmol), tris(dibenzylideneacetone)dipalladium(0) (2.0 mg, 0.002 mmol), tri-(o-tolylphosphine) (2.5 mg, 0.008 mmol) and chlorobenzene (2.0 mL). The glass vial was purged with nitrogen, securely sealed, and heated in a microwave reactor. A temperature ramp was used such that the vial was heated with stirring at 140 °C for 120 seconds, then at 160 °C for 120 sec, and finally at 180 °C for 900 seconds.The power was 300 W during the reaction. After cooling to 50 °C, the crude product was precipitated with methanol. The precipitate was collected by filtration, dissolved in THF, filtered through a 0.45 μm filter, and precipitated with methanol again. This dissolution/precipitation procedure was repeated three more times. The final collected polymer was subjected to Soxhlet extraction (with acetone and methanol) and dried overnight at 100 °C to give 79.6 mg product as a dark-colored solid (60% yield). ^{1}H NMR ($CDCl_3$): δ 0.88-1.62 (br m, 92H), 2.57 (br, 4H), 2.74 (br, 4H), 7.00 (br, 2H), 7.42 (br, 2H), 7.65 (br, 4H), 8.55 (br, 4H) ppm. Anal. calcd.: C, 78.43; H, 8.20; N, 4.06. Found: C, 78.87; H, 8.42; N, 3.65. GPC (HT in TCB) M_w = 23,273 g/mol , M_n =6,685 g/mol, PDI = 3.48 (against PS standard).

Note that the synthesis of the polymer P14 follows a similar procedure to that employed for P13.

Single-Crystal Structure Determination.

Single crystals of 7, M2, and M4 were grown by slow evaporation of chloroform solution and slow diffusion of methanol into chloroform solution, respectively. X-ray single crystal diffraction measurements were performed on a Bruker CCD area detector instrument with graphite-monochromated MoKα (0.71073 Å) radiation. The data were collected at 153(2)K, and the structures were solved by direct methods and expanded using Fourier techniques.

Device Fabrication and Thin Film Characterization.

Prime grade n-doped silicon wafers (100) having a 300 nm thermally grown oxide layer (Process Specialties Inc.) were used as device substrates. These were rinsed with water, methanol, and acetone before film deposition. Trimethylsilyl functionalization of the Si/SiO_2 surface was carried out by exposing the silicon wafers to hexamethyldisilazane (HMDS) vapor at room temperature in a closed container under nitrogen overnight. Polymer films were spin-coated from 5 mg/mL solutions in THF or 1,2,4-trichlorobenzene and then annealed under nitrogen at various temperatures from 100 ^{o}C to 300 ^{o}C for 30 min. Spin-coated films were 25-30 nm-thick as assessed by profilometry. For FET device fabrication, top-contact electrodes (500 Å) were deposited by evaporating gold (pressure < 10^{-5} Torr); channel dimensions were 25/50/100 μm (L) by 0.2/1.0/2.5/5.0 mm (W). The capacitance of the insulator is 1 x 10^{-8} F/cm^2 for 300 nm SiO_2. TFT device measurements were carried out in a customized vacuum probe station (8 x 10^{-5} Torr) or in air. Coaxial and/or triaxial shielding was incorporated into Signaton probes to minimize the noise level. TFT characterization was performed with a Keithley 6430 subfemtoammeter and a Keithley 2400 source meter, operated by a locally written Labview program and GPIB communication. Thin films were analyzed by wide-angle X-ray film diffractometry (WAXRD) on a Rikagu ATX-G instrument with Cu Kα radiation and a monochromator using standard θ-2θ techniques. All θ-2θ scans were calibrated in situ with the reflection of the Si (100) substrates.

Electrochemistry.

Cyclic voltammetry was performed in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate ($Bu_4N^+PF_6^-$) in dry acetonitrile. Platinum wire electrodes were used as both working and counter electrodes, and Ag wire was used as the pseudo-reference electrode. A ferrocene/ferrocenium redox couple was used as an internal standard and potentials obtained in reference to a silver electrode were converted to the saturated calomel electrode (SCE) scale.

Thin films of the polymers were coated onto the Pt working electrode by drop casting from 0.5 wt % – 1.0 wt % THF solutions and dried under vacuum at 80 °C for 2 h.

Computational Methodology.

Geometry optimizations for the gas-phase neutral, radical-anion, and radical-cation states of **1** - **12** were carried out at the density functional theory level using the B3LYP functionals[1-3] and a 6-31G** split valence plus double polarization basis set. To ease the computational cost, all alkyl chains in the molecular structures were substituted by methyl groups. Excitation energies of the low-lying excited states have been calculated at the time-dependent DFT (TDDFT) level. All calculations were carried out with QChem (version 3.1).

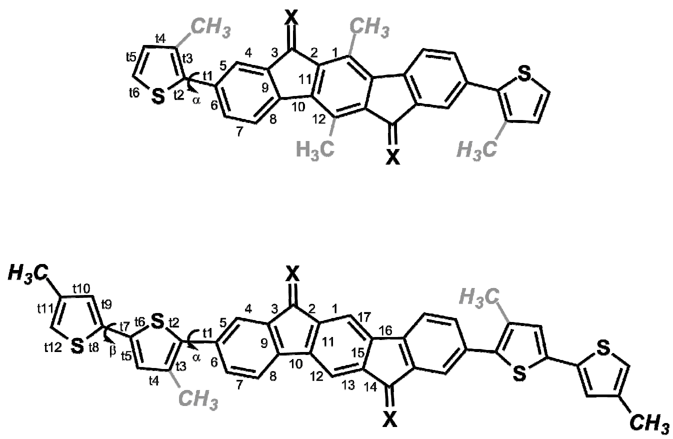

Figure S1. Bond length and number scheme used in Tables S1 – S4.

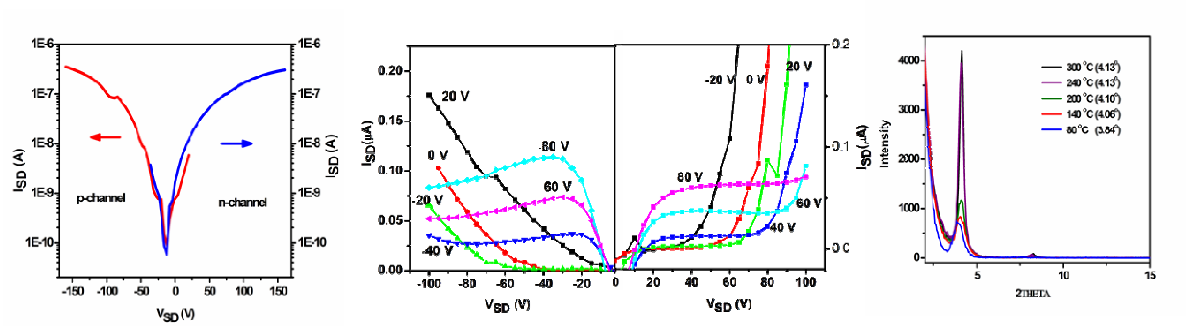

Figure S2. OFET plots and XRD scans of thin-films fabricated with **P13/P14** in ambient.

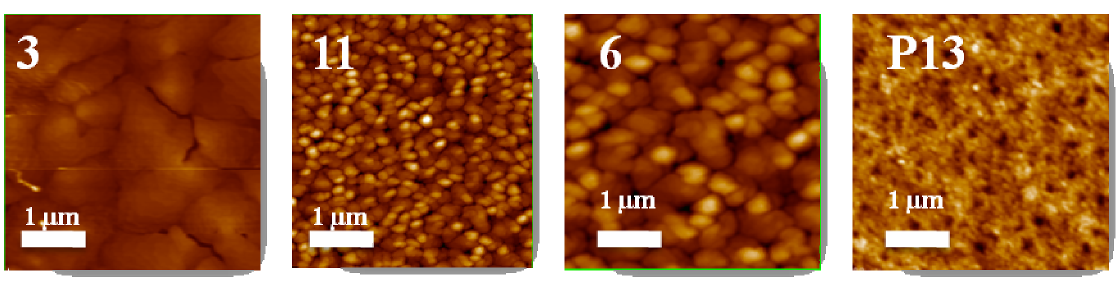

Figure S3. AFM Images of compounds **3**, **6**, **11**, and **P13**.

