Supporting Information

Incorporation of Designed Donor–Acceptor–Donor Segments in a Host Polymer for Strong Near-Infrared Emission from a Large-Area Light-Emitting Electrochemical Cell

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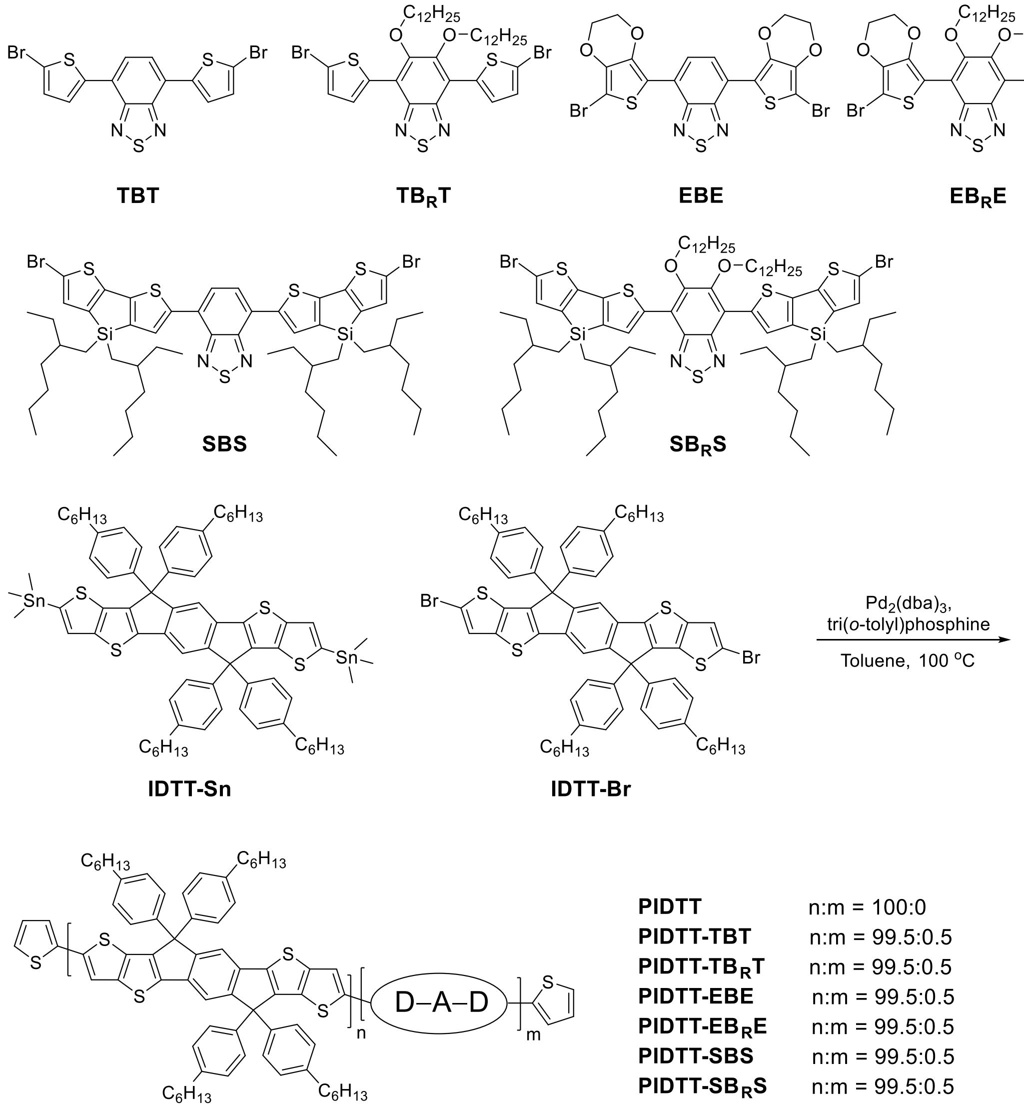
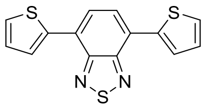
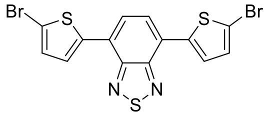


Scheme S1. The chemical structures of the IDTT and DAD monomers and a schematic representation of the synthesis of the PIDTT-based copolymers.

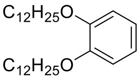
The synthesis of 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (B) was reported previously.[1] The bis(trimethylstannyl)-substituted indacenodithieno[3,2-*b*]thiophene monomer (IDTT-Sn), the dibromo-substituted indacenodithieno[3,2-*b*]thiophene monomer (IDTT-Br), and 4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophene were purchased from Solarmer Energy, Inc., while the other reagents and solvents were obtained from Sigma-Aldrich. All purchased materials were used as received. All reactions were performed under N_2 atmosphere unless otherwise noted.



