Electronic Supplementary Material (ESI) for Chemical Science

Structural Dependence of the Optical Properties of Narrow Bandgap Semiconductors with Orthogonal Donor-Acceptor Geometries

Bruno Grimm,[1] Chad Risko,[2] Jason D. Azoulay,[1] Jean-Luc Brédas*[2] and Guillermo C. Bazan*[1]

[1]Center of Polymers and Organic Solids, Department of Chemistry and Biochemistry, and Department of Materials, The University of California, Santa Barbara, California, 93106, United States

[2]School of Chemistry and Biochemistry and Center of Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia, 30332-0400, United States

Experimental Section

General Details: Preparations were carried out on a bench top or under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and a Vacuum Atmospheres inert atmosphere glove box. Toluene was dried over sodium/benzophenone, distilled under vacuum, and stored over molecular sieves (4 Å). Both dichloromethane and xylene (mixed isomers) were dried over calcium hydride, distilled under vacuum, and stored over molecular sieves (4 Å). Molecular sieves (4 Å) were purchased from Aldrich Chemical Company and dried at 140 oC under vacuum for 24 hours prior to use. Deuterated solvents were (CD_2Cl2, $CDCl_3$, C_6D_6, 1,1,2,2-tetrachloroethane-D_2) purchased from Cambridge Isotopes Laboratory and used as received. All reactants and reagents are commercially available and used as received, unless otherwise noted.

Materials: Compound **S2** was prepared by a method reported elsewhere.[i] Compounds 4-hexyl aniline was purchased from TCI America, 4*H*-cyclopenta-[2,1-b:3,4-b']-dithiophene-4-one **1** from Luminescence Technology Corp. (Lumtec) and used as received.

GPC: Gel permeation chromatography (room temperature in chloroform) was performed on a Waters 2690 Separation Module with Waters 2414 and 2998 PDA detectors.

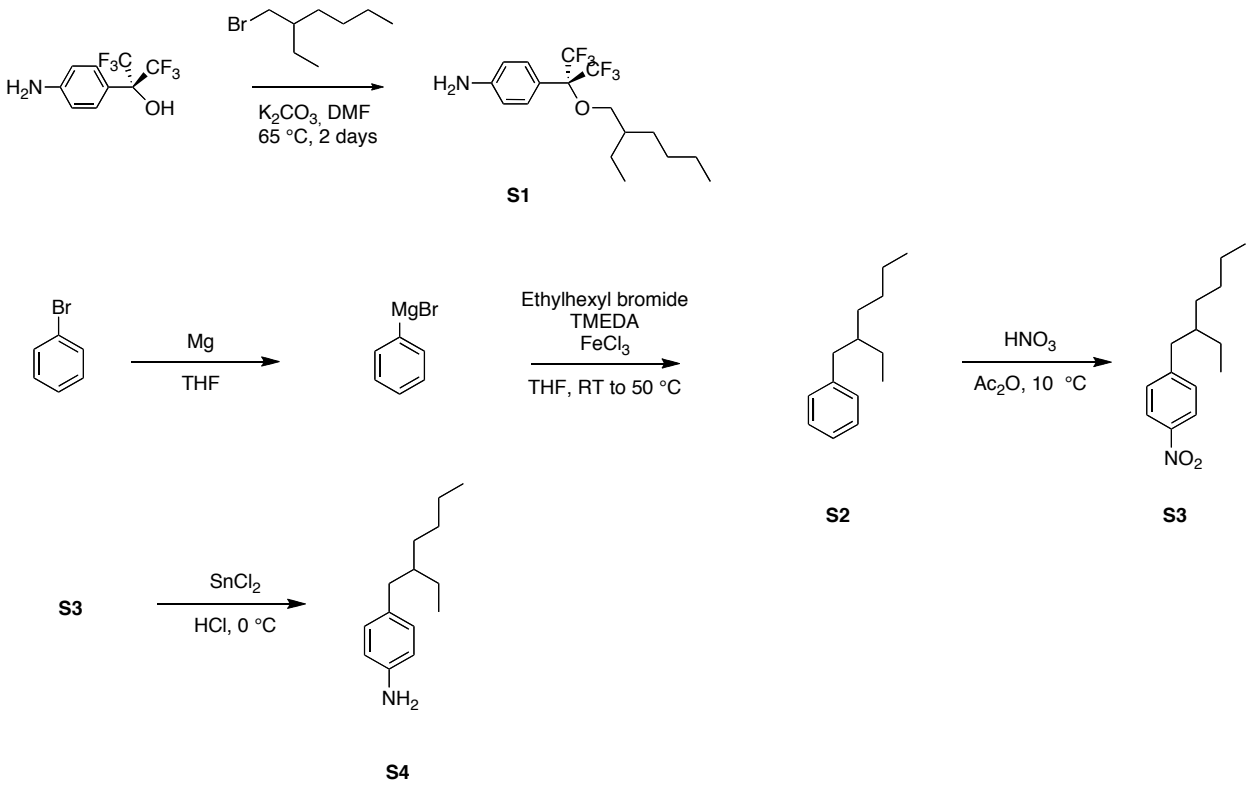
NMR: ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy spectra were recorded on Bruker Avance-500 MHz and Varian VNMRS 600MHz SB spectrometers at 25˚C unless otherwise noted. ^{1}H and ^{13}C NMR spectra are referenced to $SiMe_4$ using the residual solvent peak impurity of the given solvent. Chemical shifts are reported in ppm and coupling constants in Hz as absolute values.

UV-vis: UV-visible spectra were recorded using a Beckman Coulter DU 800 series or Perkin Elmer Lambda 750 spectrophotometer at room temperature unless otherwise noted. All UV-vis experiments were run in $CHCl_3$.

CHN: Combustion analyses were performed by the MSI analytical lab at the University of California, Santa Barbara.

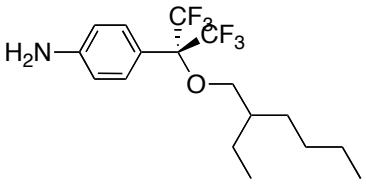
Mass Spectrometry: Full scan, low resolution EI/FD/FI mass spectrometry was carried out at the Department of Chemsitry spectrometry facility, University of Californa, Santa Barbara.

Synthesis of compounds S1 to 13



Scheme S1: Synthesis of anilines **S1** and **S4**.

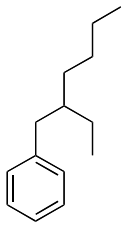
4-(2-(2-ethylhexyloxy)-1,1,1,3,3,3-hexafluoropropan-2-yl) aniline (S1)



2-(4-Aminophenyl)-1,1,1,3,3,3-hexafluoro-2-propanol (4 g, 15.40 mmol), K_2CO_3 (3.2 g, 32 mmol) and ethylhexyl bromide (3.57 g, 18.5 mmol) were combined in an oven dried schlenk flask. The flask was evacuated and back-filled with argon three times. Anhydrous DMF (50 mL) was added and the mixture was heated to 65 ˚C and stirred for two days. The mixture was then poured into a separatory funnel containing 50 mL of DI water and 50 mL of diethyl ether. The organic layer was further washed with 3 x 50 mL DI water. The organic layer was dried over anhydrous $MgSO_4$, and all volatiles were removed *in vacuo*. Purification by column chromatography using hexanes (with 1% triethylamine) as the eluent gave 2.96 g (66.8%) of the

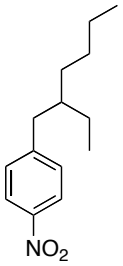
product. ^{1}H NMR (500 MHz, [d_1]-chloroform, 298 K): δ = 7.47 (d, 2H, *J* = 8.3 Hz), 6.63 (d, 2H, *J* = 8.9 Hz), 3.86 (s, 2H), 3.05 (d, 2H, *J* = 6.2 Hz), 1.61 – 1.55 (m, 1H), 1.49 – 1.26 (m, 8H), 0.96 – 0.89 (m, 6H). ^{13}C NMR (151 MHz, [d_1]-chloroform, 298 K): δ =150.04, 127.68, 122.08 (q), 117.00, 112.26, 77.26 (m), 46.84, 39.21, 31.44, 29.12, 24.62, 23.23, 14.20, 11.04. ^{19}F NMR (564.56 MHz, [d_1]-chloroform, 298 K): δ = -75.89 (s, 6F). LRMS (FI) *m/z*, calcd. for $C_{17}H_{23}F_6NO$ (M^+): 371,17; found: 371.

(2-ethylhexyl)benzene S2



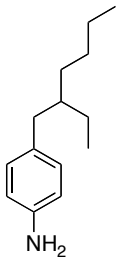
Bromobenzene (4 g, 25.5 mmol) in dry THF (12 mL) was added dropwise over 30 min to a suspension of magnesium ribbons (0.68 g, 28 mmol) in 50 mL dry THF. After complete addition, the solution was refluxed for 3 hours. After cooling to room temperature, the phenylmagnesium bromide was transferred over the course of 1.5 hours via dropping funnel at room temperature to a solution of $FeCl_3$ (144 mg, 0.89 mmol), tetramethylethylenediamine TMEDA (4.44 g, 38.2 mmol) and 2-ethylhexyl bromide (3.44 g, 17.8 mmol) in 40 mL dry THF at such a rate that the reaction mixture was kept pale yellow rather than dark red. The reaction mixture was then quenched with 20 mL water and 100 mL 2 M hydro chloric acid. After phase separation, the aqueous phase was extracted with diethyl ether (3 × 75 mL) and the combined organic phases were washed with brine and dried (anhydrous magnesium sulfate). All solvents were removed *in vacuo*. The reaction product was dissolved in a solution of water/DMSO (2:1) and K_2CO_3 (4.9 g, 35.6 mmol) and heated to reflux over night. The reaction mixture was cooled to room temperature and neutralized with HCl_{conc}. The crude mixture was extracted with with diethyl ether and the combined organic phases were washed with NH_4Cl and brine. After drying with $MgSO_4$ the crude product was purified by column chromatography using hexane as eluent. The product was obtained as colorless liquid (2.17 g, 64 %). ^{1}H NMR (600 MHz, [d_2]-methylene chloride, 298 K): δ = 7.36 – 7.22 (m, 2H), 7.22 – 7.07 (m, 3H), 2.59 – 2.49 (m, 2H), 1.59 (m, 1H), 1.39 – 1.20 (m, 8H), 0.97 – 0.79 (m, 6H). ^{13}C NMR (151 MHz, [d_2]-methylene chloride, 298 K): δ = 142.03, 129.34, 128.20, 125.63, 41.24, 40.30, 32.50, 29.01, 25.57, 23.19, 14.28, 10.93. LRMS (FI) *m/z*, calcd. for $C_{14}H_{22}$ (M^+): 190.17; found: 190.

1-(2-ethylhexyl)-4-nitrobenzene S3



(2-ethylhexyl)benzene (**S2**) (1.88 g, 9.90 mmol) was dissolved in 10 mL acetic anhydrid at 10 °C. After slow addition of 0.48 mL 70 % nitric acid (10.88 mmol), the colored solution was stirred for three hours at 10 °C. After diluting the reaction mixture with water, sodium hydroxide was added carefully until a neutral pH was reached. The reaction mixture was extracted with diethyl ether (3 × 50 mL) and the organic layers were washed with sodium bicarbonate and brine, and dried with $MgSO_4$. Removing all volatiles *in vacuo* gave a yellow liquid. Due to the presence of multiple isomers, two flash chromatographies (hexane : CH_2Cl_2 = 9:1 and 4:1) were necessary to purify the target compound. This procedure yielded 500 mg of **S3** (22 %). ^{1}H NMR (600 MHz, [d_2]-methylene chloride, 298 K): δ = 8.23 – 7.90 (m, 2H), 7.33 – 7.30 (m, 2H), 2.66 – 2.63 (m, 2H), 1.65 – 1.58 (m, 1H), 1.38 – 1.13 (m, 6H), 0.93 – 0.82 (m, 6H). ^{13}C NMR (151 MHz, [d_2]-methylene chloride, 298 K): δ = 150.88, 146.83, 130.51, 123.83, 41.66, 40.60, 32.85, 29.31, 26.04, 23.53, 14.41, 11.07. LRMS (FI) *m/z*, calcd. for $C_{14}H_{21}NO_2$ (M^+): 235.16; found: 235.

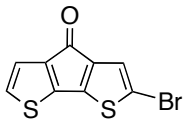
4-(2-ethylhexyl)aniline S4



$SnCl_2$ (1.5 g, 8.0 mmol) in a round bottom flask was cooled with a water bath and 1-(2-ethylhexyl)-4-nitrobenzene (**S4**) (0.5 g, 2.13 mmol) dissolved in 38 % hydrochloric acid (1.9 mL) was added drop wise under vigorously stirring (strong gas evolution). The water bath was then removed and the reaction mixture was increased to 70 °C for three hours. After cooling to room temperature, the reaction mixture was neutralized with 20 % sodium hydroxide. The product was extracted with CH_2Cl_2 and the organic layers were combined and washed with sodium bicarbonate and brine. All volatiles were removed *in vacuo* and **S5** was isolated as colorless liquid (266 mg, 65 %). ^{1}H NMR (600 MHz, [d_2]-methylene chloride, 298 K): δ = 6.98 – 6.89 (m, 2H), 6.64 – 6.54 (m, 2H), 3.57 (s, 2H), 2.48 – 2.30 (m, 2H), 1.51 – 1.46 (m, 1H), 1.38 – 1.17 (m, 6H), 0.88 (m, 6H). ^{13}C NMR (151 MHz, [d_2]-methylene chloride, 298 K): δ = 144.96,

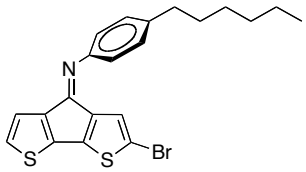
132.12, 130.42, 115.31, 41.87, 39.65, 32.85, 29.44, 25.92, 23.68, 14.50, 11.16. LRMS (FI) *m/z*, calcd. for $C_{14}H_{23}N$ (M^+): 205.18; found: 205.

Monobromo-4*H*-Cyclopenta-[2,1-*b*:3,4-*b'*]dithiophen-4-one (2)



4*H*-Cyclopenta-[2,1-*b*:3,4-*b'*]dithiophen-4-one (1.52 g, 7.91 mmol) was dissolved in anhydrous DMF (40 mL). N-Bromosuccinimide (1.41 g, 7.91 mmol) was added in one portion. The solution was vigorously stirred in the dark for 20 minutes. After this time the reaction mixture was diluted with dichloromethane (200 mL) and water (100 mL) was added. The mixture was allowed to stir over the course of an hour. The organic layer was washed with additional water (3 x 100 mL), brine and dried over $MgSO_4$. Flash chromatography using a hexane:dichloromethane gradient gave 1.39 g (5.13 mmol) of the desired product (64.8 %). ^{1}H NMR (600 MHz, [d_2]-methylene chloride, 298 K) δ = 7.11 (d, *J* = 4.9 Hz, 1H), 6.99 (s, 1H), 6.98 (d, *J* = 4.7 Hz, 1H). ^{13}C NMR (151 MHz, Methylene Chloride-d2) δ = 181.87, 149.66, 149.65, 141.63, 141.48, 128.60, 124.69, 122.08, 113.95. LRMS (FI) *m/z*, calcd. for $C_9H_3BrOS_2$ (M^+): 271.88; found: 272.

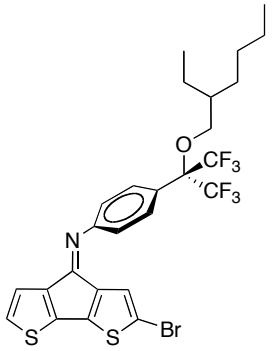
N-(2-bromopentaleno[2,1-b:3,4-b']-dithiophen-4(7H)-ylidene)-4-hexylaniline (3)



In a glovebox, a dry solution of 4-hexylaniline (539 mg, 3.04 mmol) and triethylamine (1.40 g, 13.8 mmol) in dichloromethane (10 ml) were chilled to – 35 °C. Titanium tetrachloride (525 mg, 2.77 mmol) in 1 mL toluene was added drop-wise over a period of 5 minutes to give a deep red solution, which was allowed to stir for an additional five minutes. A chilled solution of monobromo-4*H*-Cyclopenta-[2,1-*b*:3,4-*b'*]dithiophen-4-one (750 mg, 2.77 mmol) in dichloromethane (5 mL) was added at once. The solution was vigorously stirred, allowed to warm to room temperature and stirred overnight. Subsequently, 100 mL of diethyl ether was added and the resulting suspension was stirred over the course of an hour. The suspension was filtered through a pad of celite and all volatiles were removed *in vacuo*. Purification by column chromatography on silica using hexanes:chloroform (9:1, containing 1% triethylamine) as the eluent gave 874 mg (2.03 mmol, 73%) of the desired product as a red oil. ^{1}H NMR (500 MHz, [d_2]-methylene chloride) δ = 7.28 – 7.13 (m, 3.6, isomer), 6.93 – 6.83 (m, 1.8 H, isomer), 6.85 (d, *J* = 5.0 Hz, 0.4H, isomer), 6.06 (d, *J* = 5.0 Hz, 0.4 H, isomer), 6.03 (s, 0.4H, isomer), 2.70 – 2.62 (m, 2H), 1.70 – 1.62 (m, 2H), 1.42 – 1.29 (m, 6H), 0.95 – 0.85 (m, 3H). ^{13}C NMR (151 MHz, [d_2]-methylene chloride) δ = 155.31, 155.14, 148.70, 148.64, 146.00, 145.55, 144.49, 144.08, 143.26, 142.90, 140.02, 139.96, 136.48, 135.96, 128.87, 128.80, 126.98, 126.48, 125.59, 124.19, 123.85, 121.30, 119.57, 119.55, 112.27, 110.82, 35.36, 35.33, 31.71, 31.69, 31.54, 31.47,

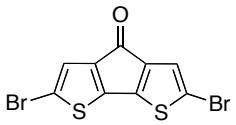
28.89, 28.84, 22.63, 22.61, 13.86, 13.82 (two isomers were observed). LRMS (FI) *m/z*, calcd. for $C_{21}H_{20}BrNS_2$ = 429.00; found 429.