Table S1. Selected bond lengths and angles of **1** – **3** in the neutral, radical-anion, and radical-cation states as determined at the B3LYP/6-31G** level. See Figure S1 for bond and angle numbering scheme.

	1					**2**					**3**				
	neutral	**anion**	**Δ(a-n)**	**cation**	**Δ(c-n)**	**neutral**	**anion**	**Δ(a-n)**	**cation**	**Δ(c-n)**	**neutral**	**anion**	**Δ(a-n)**	**cation**	**Δ(c-n)**
bond (Å)															
1	1.402	1.412	0.010	1.385	-0.017	1.411	1.423	0.012	1.392	-0.019	1.402	1.408	0.006	1.391	-0.011
2	1.505	1.466	-0.039	1.508	0.003	1.478	1.445	-0.033	1.478	0.000	1.507	1.472	-0.035	1.508	0.001
3	1.486	1.481	-0.005	1.484	-0.002	1.476	1.472	-0.004	1.473	-0.003	1.492	1.486	-0.006	1.492	0.000
4	1.386	1.392	0.006	1.381	-0.005	1.395	1.399	0.004	1.389	-0.006	1.381	1.385	0.004	1.372	-0.009
5	1.398	1.395	-0.003	1.402	0.004	1.399	1.396	-0.003	1.402	0.003	1.411	1.407	-0.004	1.421	0.010
6	1.396	1.402	0.006	1.406	0.010	1.393	1.397	0.004	1.404	0.011	1.408	1.415	0.007	1.422	0.014
7	1.403	1.399	-0.004	1.393	-0.010	1.401	1.398	-0.003	1.390	-0.011	1.399	1.394	-0.005	1.387	-0.012
8	1.396	1.403	0.007	1.410	0.014	1.393	1.398	0.005	1.408	0.015	1.395	1.403	0.008	1.406	0.011
9	1.409	1.420	0.011	1.425	0.016	1.420	1.425	0.005	1.435	0.015	1.408	1.421	0.013	1.419	0.011
10	1.498	1.479	-0.019	1.463	-0.035	1.478	1.467	-0.011	1.443	-0.035	1.485	1.464	-0.021	1.459	-0.026
11	1.406	1.448	0.042	1.444	0.038	1.423	1.442	0.019	1.446	0.023	1.416	1.443	0.027	1.430	0.014
12	1.421	1.398	-0.023	1.430	0.009	1.403	1.394	-0.009	1.429	0.026	1.406	1.399	-0.007	1.420	0.014
t1											1.466	1.464	-0.002	1.444	-0.022
t2											1.755	1.760	0.005	1.762	0.007
t3											1.378	1.379	0.001	1.394	0.016
t4											1.423	1.425	0.002	1.408	-0.015
t5											1.368	1.367	-0.001	1.379	0.011
t6											1.732	1.737	0.005	1.722	-0.010
angle (°)															
α											27.3	26.9	-0.4	1.0	-26.3

Table S2. Selected bond lengths and angles of **4** – **6** in the neutral, radical-anion, and radical-cation states as determined at the B3LYP/6-31G** level. See Figure S1 for bond and angle numbering scheme.

	4					**5**					**6**				
	neutral	**anion**	**Δ(a-n)**	**cation**	**Δ(c-n)**	**neutral**	**anion**	**Δ(a-n)**	**cation**	**Δ(c-n)**	**neutral**	**anion**	**Δ(a-n)**	**cation**	**Δ(c-n)**
bond (Å)															
1	1.410	1.421	0.011	1.399	-0.011	1.386	1.391	0.005	1.371	-0.015	1.397	1.404	0.007	1.382	-0.015
2	1.480	1.447	-0.033	1.479	-0.001	1.499	1.485	-0.014	1.504	0.005	1.480	1.468	-0.012	1.482	0.002
3	1.478	1.474	-0.004	1.478	0.000	1.498	1.484	-0.014	1.494	-0.004	1.480	1.467	-0.013	1.476	-0.004
4	1.389	1.394	0.005	1.380	-0.009	1.386	1.393	0.007	1.384	-0.002	1.397	1.403	0.006	1.394	-0.003
5	1.411	1.407	-0.004	1.421	0.010	1.401	1.396	-0.005	1.402	0.001	1.400	1.396	-0.004	1.401	0.001
6	1.406	1.408	0.002	1.420	0.014	1.397	1.406	0.009	1.404	0.007	1.396	1.401	0.005	1.403	0.007
7	1.396	1.392	-0.004	1.384	-0.012	1.403	1.398	-0.005	1.396	-0.007	1.400	1.397	-0.003	1.393	-0.007
8	1.394	1.399	0.005	1.406	0.012	1.391	1.398	0.007	1.399	0.008	1.389	1.394	0.005	1.399	0.010
9	1.418	1.424	0.006	1.429	0.011	1.410	1.424	0.014	1.420	0.010	1.417	1.426	0.009	1.427	0.010
10	1.473	1.462	-0.011	1.447	-0.026	1.482	1.462	-0.020	1.459	-0.023	1.468	1.456	-0.012	1.444	-0.024
11	1.423	1.443	0.020	1.438	0.015	1.413	1.428	0.015	1.430	0.017	1.421	1.430	0.009	1.440	0.019
12	1.405	1.396	-0.009	1.419	0.014	1.394	1.399	0.005	1.405	0.011	1.392	1.394	0.002	1.404	0.012
13						1.396	1.391	-0.005	1.385	-0.011	1.393	1.390	-0.003	1.381	-0.012
14						1.527	1.530	0.003	1.525	-0.002	1.526	1.527	0.001	1.524	-0.002
15						1.412	1.423	0.011	1.433	0.021	1.410	1.416	0.006	1.430	0.020
16						1.465	1.457	-0.008	1.431	-0.034	1.468	1.468	0.000	1.432	-0.036
17						1.402	1.400	-0.002	1.417	0.015	1.400	1.399	-0.001	1.415	0.015
t1	1.466	1.468	0.002	1.444	-0.022										
t2	1.754	1.756	0.002	1.761	0.007										
t3	1.379	1.378	-0.001	1.395	0.016										
t4	1.423	1.424	0.001	1.407	-0.016										
t5	1.369	1.368	-0.001	1.380	0.011										
t6	1.730	1.734	0.004	1.720	-0.010										
angle (°)															
α	24.2	24.3	0.1	5.4	-18.8										

Table S3. Selected bond lengths and angles of **7** – **9** in the neutral, radical-anion, and radical-cation states as determined at the B3LYP/6-31G** level. See Figure S1 for bond and angle numbering scheme.