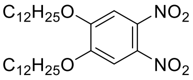
4,7-Di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (1): B (0.300 g, 1.02 mmol), $Pd_2(dba)_3$ (0.0187 g, 0.020 mmol), and tri(*o*-tolyl)phosphine (0.0248 g, 0.082 mmol) were dissolved in dry THF (8 mL). 2-(Tributylstannyl)-thiophene (1.523 g, 4.08 mmol) was added and the mixture was heated to 80 °C. After 20 h, the mixture was cooled and poured over water, and extracted with chloroform (3 × 100 mL). The combined organic phase was washed with water (3 × 100 mL) and dried over anhydrous $MgSO_4$. The mixture was concentrated and purified with column chromatography over silica gel, by using hexane as the initial eluent and gradually increasing the polarity to 3:1 (v/v) hexane/DCM. Compound **1** (0.284 g, 93%)was collected as orange solid needles after removing the solvent under vacuum. ^1H NMR (400 MHz, $C_2D_2Cl_4$, δ): 8.02 (d, J = 3.70 Hz, 2H), 7.77 (s, 2H), 7.39 (d, J = 5.11 Hz, 2H), 7.14 (t, J = 3.7 Hz, 2H); ^{13}C NMR (100 MHz, $C_2D_2Cl_4$, δ): 152.34, 139.09, 128.03, 127.42, 126.92, 125.66.



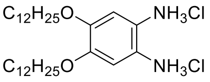
4,7-Bis(5-bromothiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (TBT): Compound **1** (0.150 g, 0.50 mmol) was dissolved in dry DMF (9 mL) and the mixture was cooled to 0 °C on an ice bath. *N*-bromosuccinimide (0.187 g, 1.05 mmol) was dissolved in small amount of DMF (*ca*. 2 mL) and added to the mixture dropwise in dark. The mixture was stirred at 0 °C for 1 h and then allowed to warm to room temperature overnight. After 21 h, another 0.009 g (0.05 mmol) of *N*-bromosuccinimide was added and the reaction was continued for 1 h. The reaction was quenched by adding water, which resulted in precipitation of TBT from the mixture. The precipitate was collected by filtration and washed with water. Then, the solid was dissolved in hot DMF and the product was recrystallized by allowing the mixture to cool down overnight. Two subsequent recrystallization steps from ethanol/DMF mixture yielded TBT (0.162 g, 71%) as red solid needles. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, δ): 7.74–7.72 (m, 4H), 7.11 (d, *J* = 3.97 Hz, 2H); MALDI-TOF MS (M_w = 455.81): *m/z* = 455.71 [M^+].



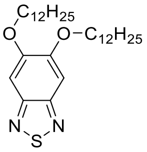
1,2-Bis(dodecyloxy)benzene (2): Catechol (10.0 g, 0.09 mol) was dissolved in dry DMF and to this mixture were added K_2CO_3 (55.3 g, 0.40 mol) and 1-bromododecane (55.0 g, 0.22 mol). The mixture was heated at 120 °C overnight. After cooling to room temperature, the mixture was poured into water, extracted with DCM and washed with water and brine. The organic phase was dried over anhydrous $MgSO_4$. The solvent was removed to yield compound **2** (27.0 g, 60%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.87 (s, 4H), 4.00 (t, *J* = 6.7 Hz, 4H), 1.87–1.75 (m, 4H), 1.46 (m, 4H), 1.38–1.19 (m, 32H), 0.87 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 149.21, 120.96, 114.07, 77.32, 77.00, 76.68, 69.24, 31.90, 29.79, 26.05, 22.68, 14.10.



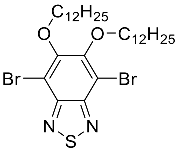
1,2-Bis(dodecyloxy)-4,5-dinitrobenzene (3): To a mixture of compound **2** (10.0 g, 22.4 mmol), dichloromethane (140 mL), and acetic acid (140 mL) at 10 °C was added slowly 20 mL of 65% nitric acid. The mixture was stirred at room temperature for 1 h and then cooled again to 10 °C, followed by dropwise addition of 50 mL of fuming nitric acid under ambient air. The mixture was stirred at room temperature overnight, poured into ice water, and extracted with DCM. The combined organic phase was washed with water, sat. $NaHCO_3$ solution, and brine, and finally dried over anhydrous $MgSO_4$. The solvent was removed and the resulting yellow solid was recrystallized from ethanol to yield compound **3** (10.3 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.30 (s, 2H), 4.10 (t, *J* = 6.5 Hz, 4H), 1.91–1.78 (m, 4H), 1.46 (m, 4H), 1.41–1.15 (m, 32H), 0.86 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 151.75, 136.42, 107.84, 70.16, 31.89, 29.42, 28.67, 25.78, 22.66, 14.09.



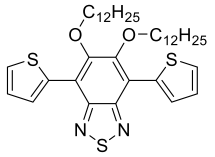
4,5-Bis(dodecyloxy)benzene-1,2-diammonium chloride (4): A mixture of compound **3** (5.0 g, 9.32 mmol), $SnCl_2$ (14.1 g, 74.36 mmol), ethanol (120 mL), and 37% HCl solution (60 mL) was heated at 85 °C overnight. The mixture was allowed to cool to room temperature and then filtered. The residue was washed with water and methanol, and dried in vacuum to yield compound **4** (4.5 g, 88%) as white solid. The product was used directly in the next reaction without further purification.