N-(2-bromopentaleno[2,1-b:3,4-b']-dithiophen-4(7H)-ylidene)-4-4-(2-(2-ethylhexyloxy)-1,1,1,3,3,3-hexafluoropropan-2-yl)aniline (4)



In the glove box, a dry solution of 4-(2-(2-ethylhexyloxy)-1,1,1,3,3,3-hexafluoropropan-2-yl)aniline (1.23 g, 3.47 mmol) and triethylamine (1.60 g, 15.8 mmol) in dichloromethane (10 ml) were chilled to – 35 °C. Titanium tetrachloride (599 mg, 3.16 mmol) in 1 mL toluene was added drop-wise over a period of 5 minutes to give a deep red solution, which was allowed to stir for an additional five minutes. A chilled solution of monobromo-4*H*-Cyclopenta-[2,1-*b*:3,4-*b'*]dithiophen-4-one (856 mg, 3.16 mmol) in dichloromethane (5 mL) was added at once. The solution was vigorously stirred, allowed to warm to room temperature and stirred overnight. Subsequently, 100 mL of diethyl ether was added and the resulting suspension was stirred over the course of an hour. The suspension was filtered through a pad of celite and all volatiles were removed *in vacuo*. Purification by column chromatography using hexanes:methlylene chloride (9:1, containing 1% triethylamine) as the eluent gave 1.3 g (71%) of the product. ^{1}H NMR (600 MHz, [d_2]-methylene chloride) δ = 7.65 – 7.59 (m, 2H), 7.26 (s, 0.6H, isomer), 7.24 (d, *J* = 4.8 Hz, 0.5H, isomer), 7.21 (d, *J* = 4.9 Hz, 0.6H, isomer), 7.10 – 7.05 (m, 2H), 6.86 (d, *J* = 5.1 Hz, 0.6H, isomer), 5.90 (d, *J* = 5.0 Hz, 0.6H, isomer), 5.77 (s, 0.6H, isomer), 3.56 – 3.51 (m, 2H), 1.72 – 1.63 (m, 1H), 1.55 – 1.24 (m, 8H), 0.94 – 0.87 (m, 6H). LRMS (FI) *m/z*, calcd. for $C_{26}H_{24}BrF_6NOS_2$ = 623.03; found 623.

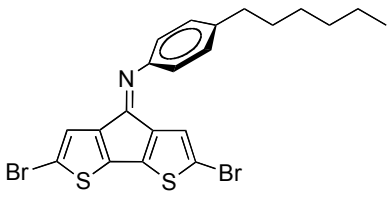
Dibromo-4*H*-Cyclopenta-[2,1-*b*:3,4-*b'*]dithiophen-4-one (5)



Under a flow of argon, 4*H*-Cyclopenta-[2,1-*b*:3,4-*b'*]dithiophen-4-one (1.00 g, 2.86 mmol) was dissolved in anhydrous DMF (25 mL). N-Bromosuccinimide (1.07 g, 6.01 mmol) was added in one portion. The solution was vigorously stirred in the dark for 20 minutes. After this time the reaction mixture was diluted with dichloromethane (200 mL) and water (100 mL) was added.

The mixture was allowed to stir over the course of an hour. The organic layer was washed with additional water (3 x 100 mL), brine and dried over $MgSO_4$. Recrystallization from ether gave 1.45 g (2.84 mmol) of the desired product (94.0 %). ^{1}H NMR (500 MHz, [d_1]-chloroform, 298 K): δ = 6.99 (s, 2H), ^{13}C NMR (125.7 MHz, [d_1]-chloroform, 298 K): 180.52, 148.72, 139.62, 124.49, 114.02. LRMS (FI) *m/z*, calcd. for $C_9H_2Br_2OS_2$ = 347.49; found 358.

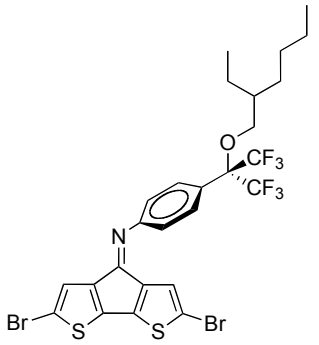
N-(2,6-dibromopentaleno[2,1-b:3,4-b']-dithiophen-4(7H)-ylidene)-4-hexylaniline (6)



In a glovebox, a dry solution of 4-hexylaniline (535 mg, 3.02 mmol) and triethylamine (1.26 g, 12.48 mmol) in dichloromethane (10 ml) was chilled to –35 °C. Titanium tetrachloride (541 mg, 2.85 mmol) in 1 mL toluene was added drop-wise over a period of 5 minutes to give a deep red solution, which was allowed to stir for an additional five minutes. A chilled solution of dibromo-4*H*-Cyclopenta-[2,1-*b*:3,4-*b'*]dithiophen-4-one (1.26 g, 3.02 mmol) in dichloromethane (5 mL) was added at once. The solution was vigorously stirred, allowed to warm to room temperature and stirred overnight. Subsequently, 100 mL of diethyl ether was added and the resulting suspension was stirred over the course of an hour. The suspension was filtered through a silica plug and removal of the solvent gave 1.45 g (2.84 mmol, 94%) of the desired product as a red solid. ^{1}H NMR (600 MHz, [d_1]-chloroform) δ = 7.27 (s, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.04 (s, 1H), 2.66 (t, *J* = 7.7 Hz, 2H), 1.68 – 1.63 (m, 2H), 1.42 – 1.27 (m, 6H), 0.95 – 0.85 (m, 3H). ^{13}C NMR (151 MHz, [d_1]-chloroform) δ = 155.01, 148.60, 145.91, 143.39, 143.09, 140.60, 135.25, 129.31, 126.88, 124.83, 120.11, 113.27, 111.77, 35.80, 32.09, 31.76, 29.21, 23.00, 14.48. LRMS (FI) *m/z*, calcd. for $C_{21}H_{19}Br_2NS_2$ = 506.93; found 507.

.

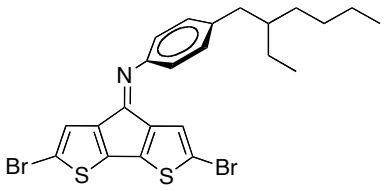
N-(2,6-dibromopentaleno[2,1-b:3,4-b']-dithiophen-4(7H)-ylidene)-4-4-(2-(2-ethylhexyloxy)-1,1,1,3,3,3-hexafluoropropan-2-yl)aniline (7)



In the glove box, a dry solution of 4-(2-(2-ethylhexyloxy)-1,1,1,3,3,3-hexafluoropropan-2-yl) aniline (535 mg, 3.02 mmol) and triethylamine (1.26 g, 12.48 mmol) in dichloromethane (10 ml)

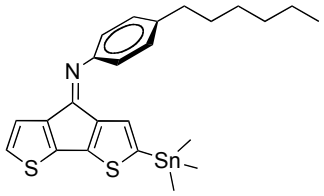
were chilled to – 35 °C. Titanium tetrachloride (541 mg, 2.85 mmol) in 1 mL toluene was added drop-wise over a period of 5 minutes to give a deep red solution, which was allowed to stir for an additional five minutes. A chilled solution of Dibromo-4*H*-Cyclopenta-[2,1-*b*:3,4-*b'*]dithiophen-4-one (1.26 g, 3.02 mmol) in dichloromethane (5 mL) was added at once. The solution was vigorously stirred, allowed to warm to room temperature and stirred overnight. Subsequently, 100 mL of diethyl ether was added and the resulting suspension was stirred over the course of an hour. The suspension was filtered through a pad of celite and all volatiles were removed *in vacuo*. Purification by column chromatography using hexane : CH_2Cl_2 (9:1) (containing 1% triethylamine) as the eluent gave 1.61 g (76 %) of the product. ^{1}H NMR (500 MHz, [d_1]-chloroform, 298 K): δ = 7.59 (d, *J* = 8.3 Hz, 2H), 7.06 (s, 1H), 6.81 – 6.79 (m, 2H), 5.79 (s, 1H), 3.56 – 3.51 (m, 2H), 1.59 – 1.53 (m, 1H), 1.47 - 1.17 (m, 8H), 0.8 – 0.83 (m, 6H). ^{13}C NMR (150.87 MHz, [d_1]-chloroform) δ = 155.43, 152.33, 146.04, 143.31, 142.56, 134.66, 129.08, 126.18, 125.19, 124.43, 122.54 (q), 119.62, 113.32, 111.97. 82.59 (m), 68.81, 40.24, 30.33, 29.04, 23.77, 23.11, 14.16, 11.18. LRMS (FD) *m/z*, Calcd. for $C_{26}H_{23}Br_2F_6NOS_2$ (M^+): 700.95; found: 701.

N-(2,6-dibromopentaleno[2,1-b:3,4-b']-dithiophen-4(7H)-ylidene)- 4-(2-ethylhexyl)aniline (8)



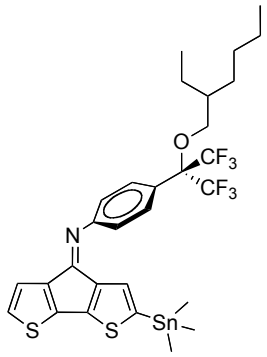
In the glove box, a dry solution of 4-(2-ethylhexyl)aniline **S5** (225 mg, 1.10 mmol) and triethylamine (558 mg, 5.48 mmol) in dichloromethane (6 ml) were chilled to – 35 °C. Titanium tetrachloride (187 mg, 0.99 mmol) in 1 mL toluene was added drop-wise over a period of 5 minutes to give a deep red solution, which was allowed to stir for an additional five minutes. A chilled solution of Dibromo-4*H*-Cyclopenta-[2,1-*b*:3,4-*b'*]dithiophen-4-one (364 mg, 1.04 mmol) in dichloromethane (3 mL) was added at once. The solution was vigorously stirred, allowed to warm to room temperature and stirred overnight. Subsequently, 50 mL of diethyl ether was added and the resulting suspension was stirred over the course of an hour. The suspension was filtered through a pad of celite and all volatiles were removed *in vacuo*. Purification by column chromatography using hexanes : $CHCl_3$ (9:1) (containing 1% triethylamine) as the eluent gave 540 mg (92 %) of the product. ^{1}H NMR (500 MHz, [d_2]-methylene chloride, 298 K): δ = 7.27 (s, 1H), 7.22 – 7.17 (m, 2H), 6.89 – 6.84 (m, 2H), 6.02 (s, 1H), 2.62 – 2.51 (m, 2H), 1.65 – 1.56 (m, 1H), 1.40 – 1.23 (m, 8H), 0.95 – 0.83 (m, 6H). ^{13}C NMR (126 MHz, [d_2]-methylene chloride, 298 K) δ 154.61, 148.43, 145.50, 143.02, 142.85, 139.27, 134.90, 129.70, 126.46, 124.21, 119.38, 112.92, 111.44, 41.83, 40.16, 32.92, 29.39, 26.14, 23.64, 14.51, 11.29. LRMS (FI) *m/z*, Calcd. for $C_{23}H_{23}Br_2NS_2$ (M^+): 534.96; found: 535.

N-(2-trimethylstannylpentaleno[2,1-b:3,4-b']-dithiophen-4(7H)-ylidene)-4-hexylaniline (9)



In a glovebox, **3** (648 mg, 1.50 mmol), Me_6Sn_2 (789 mg, 2.41 mmol) and $Pd(PPh_3)_4$ (260 mg, 0.225 mmol) were combined in a small vial and 10 mL of toluene was added. The vial was sealed, removed from the glovebox and heated in an oil bath at 80˚C for six hours. The mixture was poured into a separatory funnel containing 50 mL DI water and 50 mL of diethyl ether. The organic layer was further washed with 3 x 50 mL DI water. The organic layer was dried over anhydrous $MgSO_4$, and all volatiles were removed *in vacuo*. Purification by column chromatography on reverse phase silica using ethanol (containing 1% triethylamine) as the eluent gave 600 mg (1.17 mmol, 77.8 %) of the product. ^{1}H NMR (500 MHz, [d_2]-methylene chloride) δ =7.37 – 7.04 (m, 3.5H, isomer), 6.94 – 6.86 (m, 2H), 6.79 (d, J = 5.0 Hz, 0.4H, isomer), 6.05 – 5.95 (m, 0.8H, isomer), 2.67 – 2.44 (m, 2H), 1.73 – 1.54 (m, 2H), 1.46 – 1.28 (m, 6H), 0.91 (m, 3H), 0.59 – 0.08 (m, 9H). ^{13}C NMR (151 MHz, [d_6]-benzene, 298 K) δ 156.59, 156.43, 150.70, 150.50, 149.37, 149.05, 146.79, 146.72, 143.97, 143.57, 140.88, 140.32, 139.53, 139.45, 138.68, 138.54, 129.30, 129.22, 126.66, 126.45, 124.98, 124.70, 122.35, 122.23, 120.53, 120.48, 36.04, 36.02, 32.46, 32.35, 32.29, 32.12, 29.55, 29.51, 23.21, 14.52, -8.28, -8.39 (two isomers were observed). LRMS (FD) *m/z*, Calcd. for $C_{24}H_{29}NS_2Sn$ (M^+): 515.08; found: 515.

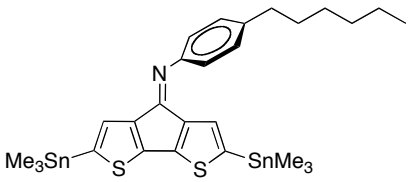
N-(2-trimethylstannylpentaleno[2,1-b:3,4-b']-dithiophen-4(7H)-ylidene)-4-4-(2-(2-ethylhexyloxy)-1,1,1,3,3,3-hexafluoropropan-2-yl)aniline (10)



In a glovebox, **4** (556 mg, 0.89 mmol), Me_6Sn_2 (466 mg, 1.42 mmol) and $Pd(PPh_3)_4$ (103 mg, 0.09 mmol) were combined in a small vial and 10 mL of toluene was added. The vial was sealed, removed from the glovebox and heated in an oil bath at 80˚C for six hours. The mixture

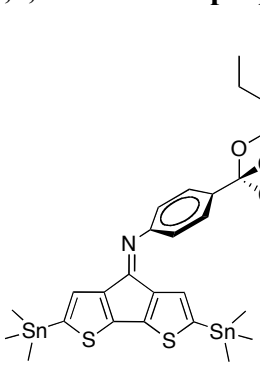
was poured into a separatory funnel containing 50 mL DI water and 50 mL of diethyl ether. The organic layer was further washed with 3 x 50 mL DI water. The organic layer was dried over anhydrous $MgSO_4$, and all volatiles were removed *in vacuo*. Purification by column chromatography on reverse phase silica using ethanol (containing 1% triethylamine) as the eluent gave 480 mg (0.68 mmol, 76%) of the product. ^{1}H NMR (600 MHz, [d_6]-benzene) δ 7.65 – 7.40 (m, 2.2H, isomer), 7.19 – 6.88 (m, 2.6H, isomer), 6.51 – 6.43 (m, 0.6H, isomer), 6.17 (d, J = 4.9 Hz, 0.4H, isomer), 6.07 (s, 0.4H, isomer), 5.97 – 5.87 (m, 0.4H, isomer), 3.62 – 3.42 (m, 2H), 1.55 (m, 1H), 1.46 – 1.11 (m, 8H), 0.92 – 0.76 (m, 6H), 0.23 – 0.06 (m, 9H). LRMS (FD) *m/z*, calcd. for $C_{29}H_{33}F_6NOS_2Sn$ (M^+): 709,09; found: 709.

N-(2,6-bis(trimethylstannyl)pentaleno[2,1-b:3,4-b']-dithiophen-4(7H)-ylidene)-4-hexylaniline (11)



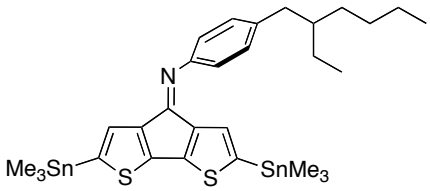
In a glovebox, **6** (687 mg, 1.34 mmol), Me_6Sn_2 (1.4 g, 4.28 mmol) and $Pd(PPh_3)_4$ (464 mg, 0.40 mmol) were combined in a small vial and 10 mL of toluene was added. The vial was sealed, removed from the glovebox and heated in an oil bath at 80˚C for six hours. The mixture was poured into a separatory funnel containing 50 mL DI water and 50 mL of diethyl ether. The organic layer was further washed with 3 x 50 mL DI water. The organic layer was dried over anhydrous $MgSO_4$, and all volatiles were removed *in vacuo*. Purification by column chromatography on reverse phase silica using ethanol (containing 1% triethylamine) as the eluent gave 675 mg (0.68 mmol, 75%) of the product. ^{1}H NMR (500 MHz, [d_2]-methylene chlroide) δ 7.29 (s, 1H), 7.20 (d, J = 8.2 Hz, 2H), 6.89 (d, J = 8.1 Hz, 2H), 5.96 (s, 1H), 2.71 – 2.52 (m, 2H), 1.68 – 1.60 (m, 2H), 1.42 – 1.27 (m, 6H), 0.93 – 0.89 (m, 3H), 0.41 (s, 9H), 0.24 (s, 9H). LRMS (FD) *m/z*, calcd. for $C_{27}H_{37}NS_2Sn_2$ (M^+): 677.04; found: 677.