	7					**8**					**9**				
	neutral	**anion**	**Δ(a-n)**	**cation**	**Δ(c-n)**	**neutral**	**anion**	**Δ(a-n)**	**cation**	**Δ(c-n)**	**neutral**	**anion**	**Δ(a-n)**	**cation**	**Δ(c-n)**
bond (Å)															
1	1.387	1.389	0.002	1.377	-0.010	1.398	1.404	0.006	1.388	-0.010	1.391	1.400	0.009	1.381	-0.010
2	1.499	1.487	-0.012	1.501	0.002	1.480	1.468	-0.012	1.480	0.000	1.502	1.466	-0.036	1.503	0.001
3	1.501	1.488	-0.013	1.500	-0.001	1.482	1.468	-0.014	1.480	-0.002	1.498	1.493	-0.005	1.499	0.001
4	1.381	1.385	0.004	1.374	-0.007	1.391	1.397	0.006	1.383	-0.008	1.383	1.387	0.004	1.373	-0.010
5	1.414	1.410	-0.004	1.422	0.008	1.413	1.407	-0.006	1.420	0.007	1.414	1.409	-0.005	1.425	0.011
6	1.408	1.418	0.010	1.421	0.013	1.407	1.412	0.005	1.418	0.011	1.409	1.415	0.006	1.424	0.015
7	1.398	1.392	-0.006	1.389	-0.009	1.396	1.392	-0.004	1.386	-0.010	1.400	1.396	-0.004	1.389	-0.011
8	1.390	1.398	0.008	1.399	0.009	1.389	1.393	0.004	1.398	0.009	1.390	1.396	0.006	1.400	0.010
9	1.410	1.425	0.015	1.419	0.009	1.417	1.426	0.009	1.426	0.009	1.410	1.421	0.011	1.420	0.010
10	1.478	1.455	-0.023	1.457	-0.021	1.464	1.451	-0.013	1.444	-0.020	1.479	1.461	-0.018	1.455	-0.024
11	1.413	1.428	0.015	1.425	0.012	1.422	1.431	0.009	1.434	0.012	1.412	1.439	0.027	1.425	0.013
12	1.394	1.402	0.008	1.403	0.009	1.392	1.395	0.003	1.402	0.010	1.396	1.389	-0.007	1.406	0.010
13	1.395	1.388	-0.007	1.387	-0.008	1.392	1.389	-0.003	1.385	-0.007					
14	1.527	1.530	0.003	1.526	-0.001	1.525	1.527	0.002	1.525	0.000					
15	1.413	1.425	0.012	1.425	0.012	1.411	1.417	0.006	1.422	0.011					
16	1.465	1.455	-0.010	1.443	-0.022	1.467	1.467	0.000	1.445	-0.022					
17	1.402	1.402	0.000	1.411	0.009	1.401	1.400	-0.001	1.409	0.008					
t1	1.466	1.462	-0.004	1.446	-0.020	1.466	1.467	0.001	1.448	-0.018	1.471	1.471	0.000	1.447	-0.024
t2	1.756	1.763	0.007	1.761	0.005	1.756	1.760	0.004	1.761	0.005	1.757	1.760	0.003	1.764	0.007
t3	1.377	1.380	0.003	1.390	0.013	1.378	1.378	0.000	1.392	0.014	1.383	1.383	0.000	1.406	0.023
t4	1.424	1.424	0.000	1.411	-0.013	1.423	1.425	0.002	1.411	-0.012	1.432	1.433	0.001	1.417	-0.015
t5	1.368	1.367	-0.001	1.376	0.008	1.368	1.367	-0.001	1.377	0.009	1.365	1.365	0.000	1.375	0.010
t6	1.733	1.738	0.005	1.723	-0.010	1.733	1.736	0.003	1.723	-0.010	1.729	1.733	0.004	1.718	-0.011
angle (°)															
α	25.0	22.7	-2.3	8.0	-17.0	22.1	22.3	0.2	7.8	-14.3	40.9	42.5	1.6	24.3	-16.6

Table S4. Selected bond lengths and angles of **10** – **12** in the neutral, radical-anion, and radical-cation states as determined at the B3LYP/6-31G** level. See Figure S1 for bond and angle numbering scheme.

	10					**11**					**12**				
	neutral	**anion**	**Δ(a-n)**	**cation**	**Δ(c-n)**	**neutral**	**anion**	**Δ(a-n)**	**cation**	**Δ(c-n)**	**neutral**	**anion**	**Δ(a-n)**	**cation**	**Δ(c-n)**
bond (Å)															
1	1.399	1.410	0.011	1.389	-0.010	1.391	1.399	0.008	1.386	-0.005	1.399	1.410	0.011	1.394	-0.005
2	1.481	1.447	-0.034	1.479	-0.002	1.502	1.468	-0.034	1.503	0.001	1.481	1.447	-0.034	1.479	-0.002
3	1.480	1.477	-0.003	1.481	0.001	1.498	1.493	-0.005	1.499	0.001	1.479	1.475	-0.004	1.480	0.001
4	1.393	1.396	0.003	1.382	-0.011	1.382	1.385	0.003	1.375	-0.007	1.391	1.395	0.004	1.384	-0.007
5	1.412	1.409	-0.003	1.425	0.013	1.414	1.410	-0.004	1.423	0.009	1.415	1.409	-0.006	1.421	0.006
6	1.408	1.411	0.003	1.422	0.014	1.410	1.417	0.007	1.420	0.010	1.409	1.411	0.002	1.417	0.008
7	1.397	1.394	-0.003	1.386	-0.011	1.400	1.395	-0.005	1.393	-0.007	1.397	1.394	-0.003	1.391	-0.006
8	1.388	1.392	0.004	1.399	0.011	1.390	1.397	0.007	1.395	0.005	1.388	1.393	0.005	1.394	0.006
9	1.417	1.423	0.006	1.427	0.010	1.410	1.421	0.011	1.415	0.005	1.417	1.423	0.006	1.422	0.005
10	1.464	1.456	-0.008	1.442	-0.022	1.479	1.460	-0.019	1.465	-0.014	1.464	1.456	-0.008	1.452	-0.012
11	1.419	1.437	0.018	1.431	0.012	1.413	1.439	0.026	1.419	0.006	1.420	1.438	0.018	1.426	0.006
12	1.392	1.384	-0.008	1.402	0.010	1.397	1.390	-0.007	1.401	0.004	1.393	1.384	-0.009	1.398	0.005
13						1.391	1.399	0.008	1.386	-0.005	1.399	1.410	0.011	1.394	-0.005
14						1.502	1.468	-0.034	1.503	0.001	1.481	1.447	-0.034	1.479	-0.002
15						1.413	1.439	0.026	1.419	0.006	1.420	1.438	0.018	1.426	0.006
16						1.479	1.459	-0.020	1.465	-0.014	1.464	1.456	-0.008	1.452	-0.012
t1	1.471	1.474	0.003	1.447	-0.024	1.468	1.467	-0.001	1.450	-0.018	1.466	1.471	0.005	1.452	-0.014
t2	1.756	1.757	0.001	1.765	0.009	1.757	1.759	0.002	1.761	0.004	1.758	1.755	-0.003	1.760	0.002
t3	1.384	1.383	-0.001	1.408	0.024	1.384	1.387	0.003	1.407	0.023	1.387	1.385	-0.002	1.408	0.021
t4	1.431	1.433	0.002	1.416	-0.015	1.425	1.424	-0.001	1.407	-0.018	1.424	1.425	0.001	1.406	-0.018
t5	1.366	1.366	0.000	1.376	0.010	1.377	1.377	0.000	1.391	0.014	1.377	1.377	0.000	1.393	0.016
t6	1.728	1.731	0.003	1.717	-0.011	1.749	1.752	0.003	1.746	-0.003	1.746	1.749	0.003	1.745	-0.001
t7						1.449	1.447	-0.002	1.431	-0.018	1.449	1.449	0.000	1.430	-0.019
t8						1.756	1.760	0.004	1.759	0.003	1.755	1.759	0.004	1.759	0.004
t9						1.377	1.377	0.000	1.387	0.010	1.377	1.376	-0.001	1.388	0.011
t10						1.430	1.431	0.001	1.419	-0.011	1.429	1.431	0.002	1.416	-0.013
t11						1.370	1.369	-0.001	1.380	0.010	1.371	1.369	-0.002	1.381	0.010
t12						1.735	1.739	0.004	1.727	-0.008	1.736	1.738	0.002	1.726	-0.010
α(°)	41.3	43.8	2.5	24.1	-17.2	40.3	40.3	0.0	22.5	-17.8	31.8	40.6	8.8	20.9	-10.9
β						18.1	16.7	-1.4	11.3	-6.8	22.4	18.6	-3.8	9.6	-12.8

Table S5. Low-lying excited-state energies (eV and nm), oscillator strengths, and excited-state configurations for **1** as determined at the B3LYP/6-31G** level.

λ/eV	λ/nm	Osc. Str.	Configuration
2.47	502	0.02	HOMO → LUMO (99%)
3.46	358	0.02	HOMO → LUMO+1 (56%); HOMO-2 → LUMO (28%); HOMO-4 → LUMO (7%)
3.51	354	0.05	HOMO-2 → LUMO (54%); HOMO → LUMO+1 (25%); HOMO → LUMO+2 (11%)
4.00	310	0.03	HOMO-5 → LUMO (79%); HOMO-6 → LUMO (10%)
4.36	284	1.16	HOMO → LUMO+2 (81%); HOMO-2 → LUMO (12%)
4.58	271	0.01	HOMO-2 → LUMO+1 (91%)

Table S6. Low-lying excited-state energies (eV and nm), oscillator strengths, and excited-state configurations for **2** as determined at the B3LYP/6-31G** level.