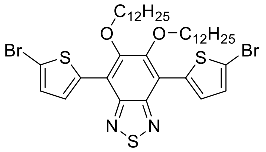
5,6-Bis(dodecyloxy)benzo[*c*][1,2,5]thiadiazole (5): Compound **4** and trimethylamine (12.53 mL) were dissolved in DCM (100 mL). Thionyl chloride (2.06 g, 17.29 mmol) was dissolved in DCM (5 mL) and added to the mixture slowly. During the addition, gas formation was observed and the color of the solution changed to brown. The mixture was refluxed for 6 h, then cooled and poured into water, extracted with DCM, and washed with water. The solvent was removed and the product was recrystallized from ethanol to afford compound **5** (2.6 g, 63%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.11 (s, 2H), 4.07 (t, *J* = 6.5 Hz, 4H), 1.97–1.83 (m, 4H), 1.57–1.44 (m, 4H), 1.44–1.17 (m, 32H), 0.86 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 154.09, 151.34, 98.36, 69.09, 31.90, 29.67, 29.63, 29.59, 29.49, 29.35, 29.33, 28.71, 25.99, 22.67, 14.09.



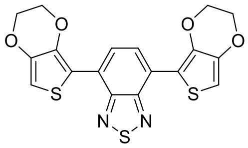
4,7-Dibromo-5,6-bis(dodecyloxy)benzo[*c*][1,2,5]thiadiazole (6): Compound **5** (2.5 g, 4.95 mmol) was dissolved in a mixture of DCM (65 mL) and acetic acid (100 mL). Bromine (8.0 g, 50.0 mmol) was added dropwise and the mixture was stirred in the dark, under ambient air for 48 h. The mixture was poured into water and extracted with DCM. The combined organic phase was washed with aqueous sodium thiosulfate solution and water, and then dried over anhydrous $MgSO_4$. The solvent was removed and the crude product was recrystallized from ethanol and purified with column chromatography over silica gel using hexane as the eluent. Compound **6** (2.0 g, 61%) was collected as white solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.14 (t, J = 6.7 Hz, 4H), 1.92–1.82 (m, 4H), 1.57–1.47 (m, 4H), 1.41–1.19 (m, 32H), 0.86 (t, J = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 154.47, 106.23, 75.13, 31.90, 30.24, 29.76–29.24, 25.97, 22.67, 14.10.



5,6-Bis(dodecyloxy)-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (7): As the procedure described for compound **1** above, compound **6** (0.300 g, 0.45 mmol), $Pd_2(dba)_3$ (0.0083 g, 0.009 mmol), and tri(*o*-tolyl)phosphine (0.0110 g, 0.036 mmol) were dissolved in dry THF (8 mL). 2-(Tributylstannyl)-thiophene (0.676 g, 1.81 mmol) was added and the mixture was heated at 80 °C for 24 h. Purification with column chromatography over silica gel using hexane as the initial eluent and gradually increasing the polarity to 4:1 (v/v) hexane/DCM yielded compound **7** (0.272 g, 90%) as yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.47 (d, J = 3.6 Hz, 2H), 7.50 (d, J = 5.0 Hz, 2H), 7.23 (t, J = 4.5 Hz, 2H), 4.10 (t, J = 7.0 Hz, 4H), 1.94–1.89 (m, 4H), 1.46–1.41 (m, 4H), 1.34–1.27 (m, 32H), 0.88 (t, J = 7.0 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$, δ): 152.01, 151.04, 134.16, 130.58, 127.32, 126.78, 117.66, 74.40, 31.98, 30.38, 29.75, 29.71, 29.68, 29.60, 29.42, 26.01, 22.74, 14.16.

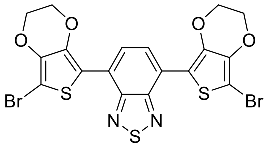


4,7-Bis(5-bromothiophen-2-yl)-5,6-bis(dodecyloxy)benzo[*c*][1,2,5]thiadiazole (TB$_R$T): As the procedure described for TBT above, compound **7** (0.150 g, 0.23 mmol) was dissolved in dry DMF (9 mL) at 0 °C. *N*-bromosuccinimide (0.085 g, 0.48 mmol) was dissolved in DMF and added to the mixture dropwise in dark. After 24 h, the reaction was quenched by adding water. Purification with column chromatography over silica gel using hexane as the initial eluent and gradually increasing the polarity to 5:1 (v/v) hexane/DCM yielded TB$_R$T (0.154 g, 82%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.25 (d, *J* = 4.1 Hz, 2H), 7.05 (d, *J* = 4.1 Hz, 2H), 4.02 (t, *J* = 7.2 Hz, 4H), 1.89–1.81 (m, 4H), 1.40–1.33 (m, 4H), 1.29–1.19 (m, 32H), 0.80 (t, *J* = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 151.39, 150.31, 135.66, 130.97, 129.62, 116.92, 115.43, 74.52, 31.95, 30.29, 29.73, 29.69, 29.66, 29.54, 29.40, 25.94, 22.71, 14.14.