N-(2,6-bis(trimethylstannyl)pentaleno[2,1-b:3,4-b']-dithiophen-4(7H)-ylidene)-4-4-(2-(2-ethylhexyloxy)-1,1,1,3,3,3-hexafluoropropan-2-yl)aniline (12)



In a glovebox, **7** (300 mg, 0.43 mmol), Me_6Sn_2 (447 mg, 1.38 mmol) and $Pd(PPh_3)_4$ (148 mg, 0.13 mmol) were combined in a small vial and 10 mL of toluene was added. The vial was sealed, removed from the glovebox and heated in an oil bath at 80˚C for six hours. The mixture was poured into a separatory funnel containing 50 mL DI water and 50 mL of diethyl ether. The organic layer was further washed with 3 x 50 mL DI water. The organic layer was dried over anhydrous $MgSO_4$, and all volatiles were removed *in vacuo*. Purification by column chromatography on reverse phase silica using ethanol (containing 1% triethylamine) as the eluent gave 302 mg (0.35 mmol, 81 %) of the product. ^{1}H NMR (600 MHz, [d_2]-methylene chloride) δ 7.60 (d, J = 8.2 Hz, 2H), 7.28 (s, 1H), 6.81 – 6.79 (m, 2H), 5.81 (s, 1H), 3.55 (m, 2H), 1.67 (m, 1H), 1.52 – 1.20 (m, 8H), 0.97 – 0.73 (m, 6H), 0.41 (s, 9H), 0.21 (s, 9H). LRMS (FD) *m/z*, calcd. for $C_{32}H_{41}F_6NOS_2Sn_2$ (M^+): 873.06; found 873.

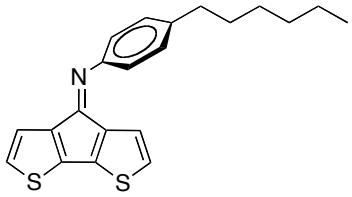
N-(2,6-bis(trimethylstannyl)pentaleno[2,1-b:3,4-b']-dithiophen-4(7H)-ylidene)-4-(2-ethylhexyl)aniline (13)



In a glovebox, **8** (260 mg, 0.48 mmol), Me_6Sn_2 (507 mg, 1.55 mmol) and $Pd(PPh_3)_4$ (102 mg, 0.10 mmol) were combined in a small vial and 10 mL of toluene was added. The vial was sealed, removed from the glovebox and heated in an oil bath at 80˚C for six hours. The mixture was poured into a separatory funnel containing 50 mL DI water and 50 mL of diethyl ether. The organic layer was further washed with 3 x 50 mL DI water. The organic layer was dried over anhydrous $MgSO_4$, and all volatiles were removed *in vacuo*. Purification by column chromatography on reverse phase silica using ethanol (containing 1% triethylamine) as the eluent gave 208 mg (0.29 mmol, 61 %) of the product. ^{1}H NMR (500 MHz, [d_2]-methylene chloride) δ 7.29 (s, 1H), 7.22 – 7.11 (m, 2H), 6.95 – 6.82 (m, 2H), 6.08 (s, 1H), 2.70 – 2.41 (m, 2H), 1.62 (m, 1H), 1.43 – 1.16 (m, 8H), 1.00 – 0.78 (m, 6H), 0.41 (s, 9H), 0.24 (s, 9H). LRMS (FI) *m/z*, calcd. for $C_{29}H_{41}NS_2Sn_2$ (M^+): 707.07; found 707.

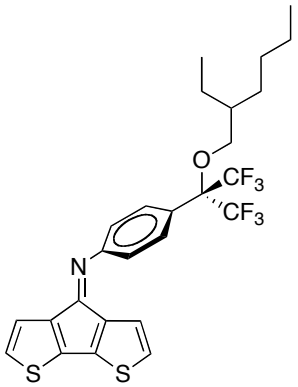
Synthesis of target compounds used in this study

N-(pentaleno[2,1-b:3,4-b']-dithiophen-4(7H)-ylidene)-4-hexylaniline (M1)



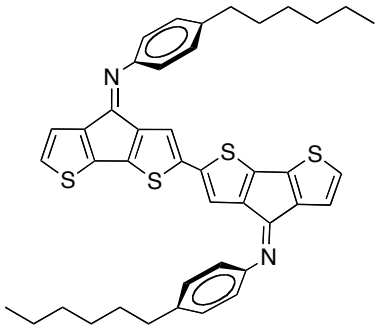
In a glovebox, a dry solution of 4-hexylaniline (507 mg, 2.86 mmol) and triethylamine (1.32 g, 13 mmol) in dichloromethane (10 ml) were chilled to – 35 °C. Titanium tetrachloride (493 mg, 2.60 mmol) in 1 mL toluene was added drop-wise over a period of 5 minutes to give a deep red solution, which was allowed to stir for an additional five minutes. A chilled solution of 4*H*-Cyclopenta-[2,1-*b*:3,4-*b'*]dithiophen-4-one (500 mg, 2.60 mmol) in dichloromethane (5 mL) was added at once. The solution was vigorously stirred, allowed to warm to room temperature and stirred overnight. Subsequently, 100 mL of diethyl ether was added and the resulting suspension was stirred over the course of an hour. The suspension was filtered through a pad of celite and all volatiles were removed *in vacuo*. Purification by column chromatography on silica using hexanes:chloroform (9:1, containing 1% triethylamine) as the eluent gave 902 mg (2.57 mmol, 99%) of the desired product as a red solid. ^{1}H NMR (600 MHz, [d_6]-benzene) δ = 7.22 (d, *J* = 4.8 Hz, 1H), 7.05 – 6.99 (m, 2H), 6.99 – 6.94 (m, 2H), 6.49 (d, *J* = 4.8 Hz, 1H), 6.18 (d, *J* = 5.0 Hz, 1H), 6.14 (d, *J* = 4.9 Hz, 1H), 2.55 – 2.47 (m, 2H), 1.60 – 1.46 (m, 2H), 1.34 – 1.16 (m, 6H), 0.99 – 0.80 (m, 3H). ^{13}C NMR (151 MHz, [d_6]-benzene) δ = 156.24, 150.10, 146.47, 146.27, 143.42, 139.39, 138.21, 129.11, 126.51, 125.06, 124.40, 122.08, 120.27, 35.84, 32.11, 31.92, 29.34, 23.03, 14.35. LRMS (FI) *m/z*, calcd. for $C_{21}H_{21}NS_2$ (M^+): 351.11; found 351. Anal. calcd. for $C_{21}H_{21}NS_2$: C, 71.75; H, 6.02; N, 3.98. Found: C, 72.00; H, 5.82; N, 4.19 %.

N-(pentaleno[2,1-b:3,4-b']-dithiophen-4(7H)-ylidene)-4-4-(2-(2-ethylhexyloxy)-1,1,1,3,3,3-hexafluoropropan-2-yl)aniline (M2)



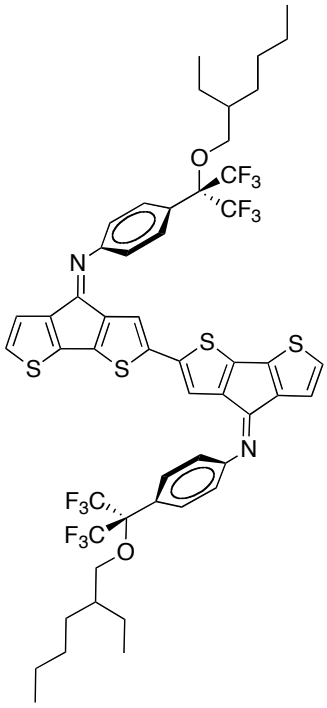
In the glove box, a dry solution of 4-(2-(2-ethylhexyloxy)-1,1,1,3,3,3-hexafluoropropan-2-yl)aniline (1.08 g, 2.64 mmol) and triethylamine (1.34 g, 13.14 mmol) in dichloromethane (10 ml) were chilled to – 35 °C. Titanium tetrachloride (0.50 mg, 2.65 mmol) in 1 mL toluene was added drop-wise over a period of 5 minutes to give a deep red solution, which was allowed to stir for an additional five minutes. A chilled solution of 4*H*-Cyclopenta-[2,1-*b*:3,4-*b'*]dithiophen-4-one (0.51 g, 2.64 mmol) in dichloromethane (5 mL) was added at once. The solution was vigorously stirred, allowed to warm to room temperature and stirred overnight. Subsequently, 100 mL of diethyl ether was added and the resulting suspension was stirred over the course of an hour. The suspension was filtered through a pad of celite and all volatiles were removed *in vacuo*. Purification by column chromatography using hexanes:CH_2Cl_2 (4:1) (containing 1% triethylamine) as the eluent gave 890 g (62 %) of the product as a red oil. ^{1}H NMR (600 MHz, [d_2]-methylene chloride) δ = 7.61 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 5.0 Hz, 1H), 7.19 (d, *J* = 4.7 Hz, 1H), 7.11 – 7.07 (m, 2H), 6.84 (d, *J* = 5.0 Hz, 1H), 5.87 (d, *J* = 5.0 Hz, 1H), 3.56 – 3.52 (m, 2H), 1.70 – 1.64 (m, 1H), 1.56 – 1.24 (m, 8H), 0.94 – 0.87 (m, 6H).^{13}C NMR (151 MHz, [d_2]-methylene chloride) δ = 156.53, 153.09, 146.46, 145.18, 143.73, 137.39, 128.96, 126.75, 125.47, 124.23, 122.67 (q), 121.70, 121.33, 119.71, 82.51 (m), 68.69, 40.07, 30.12, 28.86, 23.59, 22.91, 13.74, 10.74. LRMS (FI) *m/z*, calcd. for $C_{26}H_{25}F_6NOS_2$ = 545.13; found 545. Anal. calcd. for $C_{26}H_{25}F_6NOS_2$: C, 57.24; H, 4.62; N, 2.57. Found: C, 57.4; H, 4.7; N, 2.7 %.

Compound D1



Procedure 1: In a glovebox, a microwave tube was charged with 85 mg (0.198 mmol) of **3**, 32 mg (0.10 mmol) of Me_6Sn_2, and 23 mg (0.02 mmol) of $Pd(PPh_3)_4$; 1 ml of xylenes was added. The tube was sealed, removed from the glovebox and subjected to the following reaction conditions in a microwave reactor: 15 minutes at 120 ˚C, 15 minutes at 140 ˚C, 10 minutes at 150 ˚C and 10 minute at 170 ˚C. After this time the reaction was allowed to cool leaving a deep purple liquid containing some solid material. The mixture was dissolved in chloroform containing 1% triethylamine, filtered through a pad of celite and all volatiles removed *in vacuo*. Purification by column chromatography on base-treated silica using hexanes:chloroform (1:4 containing 1% triethylamine) as the eluent gave 62 mg (45 %) of the product. ***Procedure 2:*** In a glovebox, a microwave tube was charged with 80 mg (0.198 mmol) of **3**, 100 mg (0.208 mmol, 1.05 equivalents) of **9**, and 22 mg (0.02 mmol) of $Pd(PPh_3)_4$; 1 ml of xylenes was added. The tube was sealed, removed from the glovebox and subjected to the following reaction conditions in a microwave reactor: 15 minutes at 120 ˚C, 15 minutes at 140 ˚C, 10 minutes at 150 ˚C and 10 minute at 170 ˚C. After this time the reaction was allowed to cool leaving a viscous liquid containing some solid material. The mixture was dissolved in chloroform containing 1% triethylamine, filtered through a pad of celite and all volatiles removed *in vacuo*. Purification by column chromatography on base-treated silica using hexanes:chloroform (1:4 containing 1% triethylamine) as the eluent gave 79 g (57 %) of the product. ^{1}H NMR (500 MHz, [d_2]-methylene chloride) δ = 7.35 (s, 0.5H, isomers), 7.30 – 7.12 (m, 6.2H, isomers), 6.98 – 6.79 (m, 4.9H, isomers), 6.11 – 5.99 (m, 1.5H, isomers), 5.88 (s, 1H), 2.81 – 2.47 (m, 4H), 1.82 – 1.59 (m, 4H), 1.45 – 1.27 (m, 12H), 0.99 – 0.80 (m, 6H). ^{13}C NMR (151 MHz, [d_2]-methylene chloride) δ = 156.50, 156.45, 156.43, 156.33, 149.58, 149.53, 149.46, 149.40, 146.50, 146.43, 146.37, 146.30, 145.84, 145.77, 144.77, 144.75, 143.84, 143.70, 142.04, 141.81, 140.65, 140.62, 140.52, 139.36, 138.96, 138.35, 138.15, 137.96, 137.89, 137.83, 137.51, 129.47, 129.41, 129.39, 127.63, 127.59, 126.22, 126.17, 124.49, 124.48, 121.90, 120.27, 120.25, 120.21, 117.72, 117.62, 36.08, 36.06, 36.00, 35.98, 32.43, 32.42, 32.39, 32.37, 32.32, 32.18, 29.53, 29.51, 23.28, 23.26, 23.23, 14.52, 14.51, 14.44 (isomers were obtained). LRMS (FD) *m/z*, calcd. for $C_{42}H_{40}N_2S_4$ = 700.21; found 700. Anal. calcd. for $C_{42}H_{40}N_2S_4$: C, 71.96; H, 5.75; N, 4.00. Found: C, 71.70; H, 5.98; N, 4.14 %.

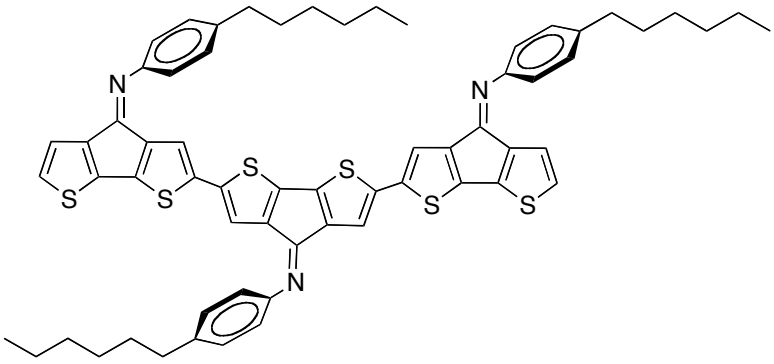
Compound D2



Procedure 1: In a glovebox, a microwave tube was charged with 190 mg (0.30 mmol) of **4**, and 160 mg (0.14 mmol) of Me_6Sn_2 and 35 mg (0.03 mmol) of $Pd(PPh_3)_4$. 1 ml of xylenes was added and the tube was sealed, removed from the glovebox and subjected to the following reaction conditions in a microwave reactor: 15 minutes at 120 ˚C, 15 minutes at 140 ˚C, 10 minutes at 150 ˚C and 10 minute at 170 ˚C. After this time the reaction was allowed to cool leaving a viscous deep purple liquid containing some solid material. The mixture was dissolved in chloroform containing 1% triethylamine and filtered through a pad of celite. All volatiles were removed *in vacuo*. Purification by column chromatography on base-treated silica using hexane:chloroform (2:1) (containing 1% triethylamine) as the eluent gave 160 mg (48 %) of the product. ***Procedure 2:*** In a glovebox, a microwave tube was charged with 88 mg (0.14 mmol) of **4**, and 127 mg (0.18 mmol) of **10** and 32 mg (0.03 mmol) of $Pd(PPh_3)_4$. 1 ml of xylenes was added and the tube was sealed, removed from the glovebox and subjected to the following reaction conditions in a microwave reactor: 15 minutes at 120 ˚C, 15 minutes at 140 ˚C, 10 minutes at 150 ˚C and 10 minute at 170 ˚C. After this time the reaction was allowed to cool leaving a viscous deep purple liquid containing some solid material. The mixture was dissolved in chloroform containing 1% triethylamine and filtered through a pad of celite. All volatiles were removed *in vacuo*. Purification by column chromatography on base-treated silica using hexane:chloroform (2:1) (containing 1% triethylamine) as the eluent gave 190 mg (62 %) of the product. ^{1}H NMR (500 MHz, [d_2]-methylene chloride) δ = 7.74 – 7.51 (m, 4H), 7.36 (s, 0.5H, isomers), 7.28 – 7.16 (m, 1.6H, isomers), 7.16 – 7.04 (m, 4.4H, isomers), 6.91 – 6.79 (m, 1.1H, isomers), 5.93 – 5.85 (m, 1.1H, isomers), 5.82 (s, 0.5H, isomers), 5.67 (s, 0.4H, isomers), 3.64 – 3.48 (m, 4H), 1.73 – 1.61 (m, 2H), 1.57 – 1.20 (m, 16H), 0.98 – 0.80 (m, 12H). ^{13}C NMR (151 MHz, [d_6]-benzene) δ 156.97, 156.79, 156.59, 156.43, 154.16, 154.01, 153.81, 153.69, 146.78, 146.55, 146.22, 145.41, 145.21, 144.96, 144.07, 143.83, 142.29, 142.14, 139.26, 138.13, 138.09,

137.96, 137.50, 137.47, 129.46, 126.35, 126.22, 124.84, 124.79, 124.42, 123.70, 123.64, 122.51, 122.02, 121.95, 120.23, 120.18, 120.13, 120.07, 119.92, 118.18, 117.86, 83.39, 83.19, 68.96, 40.51, 40.49, 40.46, 31.98, 30.58, 30.56, 29.44, 29.32, 29.30, 29.27, 23.99, 23.30, 23.07, 14.35, 14.25, 14.24, 11.26, 11.23, 11.19 (isomers were obtained). LRMS (FD) *m/z*, calcd. for $C_{52}H_{48}F_{12}N_2O_2S_4$ = 1088.24; found 1088. Anal. calcd. for $C_{52}H_{48}F_{12}N_2O_2S_4$: C, 57.34; H, 4.44; N, 2.57. Found: C, 57.3; H, 4.7; N, 2.7 %.