λ/eV	λ/nm	Osc. Str.	Configuration
1.93	643	0.99	HOMO → LUMO (99%)
2.94	422	0.38	HOMO-1 → LUMO (83%); HOMO-3 → LUMO (12%)
3.04	408	0.01	HOMO-2 → LUMO (84%); HOMO → LUMO+1 (7%); HOMO-1 → LUMO+1 (5%)
3.15	394	0.10	HOMO-3 → LUMO (82%); HOMO-1 → LUMO (13%)
3.71	334	0.05	HOMO-1 → LUMO+1 (86%); HOMO-2 → LUMO (6%); HOMO-6 → LUMO (5%)
3.86	321	0.17	HOMO-2 → LUMO+1 (71%); HOMO → LUMO+2 (14%); HOMO-5 → LUMO (10%)
4.08	304	0.40	HOMO-5 → LUMO (61%); HOMO-4 → LUMO+1 (14%); HOMO → LUMO+2 (9%); HOMO-1 → LUMO+2 (8%)
4.12	301	0.16	HOMO-4 → LUMO+1 (68%); HOMO → LUMO+2 (14%); HOMO-5 → LUMO (10%)
4.32	287	0.80	HOMO → LUMO+2 (53%); HOMO-2 → LUMO +1(18%); HOMO-5 → LUMO (12%); HOMO-4 → LUMO+1 (10%)
4.41	281	0.05	HOMO-6 → LUMO (85%); HOMO-1 → LUMO (6%)
4.52	274	0.01	HOMO-1 → LUMO+2 (76%); HOMO → LUMO+3 (14%)

Table S7. Low-lying excited-state energies (eV and nm), oscillator strengths, and excited-state configurations for **3** as determined at the B3LYP/6-31G** level.

λ/eV	λ/nm	Osc. Str.	Configuration
2.11	589	0.11	HOMO → LUMO (98%)
3.38	367	0.32	HOMO → LUMO+2 (60%); HOMO-6 → LUMO (15%); HOMO-4 → LUMO (10%); HOMO-7 → LUMO (7%)
3.43	362	0.02	HOMO-2 → LUMO (89%); HOMO-7 → LUMO (7%)
3.69	336	1.38	HOMO-4 → LUMO (53%); HOMO → LUMO+2 (30%); HOMO-6 → LUMO (9%)
3.72	333	0.33	HOMO-6 → LUMO (37%); HOMO-4 → LUMO (34%); HOMO-7 → LUMO (19%); HOMO → LUMO+2 (6%)
3.79	327	0.11	HOMO-1 → LUMO+1 (92%)
4.04	307	0.07	HOMO-9 → LUMO (85%)

Table S8. Low-lying excited-state energies (eV and nm), oscillator strengths, and excited-state configurations for **4** as determined at the B3LYP/6-31G** level.

λ/eV	λ/nm	Osc. Str.	Configuration
1.48	840	0.04	HOMO → LUMO (98%)
2.78	447	0.01	HOMO-3 → LUMO (73%); HOMO → LUMO (15%); HOMO-5 → LUMO (7%)
2.92	424	0.16	HOMO-2→ LUMO (44%); HOMO-1 → LUMO+1 (23%); HOMO-3 → LUMO (13%); HOMO-7 → LUMO (10%); HOMO → LUMO+2 (6%)
2.98	416	0.06	HOMO-1 → LUMO+1 (69%); HOMO-2 → LUMO (13%); HOMO-7 → LUMO (10%); HOMO-3 → LUMO+2 (5%)
3.16	393	0.43	HOMO-7 → LUMO (40%); HOMO → LUMO+2 (24%); HOM-2O → LUMO (20%); HOMO-3 → LUMO (7%)
3.36	369	1.67	HOMO → LUMO+2 (61%); HOMO-7 → LUMO (35%)
3.84	323	0.06	HOMO-4 → LUMO+1 (97%)
3.99	311	0.29	HOMO-6 → LUMO+1 (80%); HOMO-9 → LUMO (10%)
4.18	297	0.17	HOMO-2 → LUMO+2 (40%); HOMO-9 → LUMO (34%); HOMO-6 → LUMO+1 (10%); HOMO-3 → LUMO+2 (5%)
4.27	290	0.03	HOMO-9→ LUMO (48%); HOMO-2 → LUMO+2 (33%); HOMO → LUMO+4 (12%)
4.46	278	0.20	HOMO-3 → LUMO+2 (70%); HOMO → LUMO+5 (17%)
4.51	275	0.11	HOMO-1 → LUMO+3 (33%); HOMO → LUMO+4 (27%); HOMO-5 → LUMO+2 (22%); HOMO-2 → LUMO+2 (9%)
4.54	273	0.13	HOMO-5 → LUMO+2 (63%); HOMO → LUMO+4 (9%); HOMO-1 → LUMO+3 (7%); HOMO → LUMO+5 (5%)
4.58	271	0.02	HOMO-1 → LUMO+3 (27%); HOMO → LUMO+4 (25%); HOMO → LUMO+5 (21%); HOMO-8 → LUMO+1 (19%)

Table S9. Low-lying excited-state energies (eV and nm), oscillator strengths, and excited-state configurations for **5** as determined at the B3LYP/6-31G** level.

λ/eV	λ/nm	Osc. Str.	Configuration
2.72	455	0.08	HOMO → LUMO (95%)
3.64	340	0.59	HOMO → LUMO+2 (83%); HOMO-5 → LUMO (9%)
3.87	320	0.07	HOMO-1 → LUMO+1 (93%)
4.24	292	1.32	HOMO-5 → LUMO (65%); HOMO-4 → LUMO+1 (15%); HOMO → LUMO+2 (14%)
4.36	285	0.03	HOMO-6 → LUMO (35%); HOMO-5 → LUMO+1 (29%); HOMO-4 → LUMO (24%)
4.46	278	0.11	HOMO-4 → LUMO+1 (38%); HOMO-7 → LUMO (26%); HOMO → LUMO+4 (12%); HOMO-6 → LUMO+1 (9%); HOMO-5 → LUMO (6%)
4.49	276	0.02	HOMO-6 → LUMO (37%); HOMO-5 → LUMO+1 (29%); HOMO-7 → LUMO+1 (12%); HOMO-4 → LUMO (6%); HOMO → LUMO+5 (5%)

Table S10. Low-lying excited-state energies (eV and nm), oscillator strengths, and excited-state configurations for **6** as determined at the B3LYP/6-31G** level.

λ/eV	λ/nm	Osc. Str.	Configuration
2.16	575	0.01	HOMO → LUMO (96%)
3.23	384	0.02	HOMO-3 → LUMO+1 (90%)
3.31	374	0.02	HOMO-1 → LUMO (58%); HOMO-2 → LUMO+1 (33%)
3.47	357	0.24	HOMO → LUMO+2 (39%); HOMO-1 → LUMO+1 (26%); HOMO-2 → LUMO (15%); HOMO-5 → LUMO (11%); HOMO-4 → LUMO+1 (7%)
3.52	353	0.04	HOMO-1 → LUMO+1 (29%); HOMO-5 → LUMO (20%); HOMO-2 → LUMO (19%); HOMO-4 → LUMO+1 (17%); HOMO → LUMO+2 (9%)
3.64	340	0.71	HOMO-2 → LUMO+1 (61%); HOMO-1 → LUMO (33%)
3.86	321	1.49	HOMO → LUMO+2 (46%); HOMO-5 → LUMO (37%); HOMO-4 → LUMO+1 (6%)
3.88	320	0.08	HOMO-4 → LUMO+1 (66%); HOMO-5 → LUMO (29%)
4.23	293	0.08	HOMO-6 → LUMO (80%); HOMO-2 → LUMO+2 (11%)
4.27	291	0.08	HOMO-6 → LUMO+1 (63%); HOMO-1 → LUMO+2 (28%)
4.44	280	0.02	HOMO-2 → LUMO+2 (68%); HOMO → LUMO+4 (17%); HOMO-6 → LUMO (12%)

Table S11. Low-lying excited-state energies (eV and nm), oscillator strengths, and excited-state configurations for **7** as determined at the B3LYP/6-31G** level.