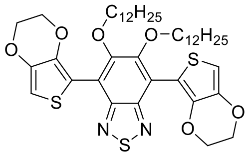


4,7-Bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)benzo[*c*][1,2,5]thiadiazole (8): B (0.147 g, 0.50 mmol), $Pd_2(dba)_3$ (0.0229 g, 0.025 mmol), tris(*o*-methoxyphenyl)phosphine (0.0176 g, 0.050 mmol), K_2CO_3 (0.242 g, 1.75 mmol), and PivOH (0.0153 g, 0.150 mmol) were dissolved in dry toluene (3 mL). 3,4-Ethylenedioxythiophene (1.422 g, 10.0 mmol) was added and the mixture was heated to 120 °C. After 60 h, the mixture was cooled and diluted with chloroform. The solids were removed by filtration, after which the mixture was concentrated and the crude product was purified with column chromatography over silica gel using hexane as the initial eluent and gradually increasing the polarity to 1:2 (v/v) hexane/chloroform. Recrystallization from hexane yielded compound **8** (0.116 g, 56%) as red solid needles. ^{1}H

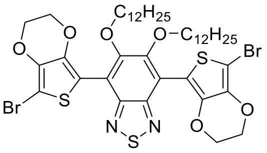
NMR (400 MHz, $C_2D_2Cl_4$, δ): 8.35 (s, 2H), 6.50 (s, 2H), 4.34–4.24 (m, 8H); ^{13}C NMR (100 MHz, $C_2D_2Cl_4$, δ): 152.06, 141.52, 140.26, 126.49, 123.37, 113.37, 101.90, 64.92, 64.30.



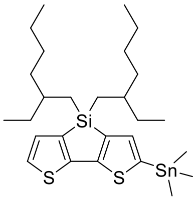
4,7-Bis(7-bromo-2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)benzo[*c*][1,2,5]thiadiazole (EBE): Compound **8** (0.083 g, 0.20 mmol) was dissolved in dry DMF (20 mL) at 0 °C. *N*-bromosuccinimide (0.075 g, 0.42 mmol) was dissolved in small amount of DMF (*ca.* 1 mL) and added to the mixture dropwise in dark. After 24 h reaction, another 0.007 g (0.04 mmol) of *N*-bromosuccinimide was added and the reaction was continued for 1 h. Then, the reaction was quenched with water and the mixture was extracted with the mixture of THF/DEE and brine. The organic phase was dried over anhydrous $MgSO_4$. The solvent was removed and the crude product was purified with column chromatography over silica gel using 2:1 (v/v) hexane/ethyl acetate as the eluent. A subsequent column using 3:2 (v/v) hexane/DCM as the eluent yielded EBE (0.048 g, 42%) as dark red solid. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, δ): 8.32 (s, 2H), 4.35–4.31 (m, 8H); MALDI-TOF MS (M_w = 571.82): m/z = 568.17 [M$^+$].



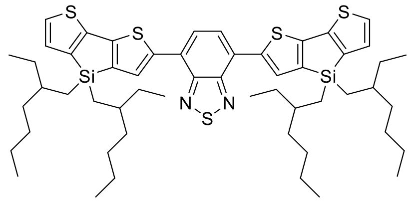
4,7-Bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-5,6-bis(dodecyloxy)benzo[*c*][1,2,5]-thiadiazole (9): As the procedure described for compound **8** above, compound **6** (0.199 g, 0.30 mmol), $Pd_2(dba)_3$ (0.0137 g, 0.015 mmol), tris(*o*-methoxyphenyl)phosphine (0.0106 g, 0.030 mmol), K_2CO_3 (0.145 g, 1.05 mmol), and PivOH (0.0092 g, 0.090 mmol) were dissolved in dry toluene (10 mL). 3,4-Ethylenedioxythiophene (0.853 g, 6.00 mmol) was added and the mixture was heated at 120 °C for 48 h. Column chromatography over silica using hexane as the initial eluent and gradually increasing the polarity to 4:1 (v/v) hexane/chloroform, and a subsequent column using 14:1 (v/v) hexane/ethyl acetate as the eluent yielded compound **9** (0.073 g, 31%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.50 (s, 2H), 4.20–4.16 (m, 8H), 3.95 (t, *J* = 6.5 Hz, 4H), 1.63–1.56 (m, 4H), 1.26–1.19 (m, 36H), 0.82 (t, *J* = 6.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 154.73, 151.85, 141.19, 139.82, 115.84, 108.11, 100.67, 74.49, 64.66, 64.48, 31.88, 30.22, 29.62, 29.41, 29.33, 25.90, 22.65, 14.08.



4,7-Bis(7-bromo-2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-5,6-bis(dodecyloxy)benzo[*c*]-[1,2,5]thiadiazole (EB$_R$E): Compound **9** (0.050 g, 0.064 mmol) was dissolved in dry THF (9 mL) at room temperature. *N*-bromosuccinimide (0.024 g, 0.134 mmol) was dissolved in THF and added dropwise in dark. After 25 h, the reaction was quenched with water, extracted with chloroform and washed with water. The organic phase was dried over anhydrous $MgSO_4$. The solvent was removed and the crude product was purified with column chromatography over silica gel using hexane as the initial eluent and gradually increasing the polarity to 5:1 (v/v) hexane/DCM. EB$_R$E (0.040 g, 66%) was obtained as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.27–4.16 (m, 8H), 3.95 (t, *J* = 6.5 Hz, 4H), 1.64–1.57 (m, 4H), 1.29–1.20 (m, 36H), 0.81 (t, *J* = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 154.74, 151.49, 139.64, 139.30, 115.24, 108.18, 88.81, 74.65, 64.92, 64.59, 31.91, 30.26, 29.70, 29.67, 29.65, 29.46, 29.36, 25.97, 22.68, 14.10.