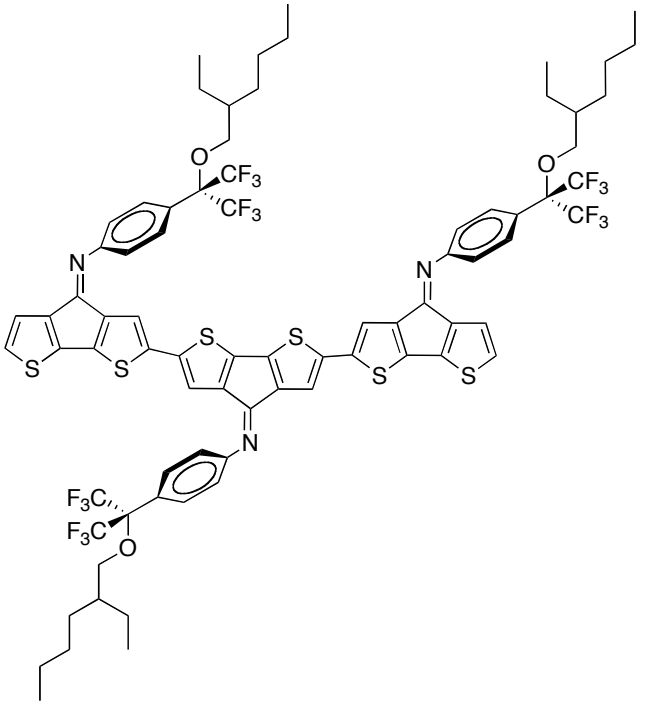
Compound T1



In a glovebox, a microwave tube was charged with 94 mg (1.85 mmol) of **6**, 200 mg (3.89 mmol, 2.1 equivalents) of **11**, and 43 mg of $Pd(PPh_3)_4$. 1 ml of xylenes was added. The tube was sealed, removed from the glovebox and subjected to the following reaction conditions in a microwave reactor: 5 minutes at 120 ˚C, 5 minutes at 140 ˚C, 30 minutes at 170 ˚C and 1 minute at 190 ˚C. After this time the reaction was allowed to cool leaving a black liquid containing some solid material. The mixture was dissolved in chloroform containing 1% triethylamine, then precipitated into methanol and collected via filtration. Purification by column chromatography on base-treated silica using hexanes:dichloromethane (2:1, containing 1% triethylamine) as the eluent gave 107 g (55 %) of the product. ^{1}H NMR (500 MHz, [d_2]-methylene chloride) δ 7.42 – 7.05 (m, 10H), 7.03 – 6.71 (m, 8H), 6.06 – 5.99 (m, 2H), 5.90 – 5.87 (m, 0.5H), 2.75 – 2.59 (m, 6H), 1.81 – 1.57 (m, 6H), 1.47 – 1.17 (m, 18H), 0.95 – 0.77 (m, 9H). ^{13}C NMR (151 MHz, [d_1]-chloroform) δ = 156.44, 156.41, 156.39, 156.36, 156.34, 156.27, 156.24, 156.18, 149.16, 149.14, 149.12, 149.04, 148.99, 148.91, 146.34, 146.31, 146.24, 146.20, 146.12, 146.09, 146.07, 146.06, 146.01, 146.00, 145.79, 145.72, 145.66, 145.60, 145.55, 145.51, 145.49, 144.74, 144.69, 144.64, 144.60, 144.49, 144.39, 144.36, 143.62, 143.58, 143.52, 143.48, 142.47, 142.42, 142.34, 142.21, 141.95, 141.89, 141.68, 141.63, 141.59, 141.56, 141.42, 141.32, 140.72, 140.68, 140.59, 140.55, 140.53, 140.41, 140.40, 140.36, 140.34, 140.30, 140.28, 140.26, 140.21, 140.19, 140.16, 139.72, 139.69, 139.35, 139.30, 139.07, 138.97, 138.72, 138.65, 138.63, 138.30, 138.24, 138.14, 138.04, 138.01, 137.84, 137.77, 137.75, 137.73, 137.70, 137.67, 137.62, 137.58, 137.55, 137.26, 137.16, 129.29, 129.26, 129.24, 129.21, 129.18, 129.17, 127.27, 127.21, 125.81, 125.79, 124.42, 121.94, 121.92, 120.25, 120.21, 120.18, 120.04, 119.94, 117.65, 117.53, 117.50, 117.42, 117.33, 117.30, 117.25, 35.95, 35.92, 35.89, 35.85, 35.84, 32.25, 32.21, 32.19, 32.17, 32.13, 32.09, 32.04, 32.03, 31.87, 29.30, 29.26, 23.09, 23.06, 23.04, 23.00, 14.58, 14.57, 14.54, 14.52, 14.46, 14.44 (isomers

were obtained). LRMS (FD) *m/z*, calcd. for $C_{63}H_{59}N_3S_6$ = 1049,30; found 1049. Anal. calcd. for $C_{63}H_{59}N_3S_6$: C, 72.03; H, 5.66; N, 4.00. Found: C, 72.1; H, 5.99; N, 4.10 %.

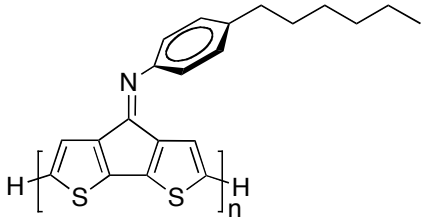
Compound T2



In a glovebox, a microwave tube was charged with 97 mg (0.14 mmol) of **7**, 200 mg (0.28 mmol) of **10**, and 12 mg (0.01 mmol) of $Pd(PPh_3)_4$; 1 ml of xylenes was added. The tube was sealed, removed from the glovebox and subjected to the following reaction conditions in a microwave reactor: 5 minutes at 120 ˚C, 5 minutes at 140 ˚C, 30 minutes at 170 ˚C and 1 minute at 190 ˚C. After this time the reaction was allowed to cool leaving a black colored liquid containing some solid material. The mixture was dissolved in chloroform, then precipitated into methanol and collected via filtration. Purification by column chromatography on base-treated silica using hexane:chloroform (2:1) (containing 1% triethylamine) as the eluent gave 114 mg g (50 %) of the product ^{1}H NMR (600 MHz, [d_2]-methylene chloride) δ = 7.85 – 7.48 (m, 6H), 7.48 – 6.41 (m, 10H), 6.00 – 5.39 (m, 4H), 3.70 – 3.47 (m, 6H), 1.74 – 1.62 (m, 3H), 1.52 – 1.14 (m, 24H), 0.99 – 0.77 (m, 18H). ^{13}C NMR (151 MHz, [d_2]-methylene chloride) δ = 157.15, 157.07, 157.00, 156.96, 156.86, 156.80, 156.77, 156.70, 156.66, 156.63, 156.60, 154.04, 153.97, 153.82, 153.78, 153.74, 153.70, 153.58, 153.55, 153.51, 153.47, 153.45, 153.39, 146.91, 146.68, 146.54, 146.08, 146.05, 145.80, 145.66, 145.60, 145.50, 145.39, 145.33, 145.29, 145.25, 145.15, 145.11, 144.94, 144.91, 144.55, 144.28, 144.15, 144.09, 142.47, 142.34, 142.31, 142.16, 142.07, 140.24, 140.17, 139.65, 139.49, 139.43, 139.29, 139.02, 138.97, 138.80, 138.72, 138.33, 138.29, 138.27, 138.16, 138.10, 137.89, 137.78, 137.70, 137.65, 137.61, 137.57, 137.54, 137.51, 129.67, 129.59, 128.08, 128.05, 128.03, 127.86, 127.86, 126.67, 126.63, 126.23, 126.16, 125.33, 125.30, 125.27, 125.14,

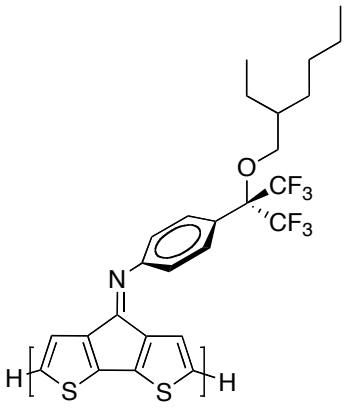
125.11, 125.07, 125.03, 124.32, 124.28, 124.26, 124.24, 123.98, 123.90, 123.85, 122.38, 122.37, 122.34, 122.32, 121.89, 121.86, 121.85, 121.84, 121.81, 121.68, 120.46, 120.40, 120.34, 120.31, 120.26, 120.22, 120.19, 120.14, 119.38, 119.35, 119.30, 117.75, 117.54, 117.46, 117.42, 117.36, 117.29, 83.31, 83.12, 82.93, 69.33, 40.73, 40.70, 40.69, 40.69, 30.74, 30.74, 30.72, 30.70, 30.67, 29.53, 29.50, 29.47, 24.20, 24.15, 23.54, 23.53, 14.38, 14.35, 11.46, 11.45, 11.44, 11.41, 11.36, 11.35 (isomers were obtained). LRMS (FD) *m/z*, calcd. for $C_{78}H_{71}F_{18}N_3O_3S_6$ = 1631.35; found 1631. Anal. calcd. for $C_{78}H_{71}F_{18}N_3O_3S_6$: C, 57.38; H, 4.38; N, 2.57. Found: C, 57.7; H, 4.5; N, 2.7 %.

Polymer P1



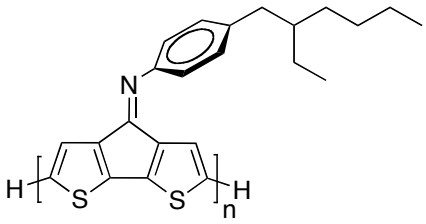
In a glovebox, a microwave tube was charged with 147 mg (0.29 mmol) of **6**, 192 mg (0.28 mmol) of **11**, and 27 mg (0.02 mmol) of $Pd(PPh_3)_4$; 1 mL of xylenes was added. The tube was sealed, removed from the glovebox and subjected to following reaction conditions in a microwave reactor: 80 °C for 5 min, 120 °C for 5 min, 150 °C for 2 min, and 180 °C for 30 min. After this time the reaction was allowed to cool leaving a viscous liquid with some solid material. The mixture was dissolved in in 1,2-dichlorobenzene, then precipitated in methanol and collected in a cellulose extraction thimble. The material was washed successively with methanol (12h), acetone (6h), and hexane (4h). The polymer comes out with chloroform (within 6h) from the thimble. Drying under reduced pressure gave 79 mg (78 %) of **P1** as black solid. Analysis via GPC at room temperature in chloroform relative to polystyrene standards resulted in M_n = 1498 g mol^{-1} and PDI = 1.2. ^{1}H NMR (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 373 K) δ = 7.40 – 6.8 (m, 5H), 6.18 (1H, partly overwhelmed by solvent signal), 2.83 – 2.68 (m, 2 H), 1.86 – 0.81 (m, 11H).

Polymer P2



In a glovebox, a microwave tube was charged with 110 mg (0.16 mmol) of **7**, 150 mg (0.17 mmol) of **12**, and 7 mg (0.01 mmol) of $Pd(PPh_3)_4$; 1 mL of xylenes was added. The tube was sealed, removed from the glovebox and subjected to following reaction conditions in a microwave reactor: 80 °C for 5 min, 120 °C for 5 min, 150 °C for 2 min, and 180 °C for 30 min. After this time the reaction was allowed to cool leaving a viscous liquid with some solid material. The mixture was dissolved in 1,2-dichlorobenzene, then precipitated in methanol and collected in a cellulose extraction thimble. The material was washed successively with methanol (12h), acetone (6h), and hexane (4h). The polymer was washed off the thimble with chloroform (within 6h). Drying under reduced pressure gave 72 mg (85 %) of **P2** as black solid. Analysis via GPC at room temperature in chloroform relative to polystyrene standards resulted in M_n = 18673 g mol^{-1} and PDI = 1.9. ^{1}H NMR (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 373 K) δ = 7.85 – 6.00 (m, 5 H), 5.80 (1H, partly overwhelmed by solvent signal), 3.81 – 3.60 (m, 2H), 1.75 – 1.29 (m, 9H), 1.17 – 0.64 (m. 6H).

Polymer P3



In a glovebox, a microwave tube was charged with 77 mg (0.14 mmol) of **8**, 122 mg (0.17 mmol) of **13**, and 7 mg (0.01 mmol) of $Pd(PPh_3)_4$; 1 mL of xylenes was added. The tube was sealed, removed from the glovebox and subjected to following reaction conditions in a microwave reactor: 80 °C for 5 min, 120 °C for 5 min, 150 °C for 2 min, and 180 °C for 30 min. After this time the reaction was allowed to cool leaving a viscous liquid with some solid material. The mixture was dissolved in 1,2-dichlorobenzene, then precipitated in methanol and collected in a cellulose extraction thimble. The material was washed successively with methanol (12h), acetone

(6h), and hexane (4h). The polymer was washed off the thimble with chloroform (within 6h). Drying under reduced pressure gave 50 mg (87 %) of **P3** as black solid. Analysis via GPC at room temperature in chloroform relative to polystyrene standards resulted in M_n = 49959 g mol^{-1} and PDI = 2.7. ^{1}H NMR (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 373 K) δ = 7.46 – 6.76 (m, 5H), 6.21 (1H, partly overwhelmed by solvent signal), 2.90 – 2.39 (m, 2H), 1.88 – 0.75 (m, 15H).

^{1}H NMR Spectra of molecules and polymers used in this study

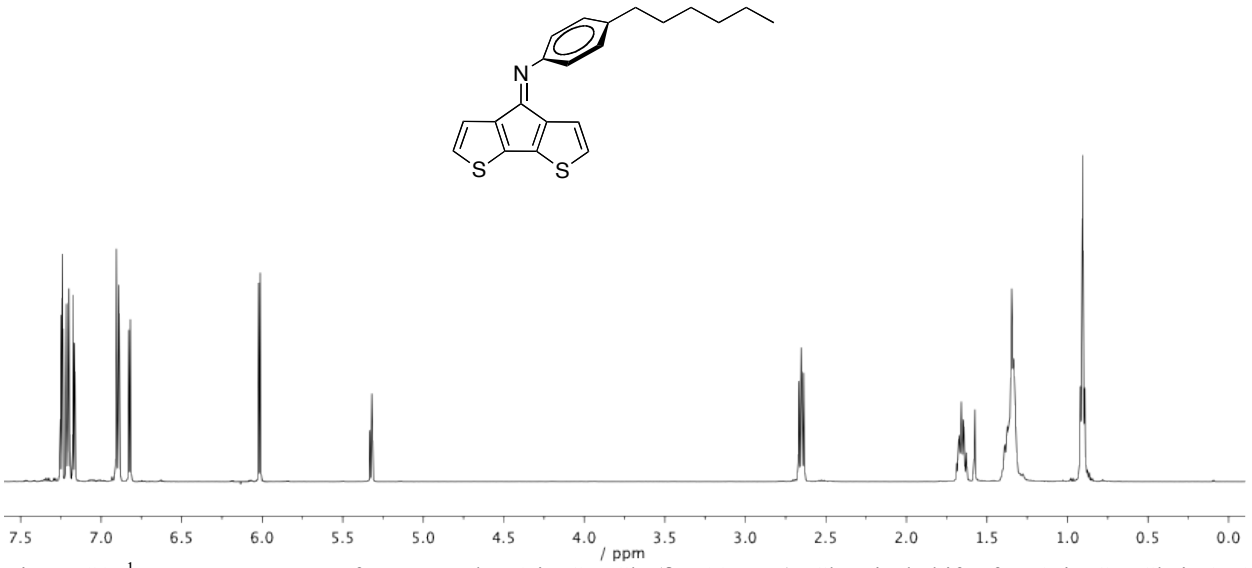


Figure S1. ^{1}H NMR spectrum of compound **M1** in CD_2Cl_2 (δ 5.33 ppm). Chemical shift of H_2O in CD_2Cl_2 is 1.52 ppm.