λ/eV	λ/nm	Osc. Str.	Configuration
2.48	501	0.30	HOMO → LUMO (93%)
3.22	385	0.15	HOMO-1 → LUMO+1 (77%); HOMO → LUMO+2 (11%); HOMO → LUMO (5%)
3.29	376	1.33	HOMO → LUMO+2 (82%); HOMO-1 → LUMO+1 (13%)
3.63	342	0.02	HOMO-2 → LUMO (91%)
4.08	304	0.38	HOMO-5 → LUMO (43%); HOMO-5 → LUMO+1 (19%); HOMO-6 → LUMO (15%); HOMO-8 → LUMO (10%)
4.10	302	0.07	HOMO-6 → LUMO (45%); HOMO-5 → LUMO (23%); HOMO-6 → LUMO+1 (18%)
4.11	302	0.05	HOMO-3 → LUMO (33%); HOMO-4 → LUMO+1 (19%); HOMO-7 → LUMO (18%); HOMO-3 → LUMO+1 (11%); HOMO → LUMO+3 (5%)
4.13	300	0.63	HOMO-8 → LUMO (35%); HOMO-7 → LUMO+1 (20%); HOMO → LUMO+3 (7%); HOMO-3 → LUMO (7%); HOMO-6 → LUMO (6%); HOMO-4 → LUMO+1 (6%)
4.14	299	0.10	HOMO-7 → LUMO (40%); HOMO-4 → LUMO+1 (13%); HOMO → LUMO+3 (10%); HOMO-3 → LUMO (8%); HOMO-8 → LUMO (6%); HOMO-6 → LUMO (6%)
4.25	292	0.04	HOMO-2 → LUMO+2 (23%); HOMO-10 → LUMO (19%); HOMO-7 → LUMO+1 (17%); HOMO → LUMO+4 (14%); HOMO → LUMO+5 (6%); HOMO-8 → LUMO (6%)
4.30	289	0.08	HOMO-7 → LUMO+1 (32%); HOMO-1 → LUMO+3 (21%); HOMO-8 → LUMO (18%); HOMO → LUMO+4 (10%)
4.35	285	0.26	HOMO-1 → LUMO+3 (40%); HOMO-2 → LUMO+2 (23%); HOMO-9 → LUMO (7%); HOMO → LUMO+4 (7%)
4.36	285	0.07	HOMO-9 → LUMO (57%); HOMO-8 → LUMO+1 (9%); HOMO → LUMO+6 (6%); HOMO-1 → LUMO+3 (5%)
4.41	281	0.01	HOMO-5 → LUMO+1 (43%); HOMO-5 → LUMO (15%); HOMO-11 → LUMO (13%); HOMO-10 → LUMO (8%)
4.42	281	0.01	HOMO-6 → LUMO+1 (49%); HOMO-6 → LUMO (15%); HOMO-10 → LUMO (9%); HOMO → LUMO+5 (6%); HOMO-1 → LUMO+3 (5%)
4.43	280	0.07	HOMO-6 → LUMO+1 (18%); HOMO-1 → LUMO+3 (13%); HOMO → LUMO+5 (12%); HOMO-10 → LUMO (11%); HOMO-9 → LUMO+1 (8%); HOMO-5 → LUMO+1 (8%); HOMO-6 → LUMO (7%); HOMO → LUMO+4 (5%)
4.46	278	0.01	HOMO-4 → LUMO+2 (64%); HOMO → LUMO+4 (8%); HOMO-8 → LUMO+1 (5%)
4.47	278	0.01	HOMO-8 → LUMO+1 (43%); HOMO-11 → LUMO (13%); HOMO-4 → LUMO+2 (8%); HOMO-10 → LUMO+1 (8%)
4.56	272	0.07	HOMO-9 → LUMO+1 (29%); HOMO-2 → LUMO+2 (19%); HOMO-11 → LUMO+1 (16%); HOMO → LUMO+4 (13%); HOMO → LUMO+5 (9%)

Table S12. Low-lying excited-state energies (eV and nm), oscillator strengths, and excited-state configurations for **8** as determined at the B3LYP/6-31G** level.

λ/eV	λ/nm	Osc. Str.	Configuration
1.87	663	0.06	HOMO → LUMO (92%); HOMO-1 → LUMO+1 (5%)
2.99	415	0.02	HOMO-2 → LUMO (92%)
3.17	391	1.29	HOMO → LUMO+2 (89%)
3.30	376	0.02	HOMO-3 → LUMO (50%); HOMO-4 → LUMO (17%); HOMO-3 → LUMO+1 (16%); HOMO-4 → LUMO+1 (11%)
3.32	374	0.02	HOMO-4 → LUMO (35%); HOMO → LUMO+1 (24%); HOMO-3 → LUMO+1 (9%); HOMO-5 → LUMO (9%); HOMO-3 → LUMO (9%); HOMO-5 → LUMO+1 (9%)
3.36	370	0.05	HOMO-6 → LUMO (60%); HOMO-6 → LUMO+1 (24%); HOMO-3 → LUMO+1 (5%)
3.48	357	0.23	HOMO-3 → LUMO+1 (41%); HOMO-4 → LUMO (31%); HOMO-7 → LUMO+1 (8%); HOMO-8 → LUMO (5%)
3.50	354	0.05	HOMO-7 → LUMO (31%); HOMO-1 → LUMO+2 (25%); HOMO-4 → LUMO+1 (16%); HOMO-8 → LUMO+1 (15%); HOMO → LUMO+3 (5%)
3.60	345	0.02	HOMO-6 → LUMO+1 (65%); HOMO-6 → LUMO (23%)
3.63	342	0.48	HOMO-4 → LUMO+1 (37%); HOMO-3 → LUMO (21%); HOMO-7 → LUMO (12%); HOMO-6 → LUMO (10%)
3.64	341	0.06	HOMO-6 → LUMO+1 (93%); HOMO-6 → LUMO (93%)
3.67	338	0.94	HOMO-7 → LUMO+1 (45%); HOMO-8 → LUMO (25%); HOMO-3 → LUMO+1 (8%); HOMO → LUMO+2 (5%)
3.69	336	0.02	HOMO-1 → LUMO+2 (53%); HOMO-7 → LUMO (21%); HOMO → LUMO+3 (9%); HOMO-9 → LUMO (7%)
3.77	329	0.02	HOMO-9 → LUMO (47%); HOMO → LUMO+3 (20%); HOMO-8 → LUMO+1 (11%); HOMO-1 → LUMO+2 (7%); HOMO-7 → LUMO (5%)
3.80	326	0.15	HOMO-8 → LUMO (37%); HOMO-9 → LUMO+1 (31%); HOMO-7 → LUMO+1 (21%)
3.93	316	0.01	HOMO-9 → LUMO+1 (56%); HOMO-8 → LUMO (13%); HOMO-7 → LUMO+1 (11%); HOMO-9 → LUMO (6%); HOMO-8 → LUMO+1 (6%)
4.03	308	0.03	HOMO → LUMO+3 (57%); HOMO-8 → LUMO+1 (19%); HOMO-1 → LUMO+2 (8%); HOMO-9 → LUMO (5%)
4.17	298	0.05	HOMO-2 → LUMO+2 (63%); HOMO-4 → LUMO+2 (14%); HOMO → LUMO+4 (10%)
4.27	291	0.48	HOMO-1 → LUMO+3 (79%); HOMO-2 → LUMO+2 (6%); HOMO-4 → LUMO+2 (5%)
4.29	289	0.04	HOMO-3 → LUMO+2 (77%); HOMO → LUMO+6 (6%)

Table S13. Low-lying excited-state energies (eV and nm), oscillator strengths, and excited-state configurations for **9** as determined at the B3LYP/6-31G** level.