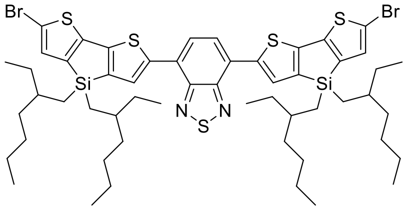


4,4-Bis(2-ethylhexyl)-2-(trimethylstannyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophene (10): To a mixture of 4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophene (2.094 g, 5.00 mmol) and dry THF (15 mL) was added 2.1 mL of *n*-BuLi solution (2.5 M in hexanes, 5.25 mmol) dropwise at –78 °C. The mixture was stirred at –78 °C for 1 h, and then allowed warm slowly to room temperature for another 1 h. The mixture was cooled again to –78 °C and trimethyltin chloride (6 mL, 1.0 M in hexanes, 6.00 mmol) was added dropwise. After keeping the mixture at –78 °C for 1 h, it was allowed to slowly warm to room temperature overnight. After 21 h, the reaction was quenched with water, extracted with DEE (3 × 100 mL), and washed with water (6 × 200 mL). The combined organic phase was dried over anhydrous $MgSO_4$. After removing the solvent in vacuum, compound **10** (2.72 g, 94%) was obtained as yellow oil. The product was used directly to the next reaction without further purification. MALDI-TOF MS (M_w = 582.18): m/z = 578.03 [M^+].

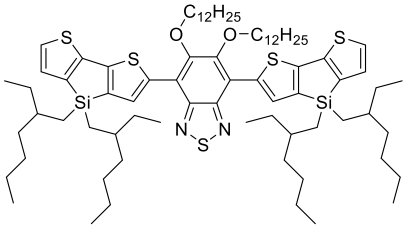


4,7-Bis(4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophen-2-yl)benzo[*c*][1,2,5]-thiadiazole (11): B (0.353 g, 1.20 mmol), compound **10** (2.094 g, 3.60 mmol), $Pd_2(dba)_3$ (0.0220 g, 0.024 mmol), and tri(*o*-tolyl)phosphine (0.0292 g, 0.096 mmol) were dissolved in dry toluene (5 mL) in a microwave tube. The tube was sealed and placed in a microwave reactor and subjected to 150 °C for 60 min. The reaction mixture was poured over water, extracted with DEE (3 × 100 mL), and washed with water (3 × 100 mL). The combined organic phase was dried over anhydrous $MgSO_4$. The solvent was removed and the crude product was purified with column chromatography over silica gel using hexane as the initial eluent and gradually increasing the polarity to 2:1 (v/v) hexane/chloroform. Compound **11** (0.863 g, 74%) was collected as purple oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.05 (t, J = 4.0 Hz, 2H), 7.76 (s, 2H), 7.19–7.17 (m, 2H), 7.01 (d, J = 4.7 Hz, 2H), 1.43–1.36 (m, 4H), 1.28–1.11 (m, 32H), 1.00–0.89 (m, 8H), 0.77–0.70 (m, 24H); ^{13}C NMR (100 MHz, $CDCl_3$, δ):

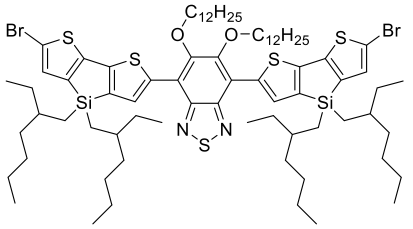
152.52, 150.29, 148.88, 143.87, 143.26, 140.05, 130.27, 129.93, 125.83, 125.69, 124.87, 35.92, 35.68, 28.92, 28.88, 22.97, 17.71, 14.16, 10.81.



4,7-Bis(6-bromo-4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophen-2-yl)benzo[*c*]-[1,2,5]thiadiazole (SBS): Compound **11** (0.535 g, 0.55 mmol) was dissolved in dry THF (20 mL) and the mixture was cooled to 0 °C on an ice bath. *N*-bromosuccinimide (0.206 g, 1.16 mmol) was dissolved in THF (5 mL) and added to the mixture dropwise in dark. After 1 h, the reaction was quenched with water and the mixture was extracted with DEE (3 × 100 mL) and washed with water (3 × 100 mL). The organic phase was dried over anhydrous $MgSO_4$ and the solvent was removed. The crude product was purified with column chromatography over silica gel using petroleum ether as the initial eluent and gradually increasing the polarity to 40:1 (v/v) petroleum ether/ethyl acetate, followed by a subsequent column using 12:1 (v/v) petroleum ether/chloroform as the eluent. SBS (0.513 g, 83%) was obtained as purple oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.03 (m, 2H), 7.76 (s, 2H), 6.97 (s, 2H), 1.39–1.36 (m, 4H), 1.22–1.10 (m, 32H), 0.99–0.87 (m, 8H), 0.79–0.71 (m, 24H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 152.42, 149.60, 149.30, 143.53, 142.93, 140.45, 132.51, 130.13, 125.63, 124.91, 111.88, 35.90, 35.64, 28.92, 28.88, 23.00, 17.61, 14.15, 10.81.