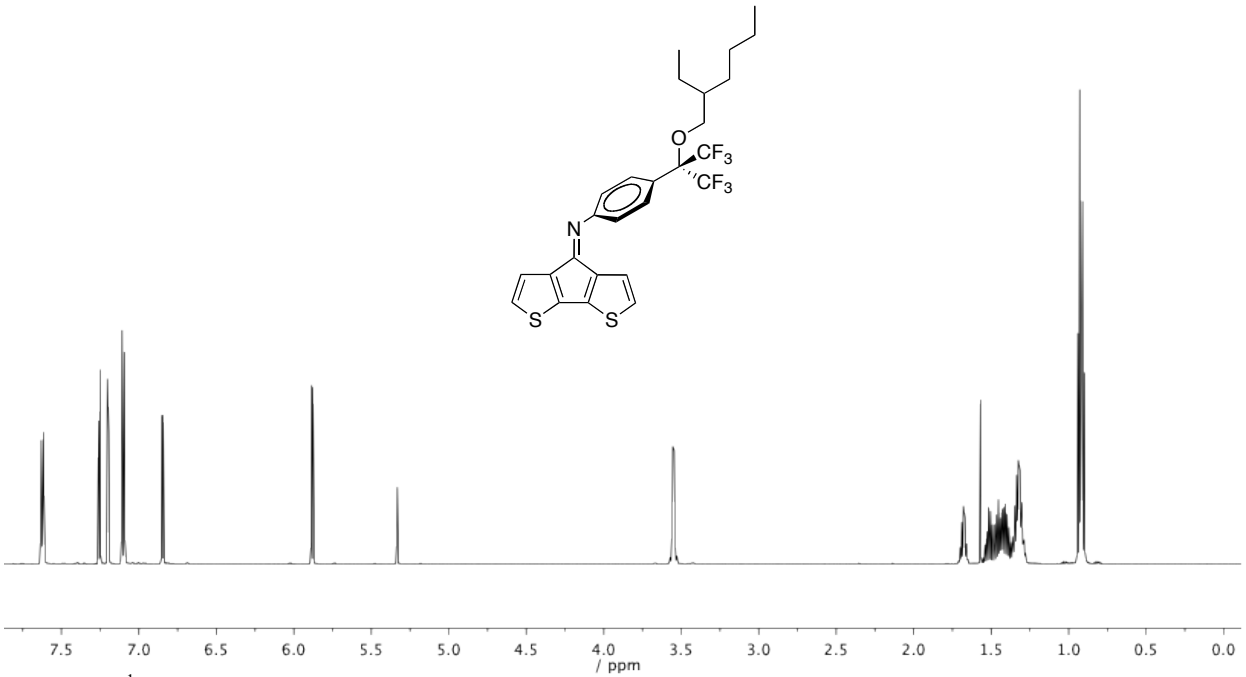


Figure S2. ^{1}H NMR spectrum of compound **M2** in CD_2Cl_2 (δ 5.33 ppm). Chemical shift of H_2O in CD_2Cl_2 is 1.52 ppm.

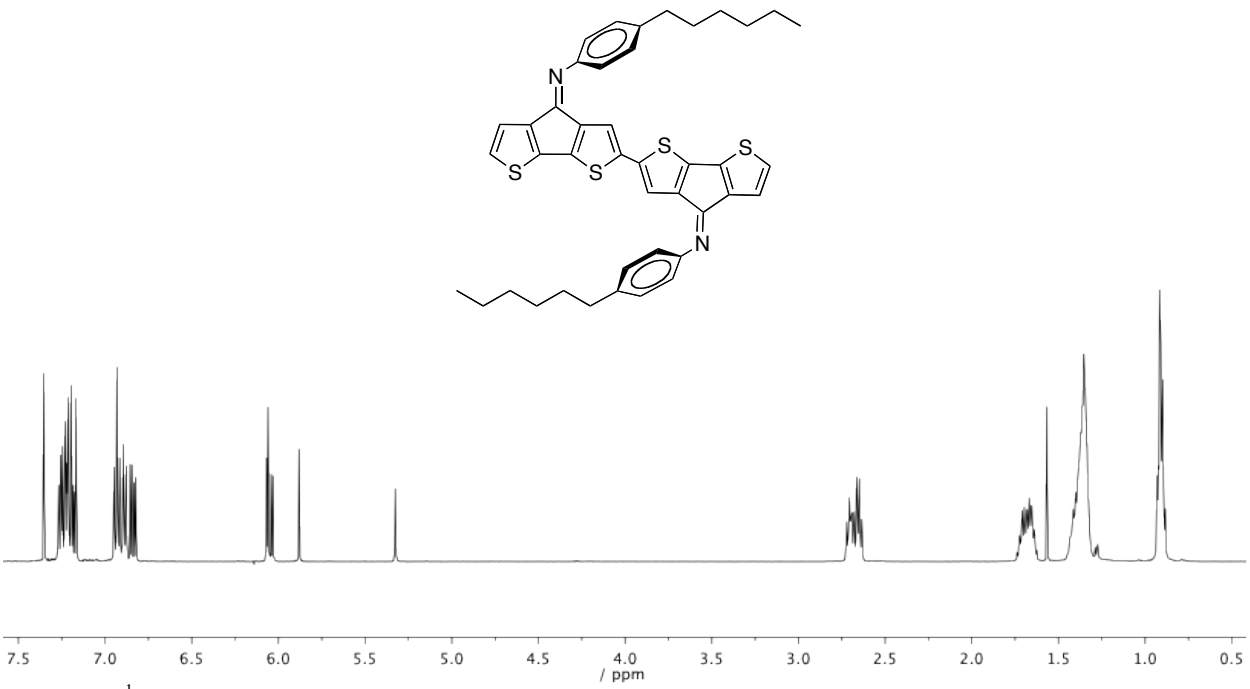


Figure S3. ^{1}H NMR spectrum of compound **D1** in CD_2Cl_2 (δ 5.33 ppm). Chemical shift of H_2O in CD_2Cl_2 is 1.52 ppm.

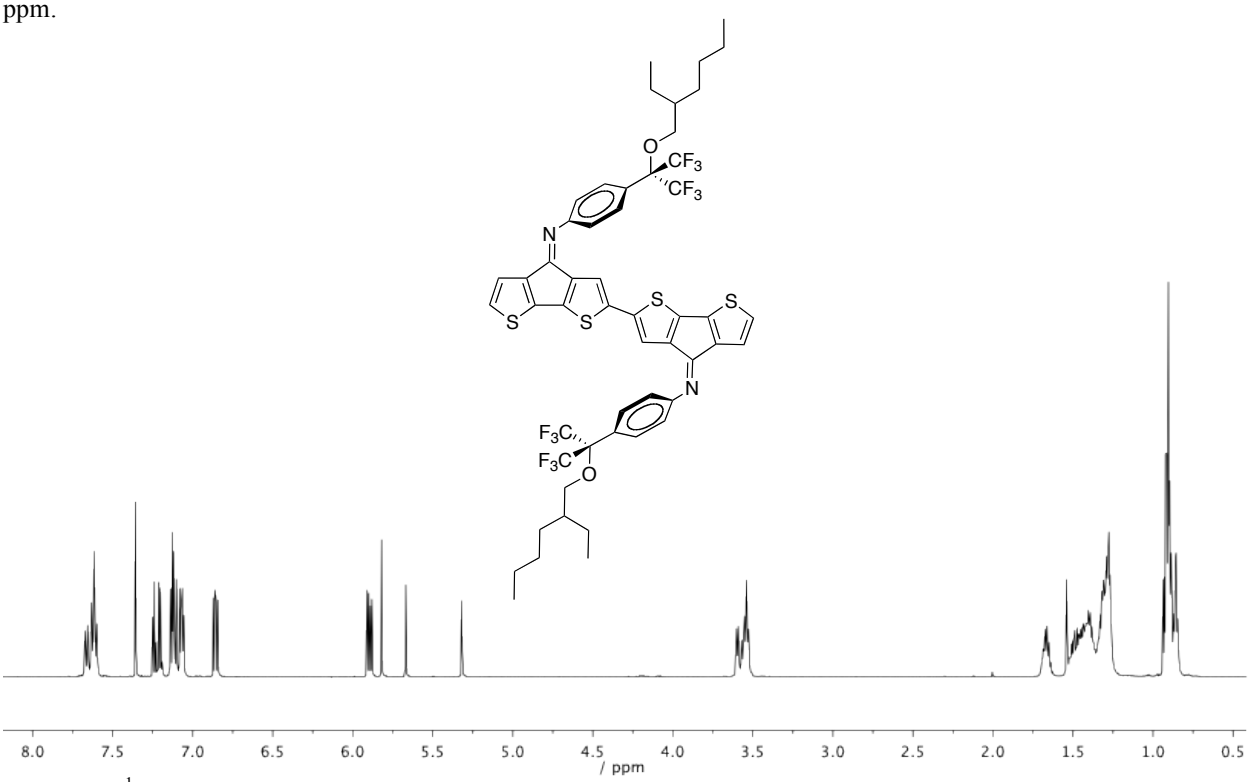


Figure S4. ^{1}H NMR spectrum of compound **D2** in CD_2Cl_2 (δ 5.33 ppm). Chemical shift of H_2O in CD_2Cl_2 is 1.52 ppm.

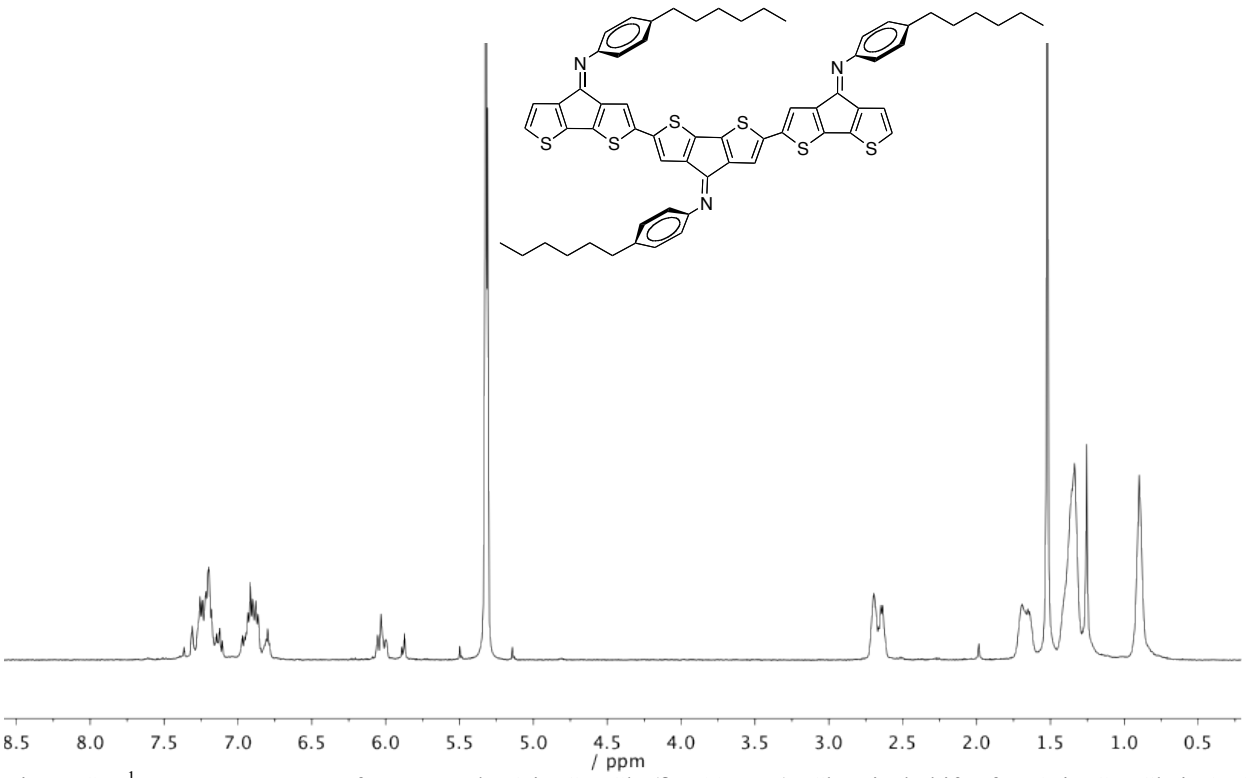


Figure S5. ^{1}H NMR spectrum of compound **T1** in CD_2Cl_2 (δ 5.33 ppm). Chemical shift of H_2O in CD_2Cl_2 is 1.52 ppm.

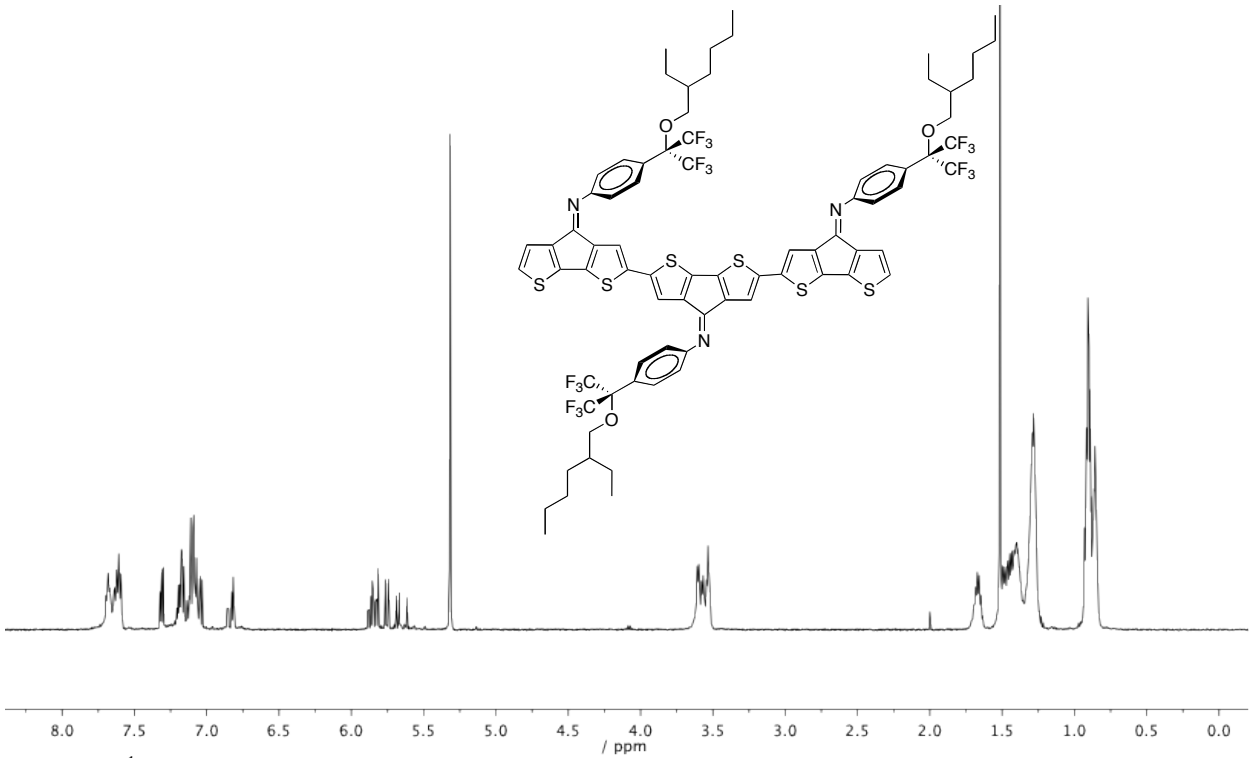


Figure S6. ^{1}H NMR spectrum of compound **T2** in CD_2Cl_2 (δ 5.33 ppm). Chemical shift of H_2O in CD_2Cl_2 is 1.52 ppm.

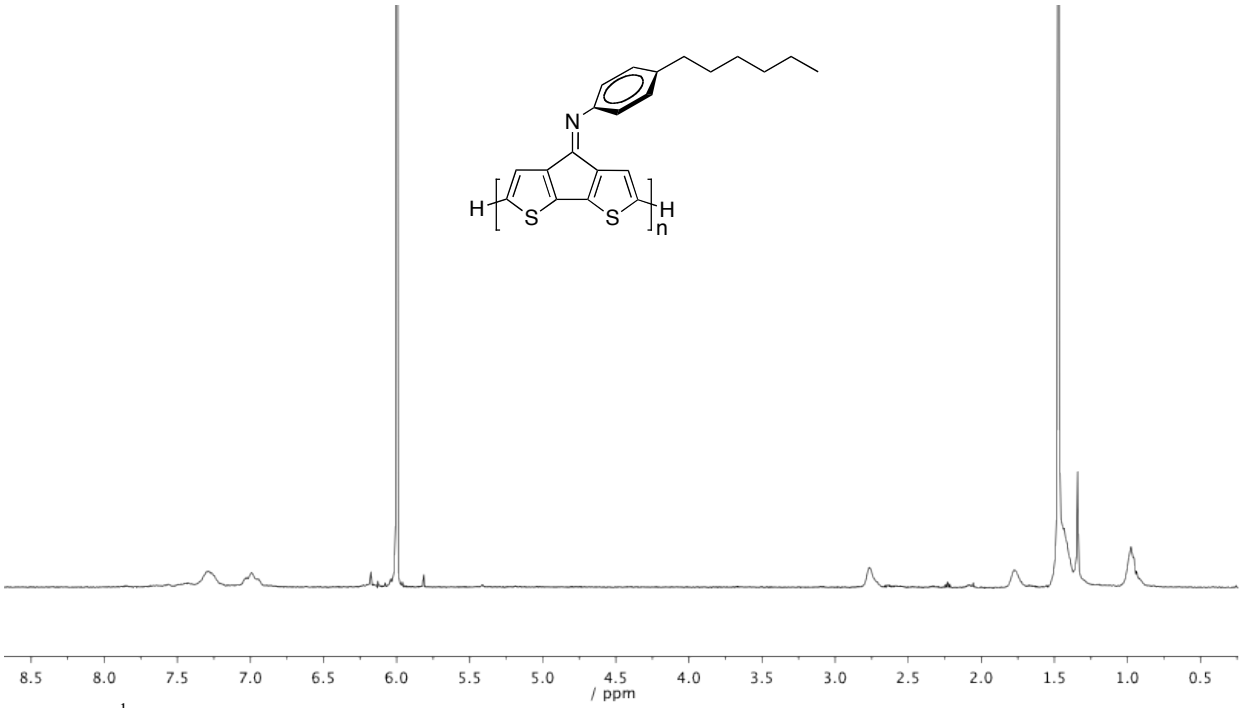


Figure S7. ^{1}H NMR spectrum of **P1** in 1,1,2,2-tetrachloroethane (δ 6.00 ppm) at 100 °C. Chemical shift of H_2O in TCE is 1.5 ppm.