λ/eV	λ/nm	Osc. Str.	Configuration
2.16	573	0.08	HOMO → LUMO (97%)
3.28	378	0.02	HOMO-2 → LUMO (76%); HOMO-4 → LUMO (11%); HOMO-6 → LUMO (8%)
3.42	362	0.69	HOMO → LUMO+2 (80%); HOMO-7 → LUMO (12%)
3.46	358	0.07	HOMO-4 → LUMO (81%); HOMO-2 → LUMO (13%)
3.78	328	0.18	HOMO-1 → LUMO+1 (91%)
3.88	319	1.00	HOMO → LUMO (72%); HOMO → LUMO (13%)
4.18	297	0.11	HOMO-9 → LUMO (77%); HOMO-7 → LUMO (5%)
4.52	274	0.26	HOMO-2 → LUMO+2 (75%); HOMO-6 → LUMO+2 (10%)

Table S14. Low-lying excited-state energies (eV and nm), oscillator strengths, and excited-state configurations for **10** as determined at the B3LYP/6-31G** level.

λ/eV	λ/nm	Osc. Str.	Configuration
1.47	844	0.02	HOMO → LUMO (98%)
2.64	470	0.01	HOMO-4 → LUMO (74%); HOMO-2 → LUMO (20%)
3.05	406	0.43	HOMO-5 → LUMO (91%)
3.19	389	0.02	HOMO-7 → LUMO (64%); HOMO → LUMO+2 (32%)
3.48	357	1.73	HOMO → LUMO+2 (63%); HOMO-7 → LUMO (32%)
3.49	355	0.01	HOMO-3 → LUMO+1 (97%)
3.97	312	0.47	HOMO-6 → LUMO+1 (86%)
4.26	291	0.11	HOMO-9 → LUMO (40%); HOMO-5 → LUMO+2 (30%); HOMO-8 → LUMO+1 (12%); HOMO-4 → LUMO+2 (9%)
4.31	288	0.05	HOMO-2 → LUMO+2 (94%)
4.46	278	0.06	HOMO → LUMO+4 (35%); HOMO-5 → LUMO+2 (16%); HOMO-9 → LUMO (15%); HOMO-8 → LUMO+1 (15%); HOMO-4 → LUMO+2 (12%)
4.53	273	0.45	HOMO-4 → LUMO+2 (56%); HOMO-5 → LUMO+2 (18%); HOMO-8 → LUMO+1 (11%)

Table S15. Low-lying excited-state energies (eV and nm), oscillator strengths, and excited-state configurations for **11** as determined at the B3LYP/6-31G** level.

λ/eV	λ/nm	Osc. Str.	Configuration
1.92	646	0.16	HOMO → LUMO (96%)
2.76	449	0.01	HOMO-2 → LUMO (93%)
3.03	409	1.59	HOMO → LUMO+2 (92%)
3.20	388	0.12	HOMO-1 → LUMO+1 (96%)
3.28	378	0.01	HOMO-1 → LUMO+2 (97%)
3.63	342	0.03	HOMO → LUMO+3 (90%)
3.69	336	0.66	HOMO-10 → LUMO (50%); HOMO-1 → LUMO+3 (14%); HOMO-12 → LUMO (12%); HOMO → LUMO+4 (11%); HOMO-2 → LUMO+2 (7%)
3.80	327	0.34	HOMO-1 → LUMO+3 (63%); HOMO-2 → LUMO+2 (23%)
3.85	322	0.03	HOMO → LUMO+4 (64%); HOMO-1 → LUMO+3 (15%); HOMO-2 → LUMO+2 (14%)
4.03	308	0.01	HOMO-12 → LUMO (42%); HOMO-10 → LUMO (34%); HOMO-13 → LUMO (11%)
4.07	305	0.01	HOMO-1 → LUMO+4 (76%); HOMO-11 → LUMO (14%)
4.16	298	0.10	HOMO-12 → LUMO (38%); HOMO-13 → LUMO (36%); HOMO-2 → LUMO+2 (10%); HOMO → LUMO+4 (5%)
4.28	290	0.34	HOMO-2 → LUMO+2 (38%); HOMO-13 → LUMO (27%); HOMO → LUMO+4 (7%); HOMO → LUMO+6 (6%); HOMO-10 → LUMO (5%)
4.47	278	0.01	HOMO-4 → LUMO+2 (42%); HOMO-3 → LUMO+1 (37%); HOMO-6 → LUMO+2 (7%)

Table S16. Low-lying excited-state energies (eV and nm), oscillator strengths, and excited-state configurations for **12** as determined at the B3LYP/6-31G** level.

λ/eV	λ/nm	Osc. Str.	Configuration
1.11	1113	0.06	HOMO → LUMO (98%)
2.25	551	0.02	HOMO-1 → LUMO+1 (99%)
2.83	438	1.41	HOMO → LUMO+2 (95%)
3.04	407	0.49	HOMO-7 → LUMO (52%); HOMO-8 → LUMO (42%)
3.17	391	0.40	HOMO-10 → LUMO (75%); HOMO-11 → LUMO (16%)
3.28	378	0.40	HOMO-11 → LUMO (73%); HOMO-10 → LUMO (19%)
3.51	353	0.02	HOMO → LUMO+3 (92%)
3.67	338	0.57	HOMO-1 → LUMO+3 (84%); HOMO-2 → LUMO+2 (8%)
3.76	330	0.01	HOMO-8 → LUMO+1 (51%); HOMO-7 → LUMO+1 (40%)
3.84	323	0.24	HOMO → LUMO+4 (66%); HOMO-1 → LUMO+3 (22%); HOMO-2 → LUMO+2 (6%)
3.89	319	0.14	HOMO-9 → LUMO+1 (60%); HOMO-2 → LUMO+2 (25%)
4.14	299	0.21	HOMO-2 → LUMO+2 (31%); HOMO → LUMO+4 (18%); HOMO-9 → LUMO+1 (17%); HOMO-13 → LUMO (9%); HOMO-4 → LUMO+2 (9%)
4.20	295	0.04	HOMO-4 → LUMO+2 (52%); HOMO → LUMO+6 (16%); HOMO-7 → LUMO+2 (7%); HOMO-6 → LUMO+2 (6%)
4.25	292	0.12	HOMO → LUMO+6 (37%); HOMO-4 → LUMO+2 (18%); HOMO-9 → LUMO+1 (8%); HOMO-6 → LUMO+2 (8%); HOMO-7 → LUMO+2 (7%); HOMO-8 → LUMO+2 (6%); HOMO-1 → LUMO+5 (5%)
4.31	287	0.01	HOMO-13 → LUMO (35%); HOMO → LUMO+6 (17%); HOMO-6 → LUMO+2 (13%); HOMO-7 → LUMO+2 (11%); HOMO-8 → LUMO+2 (8%)
4.37	284	0.10	HOMO-6 → LUMO+2 (51%); HOMO-4 → LUMO+2 (11%); HOMO-1 → LUMO+5 (7%); HOMO-7 → LUMO+2 (6%); HOMO-8 → LUMO+2 (5%)

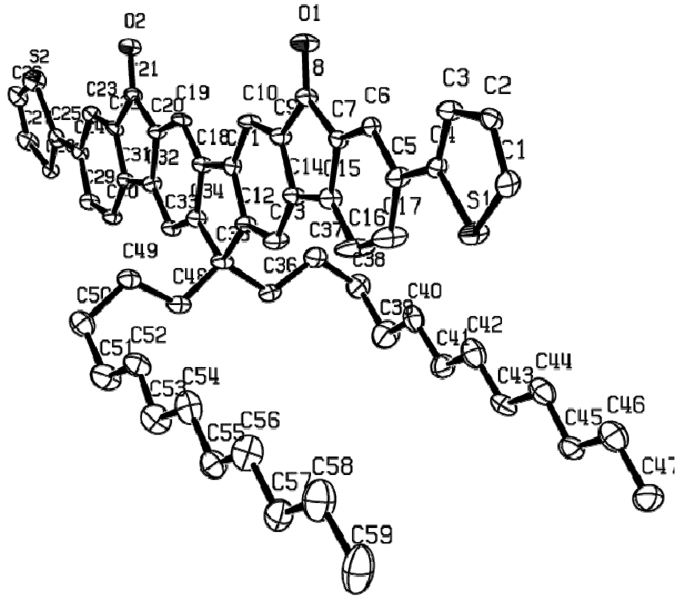

Figure S4. ORTEP drawing of compound **7** (30% thermal ellipsoids; hydrogen atoms are omitted for clarity).