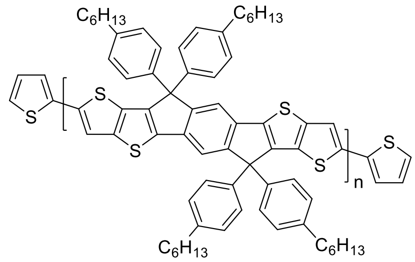


4,7-Bis(4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophen-2-yl)-5,6-bis(dodecyloxy)-benzo[*c*][1,2,5]thiadiazole (12): As the procedure described for compound **11**, compound **6** (0.663 g, 1.00 mmol), compound **10** (1.745 g, 3.00 mmol), $Pd_2(dba)_3$ (0.0183 g, 0.020 mmol), and tri(*o*-tolyl)phosphine (0.0243 g, 0.080 mmol) were dissolved in dry toluene (5 mL) in a sealed microwave tube. The tube was placed in a microwave reactor and subjected to 150 °C for 60 min. Column chromatography over silica gel using hexane as the initial eluent and gradually increasing the polarity to 6:1 (v/v) hexane/chloroform yielded compound **12** (1.041 g, 78%) as red oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.53 (t, *J* = 2.6 Hz, 2H), 7.17 (d, *J* = 4.7 Hz, 2H), 7.02 (d, *J* = 4.7 Hz, 2H), 4.08 (t, *J* = 7.2 Hz, 4H), 1.94–1.86 (m, 4H), 1.42–1.40 (m, 8H), 1.29–1.12 (m, 64H), 1.00–0.89 (m, 8H), 0.81 (t, *J* = 6.9 Hz, 6H), 0.77–0.70 (m, 24H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 151.07, 151.03, 150.90, 149.12, 143.32, 142.40, 134.88, 133.81, 129.90, 125.48, 117.46, 74.31, 35.96, 35.66, 31.93, 30.42, 29.67, 29.38, 28.97, 28.85, 26.06, 23.00, 22.69, 17.77, 14.16, 14.11, 10.78.

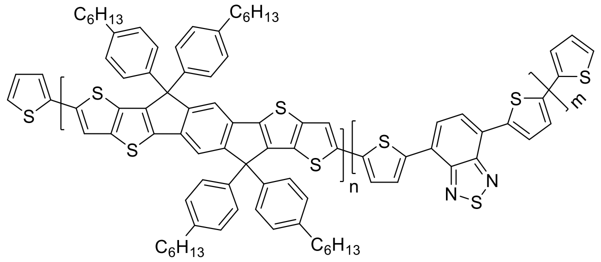


4,7-Bis(6-bromo-4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophen-2-yl)-5,6-bis(dodecyloxy)benzo[*c*][1,2,5]thiadiazole (SB_RS): As the procedure described for SBS, compound **12** (0.830 g, 0.62 mmol) was dissolved in dry THF (25 mL) and the mixture was cooled to 0 °C. *N*-bromosuccinimide (0.232 g, 1.30 mmol) was dissolved in THF and added to the mixture dropwise in dark. After 1.5 h, the mixture was allowed to warm to room temperature and the reaction was continued for 1 h. Purification with column chromatography over silica gel using petroleum ether as the initial eluent and gradually increasing the polarity to 10:1 (v/v) petroleum ether/chloroform, and a subsequent column using 40:1 (v/v) hexane/ethyl acetate as the eluent, afforded SB_RS (0.904 g, 97%) as red oil. ^{1}H NMR (600

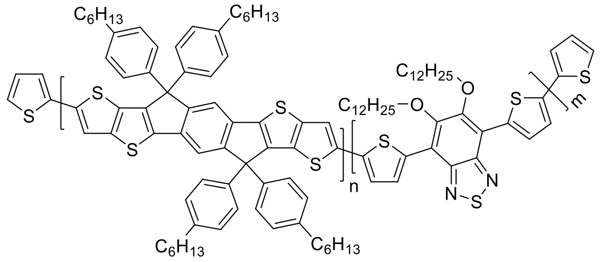
MHz, $CDCl_3$, δ): 8.62 (s, 2H), 7.04 (s, 2H), 4.14 (t, *J* = 6.9 Hz, 4H), 1.99–1.94 (m, 4H), 1.48–1.47 (m, 8H), 1.37–1.19 (m, 64H), 1.05–0.96 (m, 8H), 0.88 (t, *J* = 6.7 Hz, 6H), 0.85–0.79 (m, 24H); ^{13}C NMR (150 MHz, $CDCl_3$, δ): 151.16, 150.86, 149.61, 147.05, 143.69, 141.54, 135.39, 133.80, 132.55, 117.48, 111.49, 74.43, 36.01, 35.72, 31.99, 30.46, 29.74, 29.44, 29.01, 28.95, 26.10, 23.02, 22.75, 17.73, 14.21, 14.16, 10.84.