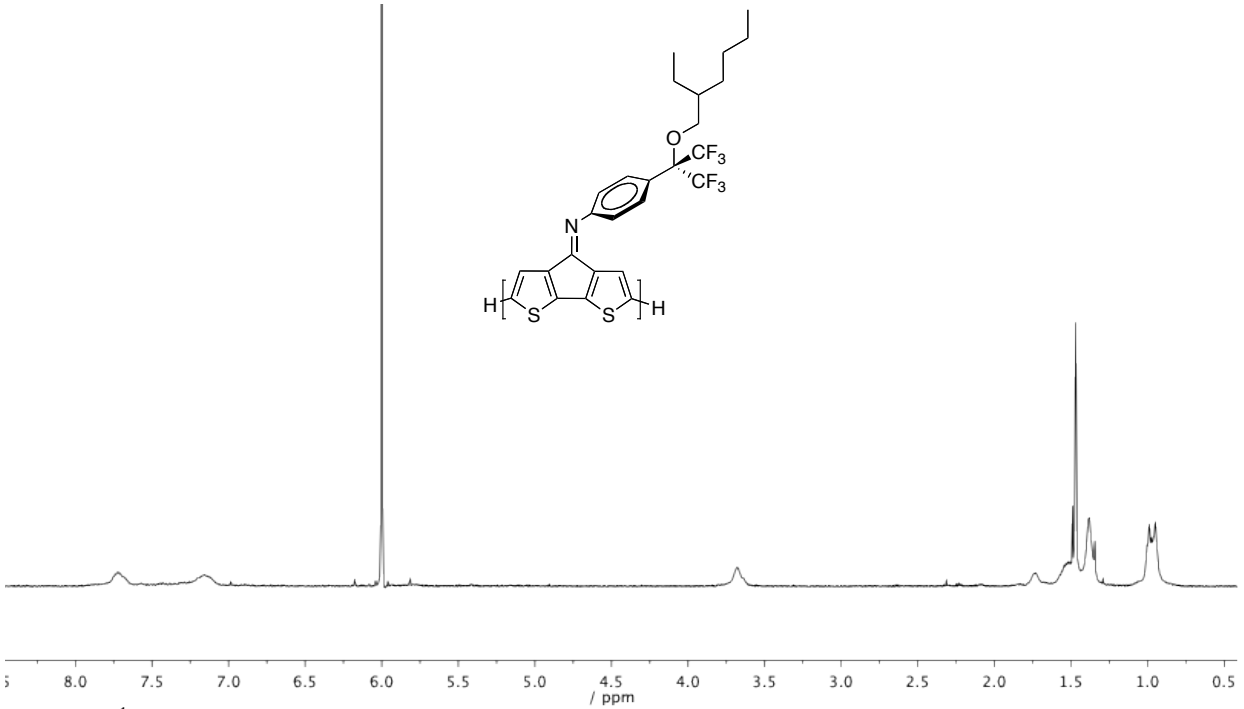


Figure S8. ^{1}H NMR spectrum of **P2** in 1,1,2,2-tetrachloroethane (δ 6.00 ppm) at 100 °C. Chemical shift of H_2O in TCE is 1.5 ppm.

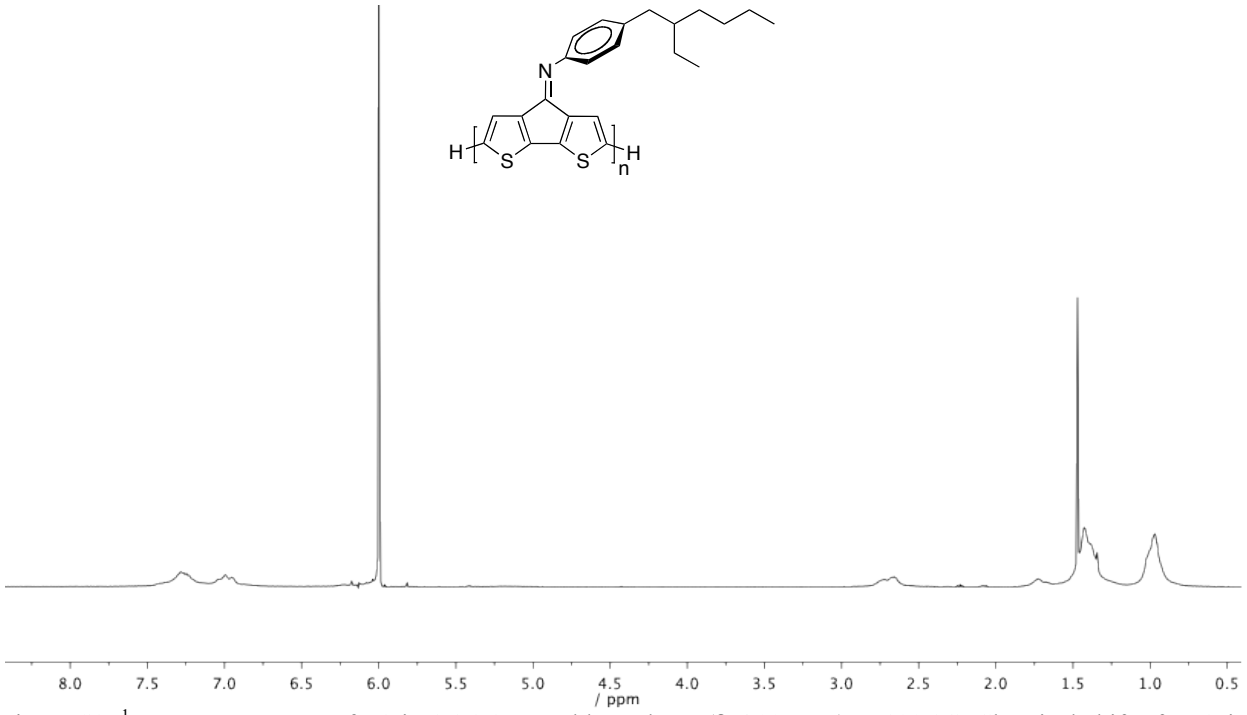


Figure S9. ^{1}H NMR spectrum of **P3** in 1,1,2,2-tetrachloroethane (δ 6.00 ppm) at 100 °C. Chemical shift of H_2O in TCE is 1.5 ppm.

Additional DFT Results

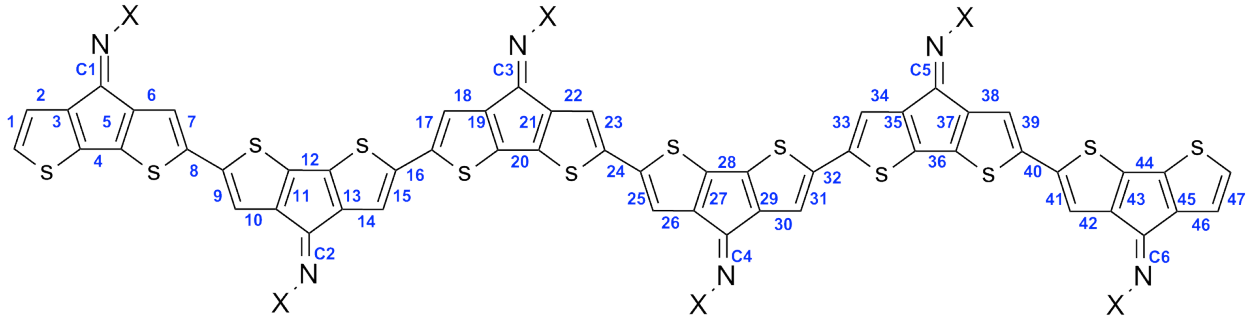


Figure S10. Bond numbering scheme used in bond-length analysis.

Table S1. Bond lengths in the S_0 state for M1', M2', M1'H, and M2'H as determined at the B3LYP/6-31G(d,p) level of theory. Bond numbering scheme is provided in Figure S10.

	M1'	M2'	Δ(M2'-M1')	M1'H	Δ(M1'H-M1')	M2'H	Δ(M2'H-M2')
1	1.371	1.372	0.001	1.372	0.001	1.372	0.000
2	1.419	1.419	0.000	1.419	0.000	1.419	0.000
3	1.384	1.384	0.000	1.382	-0.002	1.381	-0.003
4	1.451	1.452	0.001	1.448	-0.003	1.448	-0.004
5	1.391	1.390	-0.001	1.383	-0.008	1.383	-0.007
6	1.424	1.424	0.000	1.421	-0.003	1.421	-0.003
7	1.370	1.371	0.001	1.373	0.003	1.373	0.002
C1	1.283	1.282	-0.001	1.455	0.172	1.455	0.173

Table S2. Bond lengths in the S_0 state for D1', D2', D1'H, and D2'H as determined at the B3LYP/6-31G(d,p) level of theory. Bond numbering scheme is provided in Figure S10.

	D1'	D2'	Δ(D2'-D1')	D1'H	Δ(D1'H-D1')	D2'H	Δ(D2'H-D2')
1	1.372	1.372	0.000	1.373	0.001	1.373	0.001
2	1.418	1.417	-0.001	1.418	0.000	1.419	0.002
3	1.386	1.387	0.001	1.384	-0.002	1.385	-0.002
4	1.447	1.449	0.002	1.443	-0.004	1.443	-0.006
5	1.392	1.390	-0.002	1.385	-0.007	1.384	-0.006
6	1.416	1.414	-0.002	1.412	-0.004	1.410	-0.004
7	1.385	1.385	0.000	1.387	0.002	1.387	0.002
8	1.443	1.442	-0.001	1.442	-0.001	1.442	0.000
9	1.386	1.386	0.000	1.387	0.001	1.387	0.001
10	1.410	1.410	0.000	1.410	0.000	1.412	0.002
11	1.385	1.385	0.000	1.384	-0.001	1.385	0.000
12	1.447	1.448	0.001	1.443	-0.004	1.443	-0.005
13	1.393	1.392	-0.001	1.385	-0.008	1.384	-0.008
14	1.424	1.423	-0.001	1.420	-0.004	1.418	-0.005
15	1.371	1.371	0.000	1.373	0.002	1.373	0.002
C1	1.282	1.281	-0.001	1.454	0.172	1.455	0.174
C2	1.282	1.282	0.000	1.454	0.172	1.454	0.172

Table S3. Bond lengths in the S_0 state for T1', T2', T1'H, and T2'H as determined at the B3LYP/6-31G(d,p) level of theory. Bond numbering scheme is provided in Figure S10.

	T1'	T2'	Δ(T2'-T1')	T1'H	Δ(T1'H-T1')	T2'H	Δ(T2'H-T2')
1	1.371	1.372	0.001	1.373	0.002	1.373	0.001
2	1.423	1.417	-0.006	1.418	-0.005	1.418	0.001
3	1.393	1.387	-0.006	1.384	-0.009	1.384	-0.003
4	1.446	1.449	0.003	1.443	-0.003	1.443	-0.006
5	1.385	1.390	0.005	1.385	0.000	1.385	-0.005
6	1.410	1.413	0.003	1.411	0.001	1.411	-0.002
7	1.387	1.386	-0.001	1.388	0.001	1.388	0.002
8	1.441	1.441	0.000	1.440	-0.001	1.440	-0.001
9	1.386	1.387	0.001	1.389	0.003	1.389	0.002
10	1.414	1.408	-0.006	1.408	-0.006	1.408	0.000
11	1.395	1.388	-0.007	1.386	-0.009	1.386	-0.002
12	1.441	1.442	0.001	1.438	-0.003	1.438	-0.004
13	1.388	1.395	0.007	1.388	0.000	1.387	-0.008
14	1.408	1.413	0.005	1.410	0.002	1.410	-0.003
15	1.387	1.387	0.000	1.389	0.002	1.389	0.002
16	1.441	1.442	0.001	1.440	-0.001	1.440	-0.002
17	1.386	1.387	0.001	1.388	0.002	1.388	0.001
18	1.415	1.409	-0.006	1.409	-0.006	1.409	0.000
19	1.393	1.386	-0.007	1.384	-0.009	1.384	-0.002
20	1.446	1.448	0.002	1.443	-0.003	1.443	-0.005
21	1.386	1.393	0.007	1.385	-0.001	1.385	-0.008
22	1.418	1.423	0.005	1.419	0.001	1.419	-0.004
23	1.372	1.371	-0.001	1.373	0.001	1.373	0.002
C1	1.282	1.281	-0.001	1.454	0.172	1.454	0.173
C2	1.282	1.281	-0.001	1.454	0.172	1.454	0.173
C3	1.282	1.281	-0.001	1.454	0.172	1.455	0.174

Table S4. Bond lengths in the S_0 state for P1', P2', P1'H, and P2'H as determined at the B3LYP/6-31G(d,p) level of theory. Bond numbering scheme is provided in Figure S10.

	P1'	P2'	Δ(P2'-P1')	P1'H	Δ(P1'H-P1')	P2'H	Δ(P2'H-P2')
1	1.372	1.371	-0.001	1.373	0.001	1.373	0.002
2	1.418	1.423	0.005	1.418	0.000	1.419	-0.004
3	1.386	1.393	0.007	1.384	-0.002	1.385	-0.008
4	1.446	1.447	0.001	1.443	-0.003	1.443	-0.004
5	1.393	1.386	-0.007	1.385	-0.008	1.384	-0.002
6	1.415	1.409	-0.006	1.411	-0.004	1.409	0.000
7	1.386	1.387	0.001	1.388	0.002	1.388	0.001
8	1.441	1.441	0.000	1.440	-0.001	1.440	-0.001
9	1.387	1.386	-0.001	1.389	0.002	1.389	0.003
10	1.408	1.412	0.004	1.408	0.000	1.409	-0.003
11	1.388	1.393	0.005	1.387	-0.001	1.388	-0.005
12	1.440	1.443	0.003	1.437	-0.003	1.437	-0.006
13	1.396	1.389	-0.007	1.388	-0.008	1.387	-0.002
14	1.413	1.407	-0.006	1.409	-0.004	1.407	0.000
15	1.387	1.388	0.001	1.390	0.003	1.390	0.002
16	1.439	1.439	0.000	1.438	-0.001	1.438	-0.001
17	1.388	1.388	0.000	1.390	0.002	1.390	0.002
18	1.407	1.412	0.005	1.407	0.000	1.408	-0.004
19	1.389	1.395	0.006	1.387	-0.002	1.388	-0.007
20	1.439	1.441	0.002	1.436	-0.003	1.436	-0.005
21	1.396	1.389	-0.007	1.388	-0.008	1.387	-0.002
22	1.413	1.407	-0.006	1.408	-0.005	1.407	0.000
23	1.387	1.388	0.001	1.390	0.003	1.390	0.002
24	1.439	1.439	0.000	1.438	-0.001	1.438	-0.001
25	1.388	1.388	0.000	1.390	0.002	1.390	0.002
26	1.407	1.411	0.004	1.407	0.000	1.408	-0.003
27	1.389	1.394	0.005	1.387	-0.002	1.388	-0.006
28	1.439	1.442	0.003	1.436	-0.003	1.436	-0.006
29	1.396	1.390	-0.006	1.388	-0.008	1.387	-0.003
30	1.413	1.407	-0.006	1.408	-0.005	1.407	0.000
31	1.387	1.388	0.001	1.390	0.003	1.390	0.002
32	1.439	1.439	0.000	1.438	-0.001	1.438	-0.001
33	1.388	1.388	0.000	1.390	0.002	1.390	0.002
34	1.407	1.411	0.004	1.407	0.000	1.409	-0.002
35	1.388	1.393	0.005	1.387	-0.001	1.388	-0.005
36	1.440	1.443	0.003	1.437	-0.003	1.437	-0.006
37	1.396	1.390	-0.006	1.388	-0.008	1.387	-0.003
38	1.414	1.407	-0.007	1.409	-0.005	1.408	0.001
39	1.386	1.388	0.002	1.389	0.003	1.389	0.001

	P1’	P2’	Δ(P2’-P1’)	P1’H	Δ(P1’H-P1’)	P2’H	Δ(P2’H-P2’)
40	1.441	1.441	0.000	1.440	-0.001	1.440	-0.001
41	1.387	1.386	-0.001	1.388	0.001	1.388	0.002
42	1.409	1.413	0.004	1.409	0.000	1.411	-0.002
43	1.385	1.391	0.006	1.384	-0.001	1.385	-0.006
44	1.446	1.449	0.003	1.443	-0.003	1.443	-0.006
45	1.393	1.387	-0.006	1.385	-0.008	1.384	-0.003
46	1.423	1.417	-0.006	1.419	-0.004	1.418	0.001
47	1.371	1.372	0.001	1.373	0.002	1.373	0.001
C1	1.282	1.281	-0.001	1.454	0.172	1.455	0.174
C2	1.282	1.281	-0.001	1.454	0.172	1.454	0.173
C3	1.282	1.281	-0.001	1.454	0.172	1.453	0.172
C4	1.282	1.281	-0.001	1.454	0.172	1.453	0.172
C5	1.282	1.281	-0.001	1.454	0.172	1.454	0.173
C6	1.282	1.281	-0.001	1.454	0.172	1.455	0.174