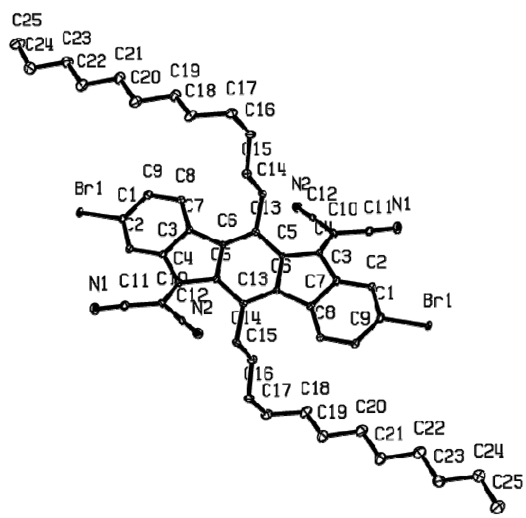

Figure S5. ORTEP drawing of compound **M2**. (30% thermal ellipsoids; hydrogen atoms are omitted for clarity).

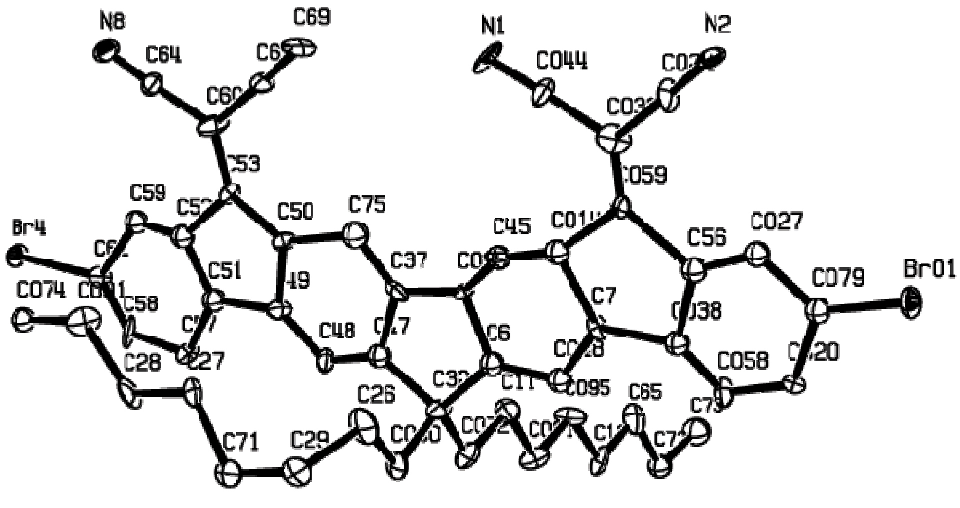

Figure S6. ORTEP drawing of compound **M4**. (30% thermal ellipsoids; hydrogen atoms are omitted for clarity).

Data Collection of Compound 7.

A orange plate crystal of C59 H66 O2 S2 having approximate dimensions of 0.258 x 0.227 x 0.023 mm was mounted using oil (Infineum V8512) on a glass fiber. All measurements were made on a CCD area detector with graphite monochromated MoK\α radiation.

Cell constants and an orientation matrix for data collection corresponded to a Triclinic cell with dimensions:

a = 12.1895(5) Å α = 112.494(2)º
b = 13.8723(5) Å β = 110.943(2)º
c = 16.2994(6) Å γ = 90.675(3)º
V = 2342.75(15) Å3

For Z = 2 and F.W. = 871.24, the calculated density is 1.235 g/cm3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

P-1

The data were collected at a temperature of 100(2)K with a theta range for data collection of 1.47 to 30.47º. Data were collected in 0.5º oscillations with 20 second exposures. The crystal-to-detector distance was 60.00 mm.

Data Reduction

Of the 26891 reflections which were collected, 12893 were unique (Rint = 0.1919). Data were collected using APEX2 V2.1-4 (Bruker, 2007) detector and processed using SAINTPLUS from Bruker.

The linear absorption coefficient, mu, for MoK\a radiation is 0.158 mm-1. A numerical absorption correction was applied. Minimum and maximum transmission factors were: 0.9603 and 0.9963, respectively. The data were corrected for Lorentz and polarization effects. No crystals examined diffracted beyond 1.1 Å resolution.

Structure Solution and Refinement

The structure was solved by direct methods and expanded using Fourier techniques3. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions, but not refined. The final cycle of full-matrix least-squares refinemene4 on F2 was based on 12893 reflections and 569 variable parameters and converged (largest parameter shift was 0.000 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma| |F_o|-|F_c| |/\Sigma|F_o| = 0.0869$$

$$wR^2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.2066$$

The weighting scheme was calc.
calc $w=1/[\sigma^2(F_o^2)+(0.1438P)^2 + 0.0000P]$ where $P=(F_o^2+2F_c^2)/3$

The standard deviation of an observation of unit weight5 was 0.830.
The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. Plots of Σ w $(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.829 and -0.401 e-/Å3, respectively.

Neutral atom scattering factors were taken from Cromer and Waber6. Anomalous dispersion effects were included in Fcalc7; the values for Df' and Df" were those of Creagh and McAuley8. The values for the mass attenuation coefficients are those of Creagh and Hubbell9. All calculations were performed using the Bruker SHELXTL3 crystallographic software package.

Table S17. Crystal data and structure refinement for compound **7**.

Identification code	compound **7**
Empirical formula	C59 H66 O2 S2
Formula weight	871.24
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 12.1895(5) Å α = 112.494(2) º b = 13.8723(5) Å β = 110.943(2) º c = 16.2994(6) Å γ = 90.675(3) º
Volume	2342.75(15) Å3
Z, Calculated density	2, 1.235 Mg/m3
Absorption coefficient	0.158 mm-1
F(000)	936
Crystal size	0.258 x 0.227 x 0.023 mm
Theta range for data collection	1.47 to 30.47 º
Limiting indices	-8<=h<=17, -19<=k<=18, -23<=l<=22
Reflections collected / unique	26891 / 12893 [R(int) = 0.1919]
Completeness to theta = 25.00	94.3 %
Absorption correction	Numerical
Max. and min. transmission	0.9963 and 0.9603
Refinement method	Full-matrix least-squares on F2

Data / restraints / parameters	12893 / 0 / 569
Goodness-of-fit on F^2	0.830
Final R indices [I>2sigma(I)]	R1 = 0.0869, wR2 = 0.2066
R indices (all data)	R1 = 0.3368, wR2 = 0.3307
Largest diff. peak and hole	0.829 and -0.401 e-/Å-3

Data Collection of Compound M2.

A green block crystal of C50 H56 Br2 N4 having approximate dimensions of 0.24 x 0.20 x 0.09 mm was mounted using oil (Infineum V8512) on a glass fiber. All measurements were made on a CCD area detector with graphite monochromated CuK\α radiation.

Cell constants and an orientation matrix for data collection corresponded to a Triclinic cell with dimensions:

a = 8.4993(4) Å α = 76.650(3)º
b = 10.0232(4) Å β = 80.592(3)º
c = 14.3879(6) Å γ = 66.240(3)º
V = 1088.09(9) Å3

For Z = 1 and F.W. = 872.81, the calculated density is 1.332 g/cm3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

P-1

The data were collected at a temperature of 100(2)K with a theta range for data collection of 4.90 to 66.73º. Data were collected in 0.5º oscillations with 10 second exposures. The crystal-to-detector distance was 50.00 mm.

Data Reduction

Of the 8558 reflections which were collected, 3412 were unique (Rint = 0.0327). Data were collected using APEX2 V2.1-4 (Bruker, 2007) detector and processed using SAINTPLUS from Bruker.

The linear absorption coefficient, mu, for CuK\a radiation is 2.649 mm-1. A numerical absorption correction was applied, minimum and maximum transmission factors were: 0.5725 and 0.7926, respectively. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods and expanded using Fourier techniques3. The non-hydrogen atoms were refined anisotropically.
Hydrogen atoms were included in idealized positions, but not refined. The final cycle of full-matrix least-squares refinemene4 on F2 was based on 3412 reflections and 254 variable parameters and converged (largest parameter shift was 0.003 times its esd) with unweighted and weighted agreement factors of:

$R1 = \Sigma| |F_o|-|F_c| |/\Sigma|F_o| = 0.0365$

$wR^2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.0928$

The weighting scheme was calc.
calc $w=1/[\sigma^2(F_o^2)+(0.0586P)^2 + 0.5517P]$ where $P=(F_o^2+2F_c^2)/3$

The standard deviation of an observation of unit weight5 was 1.053.
The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. Plots of Σ w $(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.718 and -0.469 e-/Å3, respectively.