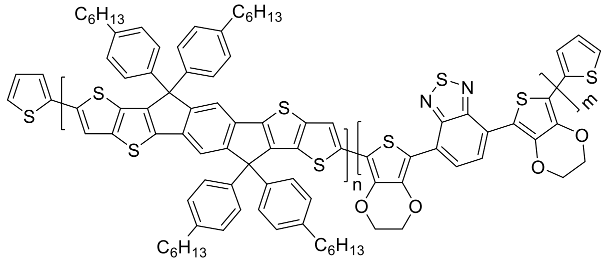
PIDTT: To a 30 mL crimp-cap vial was added IDTT-Sn (0.4036 g, 0.300 mmol), IDTT-Br (0.3532 g, 0.300 mmol), $Pd_2(dba)_3$ (0.0055 g, 0.006 mmol), and tri(*o*-tolyl)phosphine (0.0073 g, 0.024 mmol). The vial was sealed and subjected to 5 vacuum/nitrogen backfill cycles before dry toluene (14 mL) was added. The mixture was heated at 100 °C under vigorous stirring for 24 h. The polymer was end-capped by adding 2-(tributylstannyl)thiophene (0.1343 g, 0.360 mmol) and the reaction was continued for 1 h. Then, 2-bromothiophene (0.0685 g, 0.420 mmol) was added and the reaction was continued for another 2 h. The mixture was cooled to room temperature, diluted with toluene (200 mL), and extracted with 1% (aq) sodium diethyldithiocarbamate solution (300 mL) for 24 h. The organic phase was washed thoroughly with water (6 × 200 mL), then concentrated and precipitated by dropping slowly into acetone. The polymer was collected by filtration through a Soxhlet thimble and washed with Soxhlet extraction using acetone, hexane, and DCM (24 h each step). The residual polymer was dissolved in CB and further purified by passing through a silica gel column, and then precipitated again into acetone. The polymer was collected by filtration through a 0.45 μm Teflon filter. Finally, PIDTT (0.224 g, 37%) was obtained as orange solid after drying under vacuum at 40 °C overnight. GPC: $M_n = 137.5$ kg mol^{-1}, PDI = 3.1.



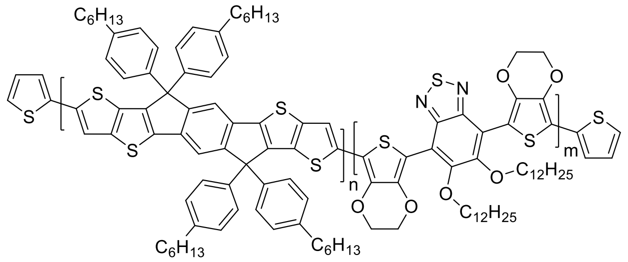
PIDTT-TBT: In a sealed 30 mL crimp-cap vial a mixture of IDTT-Sn (0.2690 g, 0.200 mmol), IDTT-Br (0.2331 g, 0.198 mmol), $Pd_2(dba)_3$ (0.0037 g, 0.004 mmol), and tri(*o*-tolyl)phosphine (0.0049 g, 0.016 mmol) was subjected to 5 vacuum/nitrogen backfill cycles. TBT (0.0229 g, 0.050 mmol) was dissolved in dry toluene (25 mL) and from that solution 1 mL (0.0009 g, 0.002 mmol) was transferred to the vial under N_2 atmosphere. Dry toluene (14 mL) was added (solvent total 15 mL) and the mixture was stirred at 100 °C for 1.5 h. The polymer was end-capped with 2-(tributylstannyl)thiophene (0.0896 g, 0.240 mmol) and 2-bromothiophene (0.0456 g, 0.280 mmol) and purified following the procedure described for PIDTT. Finally, PIDTT-TBT (0.205 g, 50%) was collected as red solid. GPC: M_n = 208.9 kg mol^{-1}, PDI = 2.9.



PIDTT-TB$_R$T: As the procedure described for PIDTT-TBT, a mixture of IDTT-Sn (0.2690 g, 0.200 mmol), IDTT-Br (0.2331 g, 0.198 mmol), $Pd_2(dba)_3$ (0.0037 g, 0.004 mmol), and tri(*o*-tolyl)phosphine (0.0049 g, 0.016 mmol) was subjected to 5 vacuum/nitrogen backfill cycles. TB$_R$T (0.0413 g, 0.050 mmol) was dissolved in dry toluene (25 mL) and from that solution 1 mL (0.0017 g, 0.002 mmol) was transferred to the reaction mixture. Dry toluene (14 mL) was added (total 15 mL) and the mixture was stirred at 100 °C for 1.5 h. The polymer was end-capped with 2-(tributylstannyl)thiophene (0.0896 g, 0.240 mmol) and 2-bromothiophene (0.0456 g, 0.280 mmol) and purified following the procedure described for PIDTT. Finally, PIDTT-TB$_{\text{R}}$T (0.178 g, 44%) was collected as red solid. GPC: M_{n} = 235.4 kg mol^{-1}, PDI = 2.6.