Table S5. $S_0 \rightarrow S_1$ vertical transition energy (E_{01}) and wavelength (λ_{01}), oscillator strength (*f*), transition dipole moment (μ_{01}), and electronic configuration determined with TDDFT at the B3LYP/6-31G(d,p) level of theory. The oligomer length is defined by m = 1 – 4, 6.

m		E_{01} [eV]	λ_{01} [131]	*f*	$\boldsymbol{\mu_{01}}$ [D]	electronic configuration
1	M1’	2.52	493	0.03	1.82	HOMO→LUMO (98%)
2	D1’	2.01	616	0.30	6.29	HOMO→LUMO (95%)
3	T1’	1.73	716	0.65	9.97	HOMO→LUMO (91%)
4		1.59	780	1.21	14.18	HOMO→LUMO (94%)
5		1.49	831	1.77	17.70	HOMO→LUMO (93%)
6	P1’	1.43	865	2.30	20.59	HOMO→LUMO (91%)
1	M2’	2.48	500	0.03	1.80	HOMO→LUMO (98%)
2	D2’	1.98	625	0.30	6.26	HOMO→LUMO (95%)
3	T2’	1.72	726	0.60	9.62	HOMO→LUMO (90%)
4		1.57	790	1.19	14.14	HOMO→LUMO (94%)
5		1.48	839	1.77	17.78	HOMO→LUMO (93%)
6	P2’	1.42	876	2.31	20.77	HOMO→LUMO (91%)

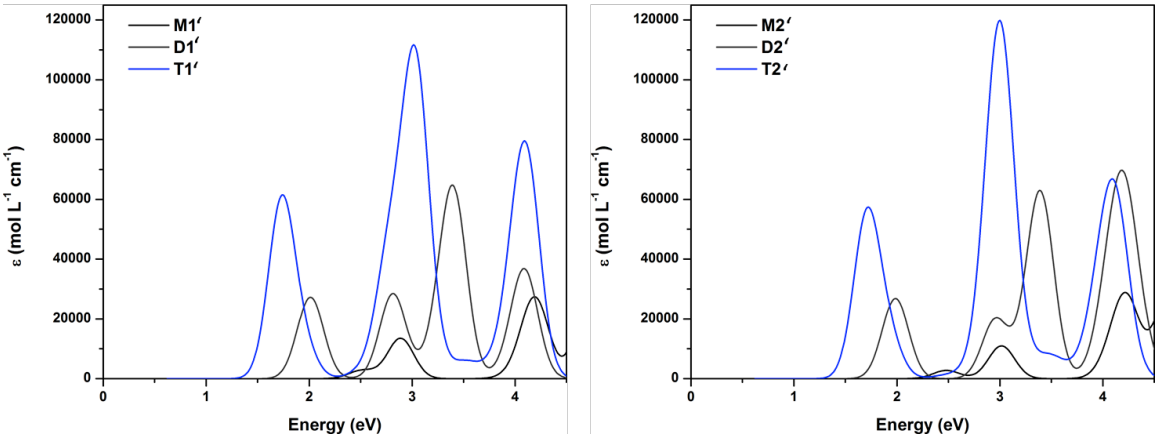


Figure S11. Simulated absorption spectra as determined with TDDFT at the B3LYP/6-31G(d,p) level of theory.

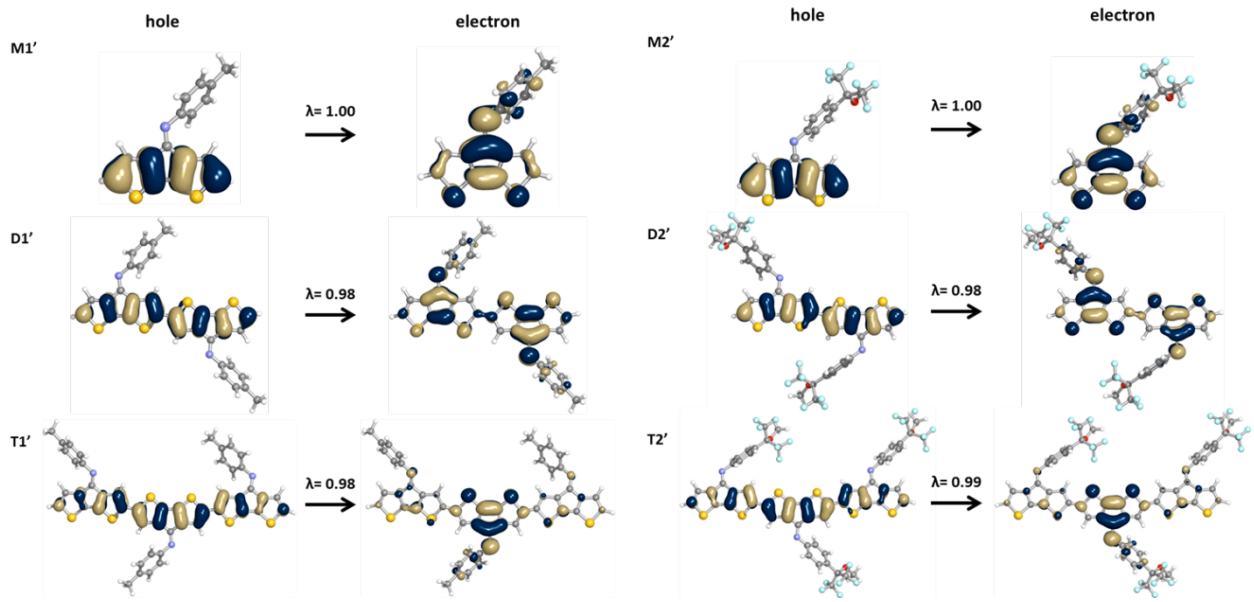


Figure S12. Natural transition orbitals (NTOs) for the $S_0 \rightarrow S_1$ transitions as determined with TDDFT at the B3LYP/6-31G(d,p) level of theory. λ is the fraction of the hole–particle contribution to the excitation.

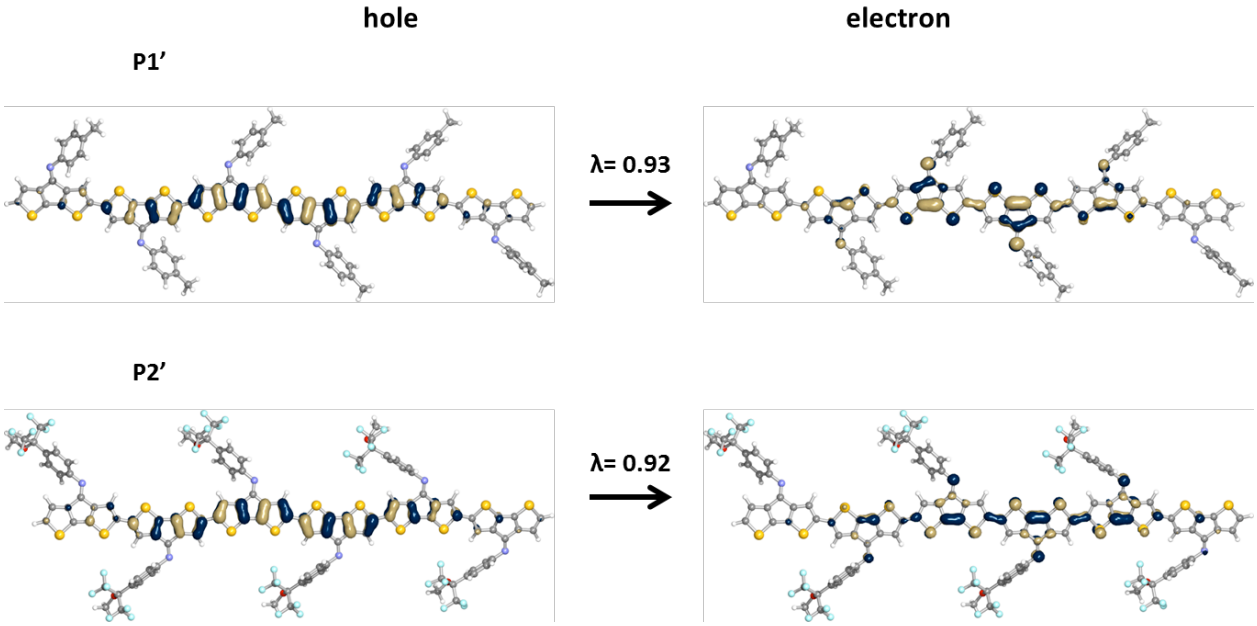


Figure S13. Natural transition orbitals (NTOs) for the $S_0 \rightarrow S_1$ transitions as determined with TDDFT at the B3LYP/6-31G(d,p) level of theory. λ is the fraction of the hole–particle contribution to the excitation.

Table S6. Optimized range-separation parameter (ω) as determined via IP fitting at the LRC-BLYP/6-31G(d,p) level of fitting. The oligomer lengths are defined by m/m' = 1 – 4, 6 and n = 1 – 4.

	m		ω ($bohr^{-1}$)[a]		m'		ω ($bohr^{-1}$)		n	ω ($bohr^{-1}$)
Orthogonal	1	M1'	0.215	Linear (hydrogenated)	1	M1'H	0.226	Linear (D-A)	1	0.201
	2	D1'	0.168		2	D1'H	0.177		2	0.153
	3	T1'	0.145		3	T1'H	0.152		3	0.132
	6	P1'	0.120		6	P1'H	0.125	(PCPDTPT')	4	0.121
	1	M2'	0.215		1	M2'H	0.211			
	2	D2'	0.169		2	D2'H	0.174			
	3	T2'	0.145		3	T2'H	0.150			
	6	P2'	0.120		6	P2'H	0.124			

[a]Recall that 1/ω defines the length scale for the transition between the short-range and long-range descriptions of the Coulomb operator in range-separated hybrid (RSH) functionals. Here, the characteristic length scales therefore range between 4 – 8 bohr.

Table S7. HOMO and LUMO energies, and HOMO-LUMO gap (E_g) as determined at the LRC-BLYP/6-31G(d,p) level of theory.

	HOMO	LUMO	E_g		HOMO	LUMO	E_g
M1'	-7.11	-0.56	6.55	M1'H	-6.82	0.54	7.36
D1'	-6.09	-1.03	5.06	D1'H	-6.13	-0.55	5.58
T1'	-5.65	-1.31	4.34	T1'H	-5.57	-0.83	4.74
P1'	-5.2	-1.64	3.56	P1'H	-5.11	-1.27	3.84
M2'	-7.23	-0.7	6.53	M2'H	-6.95	0.37	7.32
D2'	-6.21	-1.16	5.04	D2'H	-6.13	-0.55	5.58
T2'	-5.78	-1.46	4.32	T2'H	-5.70	-0.97	4.73
P2'	-5.32	-1.78	3.54	P2'H	-5.26	-1.42	3.84

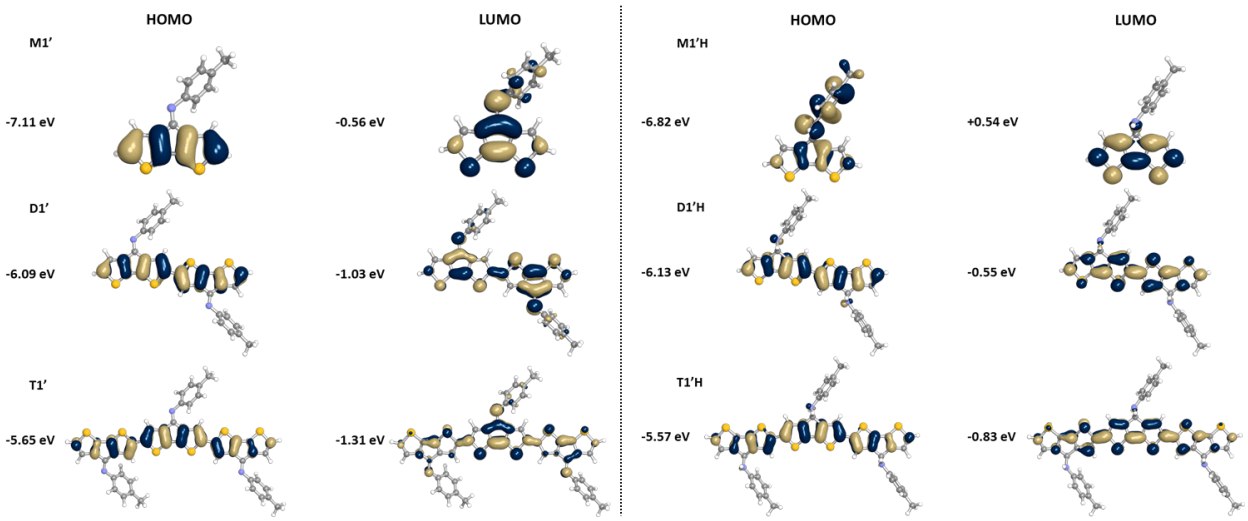


Figure S14. Depictions of the HOMOs and LUMOs for series 1 (m/m' = 1, 2, and 3) as determined at the LRC-BLYP/6-31G(d,p) level of theory.

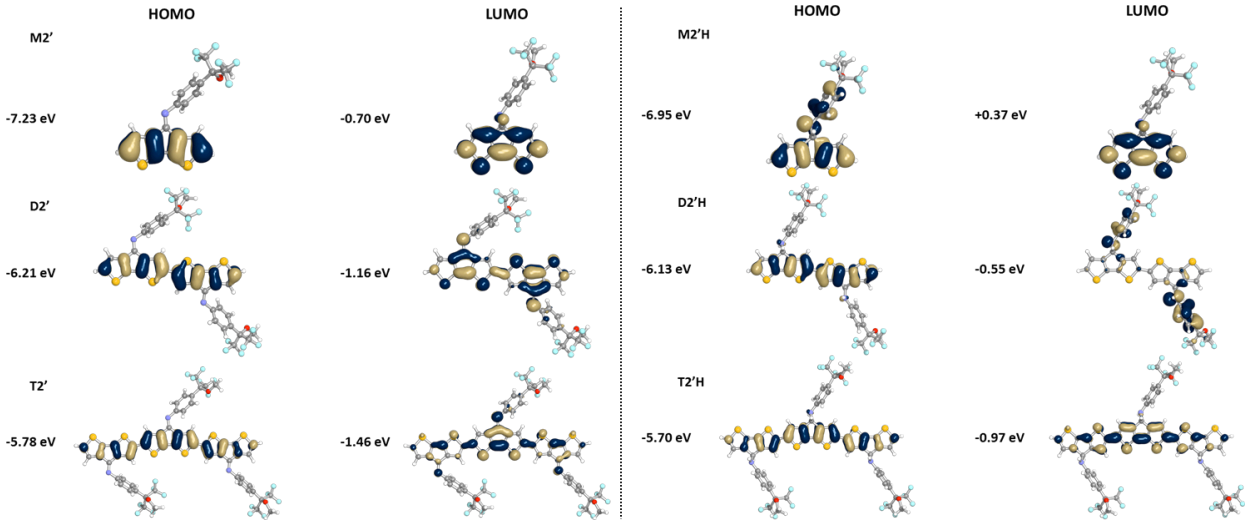


Figure S15. Depictions of the HOMOs and LUMOs for series 2 (m/m' = 1, 2, and 3) as determined at the LRC-BLYP/6-31G(d,p) level of theory.

Figure S16. Depictions of the HOMO-1's for M1' and M2' as determined at the LRC-BLYP/6-31G(d,p) level of theory.