Neutral atom scattering factors were taken from Cromer and Waber6.
Anomalous dispersion effects were included in Fcalc7; the values for Df' and Df" were those of Creagh and McAuley8. The values for the mass attenuation coefficients are those of Creagh and Hubbell9. All calculations were performed using the Bruker SHELXTL3 crystallographic software package.

Table S18. Crystal data and structure refinement for compound M2.

Identification code	Compound M2
Empirical formula	C50 H56 Br2 N4
Formula weight	872.81
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system, space group	Triclinic, P-1

Unit cell dimensions	a = 8.4993(4) Å α = 76.650(3) º
	b = 10.0232(4) Å β = 80.592(3) º
	c = 14.3879(6) Å γ = 66.240(3) º
Volume	1088.09(8) Å3
Z, Calculated density	1, 1.332 Mg/m3
Absorption coefficient	2.649 mm-1
F(000)	454
Crystal size	0.24 x 0.20 x 0.09 mm
Theta range for data collection	4.90 to 66.73 º
Limiting indices	-10<=h<=9, -9<=k<=11, -16<=l<=16
Reflections collected / unique	8558 / 3412 [R(int) = 0.0327]
Completeness to theta = 66.73	89.0 %
Absorption correction	Numerical
Max. and min. transmission	0.7926 and 0.5725
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	3412 / 0 / 254
Goodness-of-fit on F^2	1.053
Final R indices [I>2sigma(I)]	R1 = 0.0365, wR2 = 0.0928
R indices (all data)	R1 = 0.0422, wR2 = 0.0955
Largest diff. peak and hole	0.718 and -0.469 e-/Å-3

Data Collection of Compound M4.

A dark block crystal of C57 H60 Br2 N4 having approximate dimensions of 0.25 x 0.22 x 0.21 mm was mounted using oil (Infineum V8512) on a glass fiber. All measurements were made on a CCD area detector with graphite monochromated MoK\α radiation.

Cell constants and an orientation matrix for data collection corresponded to a Orthorhombic cell with dimensions:

a = 22.2091(6) Å
b = 22.2174(7) Å
c = 36.3970(10) Å
V = 17959.3(9) Å3

For Z = 16 and F.W. = 968.07, the calculated density is 1.432 g/cm3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

Iba2

The data were collected at a temperature of 100(2)K with a theta range for data collection of 1.07 to 30.55º. Data were collected in 0.5º oscillations with 10 second exposures. The crystal-to-detector distance was 60.00 mm.

Data Reduction

Of the 193890 reflections which were collected, 27207 were unique (Rint = 0.1096). Data were collected using APEX2 V2.1-4 (Bruker, 2007) detector and processed using SAINTPLUS from Bruker.

The linear absorption coefficient, mu, for MoK\a radiation is 2.024 mm-1. A numerical absorption correction was applied. Minimum and maximum transmission factors were: 0.6306 and 0.6759, respectively. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods and expanded using Fourier techniques3. The non-hydrogen atoms were refined anisotropically.
Hydrogen atoms were included in idealized positions, but not refined. The unit cell and the consistency in the reflections looked like it was tetrahdral. No solution could be found and using Platon ADDSYM (Spek, 2006) no extra symmetry is found in the reported model. The crystal under investigation was found to be merohedrally twinned. The orientation matrix for the component was found to be (0 -1 0 / -1 0 0 / 0 0 -1). The twin fraction refined to a value of 0.3405(1).The final cycle of full-matrix least-squares refinemene4 on F2 was based on 27207 reflections and 1068 variable parameters and converged (largest parameter shift was 0.005 times its esd) with unweighted and weighted agreement factors of:

$R1 = \Sigma| |F_o|-|F_c| |/\Sigma|F_o| = 0.0436$

$wR^2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.0684$

The weighting scheme was calc.
calc $w=1/[\sigma^2(F_o^2)+(0.0142P)^2 + 0.0000P]$ where $P=(F_o^2+2F_c^2)/3$

The standard deviation of an observation of unit weight5 was 1.033.
The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. Plots of $\Sigma\ w\ (|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.572 and -0.490 e-/Å3, respectively.

Neutral atom scattering factors were taken from Cromer and Waber6. Anomalous dispersion effects were included in Fcalc7; the values for Df' and Df" were those of Creagh and McAuley8. The values for the mass attenuation coefficients are those of Creagh and Hubbell9. All calculations were performed using the Bruker SHELXTL3 crystallographic software package.

Table S19. Crystal data and structure refinement for compound M4.

Identification code	Compound M4
Empirical formula	C57 H60 Br2 N4
Formula weight	968.07
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Iba2
Unit cell dimensions	a = 22.2091(6) Å b = 22.2174(7) Å c = 36.3970(10) Å
Volume	17959.3(9) Å3
Z, Calculated density	16, 1.432 Mg/m3
Absorption coefficient	2.024 mm-1
F(000)	7904

Crystal size 0.25 x 0.22 x 0.21 mm

Theta range for data collection 1.07 to 30.55 º

Limiting indices -29<=h<=31, -31<=k<=31, -51<=l<=52

Reflections collected / unique 193890 / 27207 [R(int) = 0.1096]

Completeness to theta = 30.55 99.8 %

Absorption correction Numerical

Max. and min. transmission 0.6759 and 0.6306

Refinement method Full-matrix least-squares on F2

Data / restraints / parameters 27207 / 1 / 1068

Goodness-of-fit on F^2 1.033

Final R indices [I>2sigma(I)] R1 = 0.0436, wR2 = 0.0684

R indices (all data) R1 = 0.0837, wR2 = 0.0720

Absolute structure parameter 0.079(6)

Largest diff. peak and hole 0.572 and -0.490 e-/Å-3

References.

1. Becke, A. D., Density-functional exchange-energy approximation with correct asymptotic behavior. *Physical Review A: Atomic, Molecular, and Optical Physics* **1988,** 38, (6), 3098-3100.

2. Becke, A. D., Density-functional thermochemistry. III. The role of exact exchange. *Journal of Chemical Physics* **1993,** 98, (7), 5648-52.

3. Lee, C.; Yang, W.; Parr, R. G., Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Physical Review B: Condensed Matter and Materials Physics* **1988,** 37, (2), 785-9.

4. Y. Shao, L. Fusti-Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S. T. Brown, A. T. B. Gilbert, L. V. Slipchenko,S. V. Levchenko, D. P. O'Neill, R. A. Distasio Jr., R. C. Lochan, T. Wang, G. J. O. Beran, N. A. Besley, J. M., Herbert, C. Y. Lin, T. Van Voorhis, S. H. Chien, A. Sodt, R. P. Steele, V. A. Rassolov, P. E. Maslen, P. P. Korambath, R. D. Adamson, B. Austin, J.

Baker, E. F. C. Byrd, H. Dachsel, R. J. Doerksen, A. Dreuw, B. D. Dunietz, A. D. Dutoi, T. R. Furlani, S. R. Gwaltney, A. Heyden, S. Hirata, C.-P. Hsu, G. Kedziora, R. Z. Khalliulin, P. Klunzinger, A. M. Lee, M. S. Lee, W. Liang, I. Lotan, N. Nair, B. Peters, E. I. Proynov, P. A. Pieniazek, Y. M. Rhee, J. Ritchie, E. Rosta, C. D. Sherrill, A. C. Simmonett, J. E. Subotnik, H. L. Woodcock III, W. Zhang, A. T. Bell, A. K. Chakraborty, D. M. Chipman, F. J. Keil, A. Warshel, W. J. Hehre, H. F. Schaefer III, J. Kong, A. I. Krylov, P. M. W. Gill, M. Head-Gordon, Advances in methods and algorithms in a modern quantum chemistry program package*,* *Phys. Chem. Chem. Phys.* **2006,** *8*, 3172 - 3191.