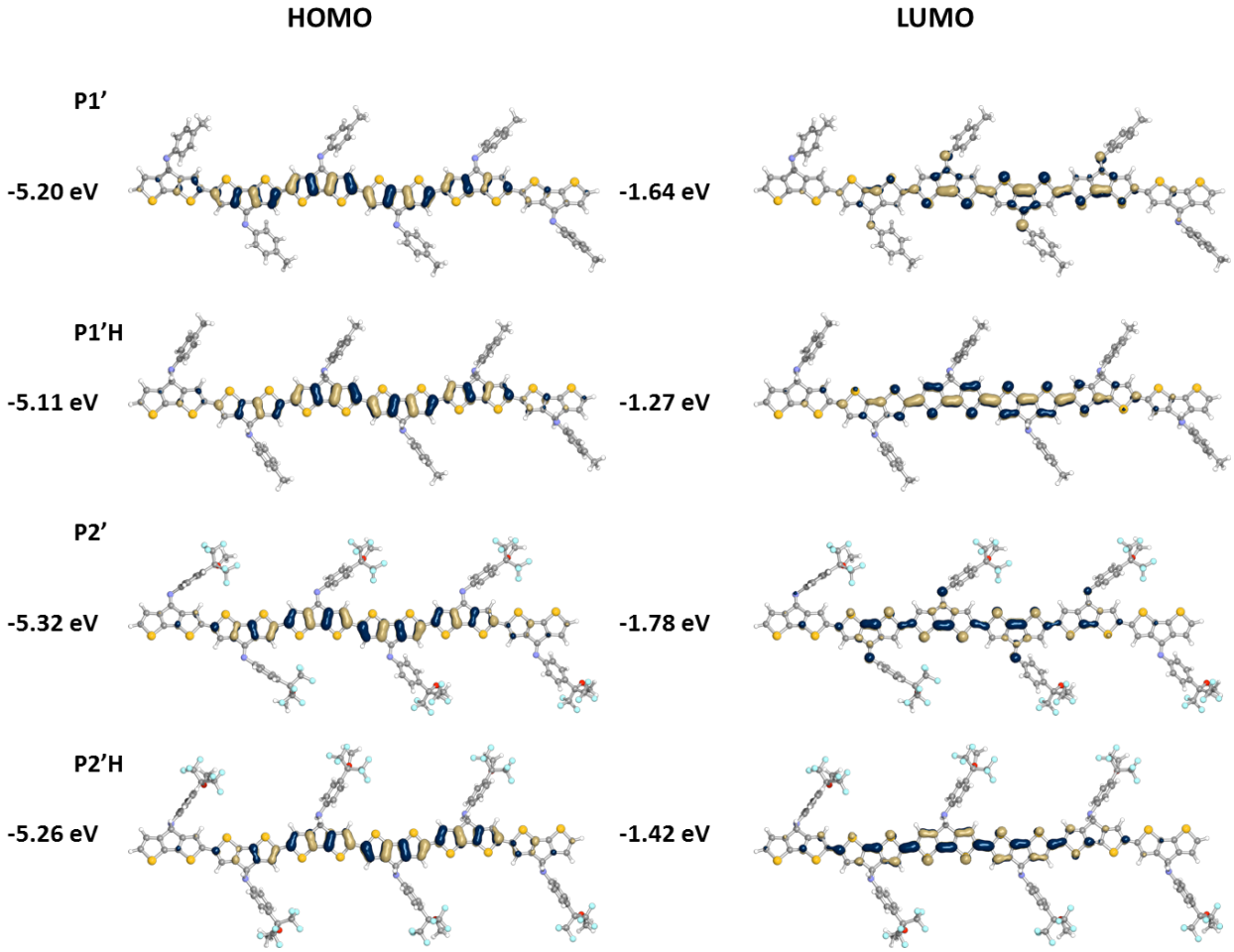


Figure S17. Depictions of the HOMOs and LUMOs for series 1 and 2 (m/m' = 6) as determined at the LRC-BLYP/6-31G(d,p) level of theory.

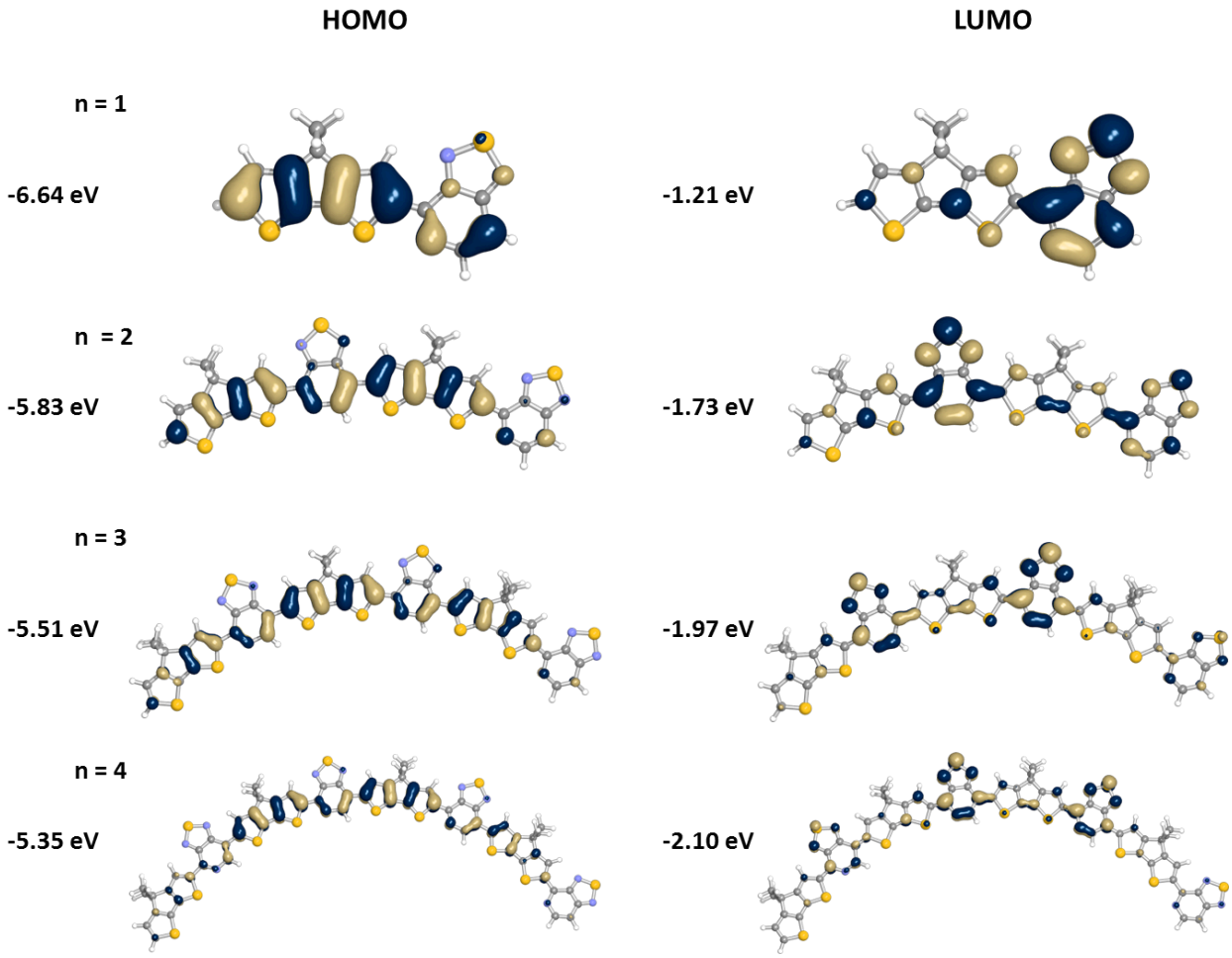


Figure S18. Depictions of the HOMOs and LUMOs for the linear D-A structures (n = 1 - 4) as determined at the LRC-BLYP/6-31G(d,p) level of theory.

Table S8. $S_0 \rightarrow S_1$ vertical transition energy (E_{01}) and wavelength (λ_{01}), oscillator strength (*f*), transition dipole moment (μ_{01}), and electronic configuration determined with TDDFT at the LRC-BLYP/6-31G(d,p) level of theory.

					μ_{01} (a.u.)				
		E_{01}	λ_{01}	*f*	x	y	z	total	Electronic configuration
Orthogonal	M1'	2.69	461	0.03	0.35	0.62	-0.06	0.71	HOMO→LUMO (97)
	D1'	2.19	566	0.28	-2.10	-0.83	0.05	2.26	HOMO-3→LUMO+1 (14); HOMO→LUMO (83)
	T1'	1.87	663	0.53	3.41	-0.12	-0.07	3.41	HOMO-5→LUMO+2 (3); HOMO-1→LUMO+1 (3); HOMO→LUMO (78); HOMO→LUMO+2 (9)
	P1'	1.56	793	1.98	7.19	0.19	-0.00	7.20	HOMO-2→LUMO+2 (5); HOMO-1→LUMO+1 (15); HOMO→LUMO (68)
	M2'	2.65	467	0.03	0.38	0.59	-0.00	0.70	HOMO→LUMO (97)
	D2'	2.16	573	0.27	-1.71	1.45	0.10	2.24	HOMO-3→LUMO+1 (13); HOMO→LUMO (84)
	T2'	1.84	673	0.49	3.23	0.62	-0.06	3.29	HOMO-5→LUMO+2 (4); HOMO-1→LUMO+1 (3); HOMO→LUMO (78); HOMO→LUMO+2 (10)
	P2'	1.54	803	1.97	-9.65	0.98	0.01	9.70	HOMO-2→LUMO+2 (6); HOMO-1→LUMO+1 (16); HOMO→LUMO (67); HOMO→LUMO+2 (2)
Linear	M1'H	3.91	317	0.19	0.69	-1.24	-0.10	1.43	HOMO-1→LUMO (29); HOMO→LUMO (67)
	D1'H	2.91	427	1.04	3.39	1.74	-0.12	3.81	HOMO-3→LUMO+1 (3); HOMO→LUMO(94)
	T1'H	2.43	510	1.85	5.57	0.15	-0.19	5.58	HOMO-4→LUMO+1 (3); HOMO-1→LUMO+1 (3); HOMO→LUMO (90)
	P1'H	1.92	644	4.46	9.73	0.32	-0.014	9.73	HOMO-2→LUMO+2 (3); HOMO-1→LUMO+1 (14); HOMO→LUMO (76)
	M2'H	3.89	318	0.21	-0.72	-1.31	-0.12	1.50	HOMO-1→LUMO (8); HOMO→LUMO (88)
	D2'H	2.90	428	1.06	-2.66	2.81	0.12	3.87	HOMO-3→LUMO+1 (3); HOMO→LUMO (94)
	T2'H	2.43	509	1.86	-5.51	-0.92	0.03	5.59	HOMO-1→LUMO+1 (5); HOMO→LUMO (91)
	P2'H	1.94	641	4.46	-9.65	0.98	0.01	9.70	HOMO-2→LUMO+2 (4); HOMO-1→LUMO+1 (13); HOMO→LUMO (74)
Linear DA	n = 1	2.66	466	0.52	-2.83	0.10	0.00	2.84	HOMO-1→LUMO (3); HOMO→LUMO (93)
	n = 2	1.87	664	1.20	5.11	0.23	0.00	5.12	HOMO-1→LUMO+1 (4); HOMO→LUMO (87); HOMO→LUMO+1 (4)
	n = 3	1.58	784	2.05	-7.26	0.28	0.00	7.27	HOMO-1→LUMO+1 (12); HOMO→LUMO (81)
(PCPDTPT')	n = 4	1.43	867	2.63	-8.67	0.31	0.00	8.67	HOMO-2→LUMO+2 (5); HOMO-1→LUMO+1 (15); HOMO→LUMO (74)

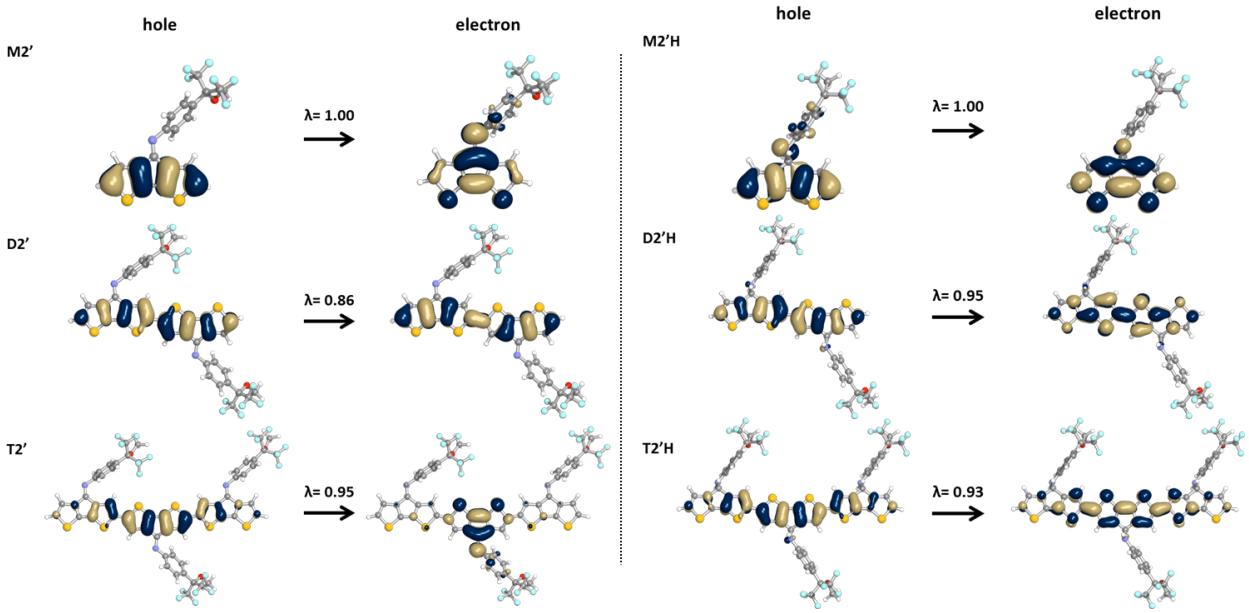


Figure S19. Natural transition orbitals (NTOs) for the $S_0 \rightarrow S_1$ transitions as determined with TDDFT at the LRC-BLYP/6-31G(d,p) level of theory. λ is the fraction of the hole–particle contribution to the excitation.

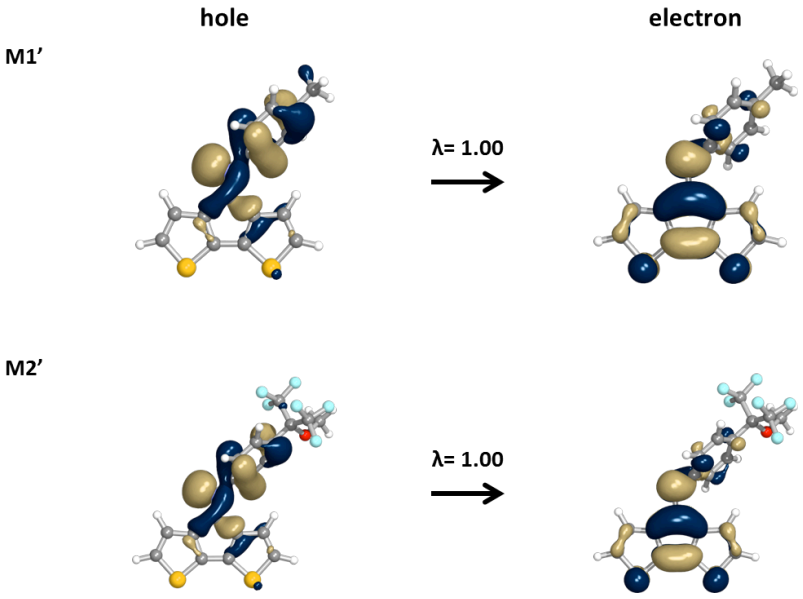


Figure S20. Natural transition orbitals (NTOs) for the $S_0 \rightarrow S_2$ transitions of M1' and M2' as determined with TDDFT at the LRC-BLYP/6-31G(d,p) level of theory. λ is the fraction of the hole–particle contribution to the excitation.

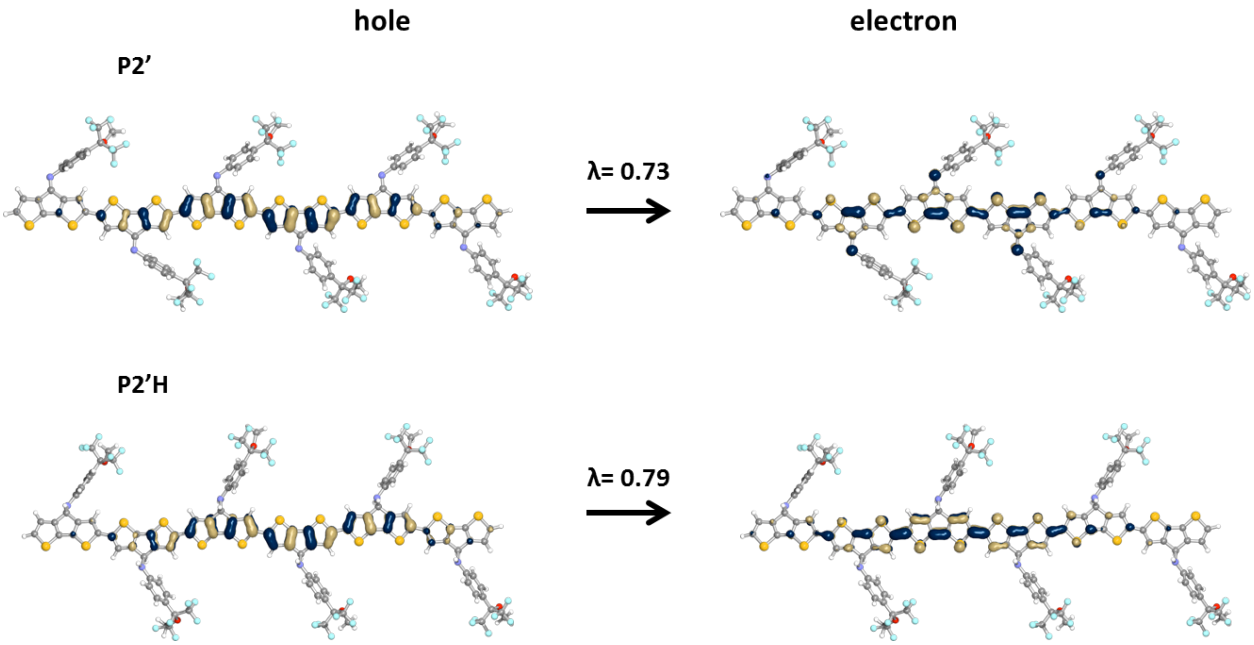


Figure S21. Natural transition orbitals (NTOs) for the $S_0 \rightarrow S_1$ transitions as determined with TDDFT at the LRC-BLYP/6-31G(d,p) level of theory. λ is the fraction of the hole–particle contribution to the excitation.

---

[i] Nakamura, M.; Matsuo, K.; Ito, S.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, *126*, 3686-3687.