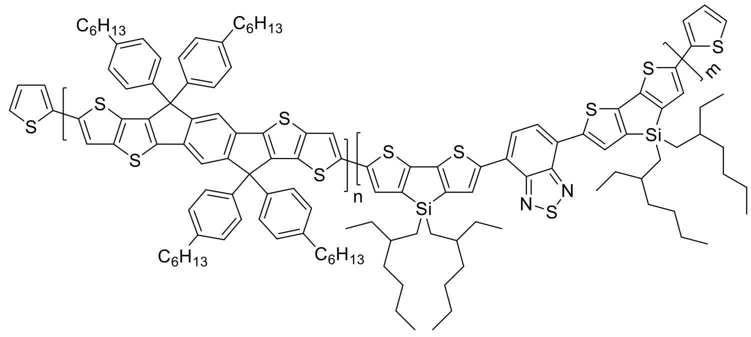


PIDTT-EBE: As the procedure described for PIDTT-TBT, a mixture of IDTT-Sn (0.2690 g, 0.200 mmol), IDTT-Br (0.2331 g, 0.198 mmol), Pd$_2$(dba)$_3$ (0.0037 g, 0.004 mmol), and tri(*o*-tolyl)phosphine (0.0049 g, 0.016 mmol) was subjected to 5 vacuum/nitrogen backfill cycles. EBE (0.0144 g, 0.025 mmol) was dissolved in dry toluene (250 mL) and from that solution 20 mL (0.0011 g, 0.002 mmol) was transferred to the reaction mixture. Dry toluene (10 mL) was added (total 30 mL) and the mixture was stirred at 100 °C for 1.5 h. The polymer was end-capped with 2-(tributylstannyl)thiophene (0.0896 g, 0.240 mmol) and 2-bromothiophene (0.0456 g, 0.280 mmol) and purified following the procedure described for PIDTT. Finally, PIDTT-EBE (0.359 g, 88%) was collected as red solid. GPC: M_{n} = 102.8 kg mol^{-1}, PDI = 3.2.

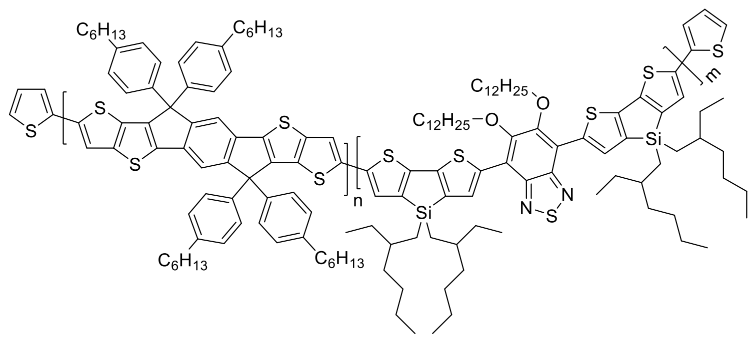


PIDTT-EB$_{\text{R}}$E: As the procedure described for PIDTT-TBT, a mixture of IDTT-Sn (0.1345 g, 0.100 mmol), IDTT-Br (0.1166 g, 0.099 mmol), Pd$_2$(dba)$_3$ (0.0018 g, 0.002 mmol), and tri(*o*-tolyl)phosphine (0.0024 g, 0.008 mmol) was subjected to 5 vacuum/nitrogen backfill cycles.

EB_RE (0.0236 g, 0.025 mmol) was dissolved in dry toluene (25 mL) and from that solution 1 mL (0.0009 g, 0.001 mmol) was transferred to the reaction mixture. Dry toluene (14 mL) was added (total 15 mL) and the mixture was stirred at 100 °C for 2 h. The polymer was end-capped with 2-(tributylstannyl)thiophene (0.0448 g, 0.120 mmol) and 2-bromothiophene (0.0228 g, 0.140 mmol) and purified following the procedure described for PIDTT. Finally, PIDTT-EB_RE (0.160 g, 79%) was collected as red solid. GPC: M_n = 108.6 kg mol^{-1}, PDI = 3.8.



PIDTT-SBS: As the procedure described for PIDTT-TBT, a mixture of IDTT-Sn (0.1345 g, 0.100 mmol), IDTT-Br (0.1166 g, 0.099 mmol), $Pd_2(dba)_3$ (0.0018 g, 0.002 mmol), and tri(*o*-tolyl)phosphine (0.0024 g, 0.008 mmol) was subjected to 5 vacuum/nitrogen backfill cycles. SBS (0.0282 g, 0.025 mmol) was dissolved in dry toluene (25 mL) and from that solution 1 mL (0.0011 g, 0.001 mmol) was transferred to the reaction mixture. Dry toluene (14 mL) was added (total 15 mL) and the mixture was stirred at 100 °C for 1.5 h. The polymer was end-capped with 2-(tributylstannyl)thiophene (0.0448 g, 0.120 mmol) and 2-bromothiophene (0.0228 g, 0.140 mmol) and purified following the procedure described for PIDTT. Finally, PIDTT-SBS (0.163 g, 80%) was collected as red solid. GPC: M_n = 140.3 kg mol^{-1}, PDI = 3.7.



PIDTT-SB$_R$S: As the procedure described for PIDTT-TBT, a mixture of IDTT-Sn (0.1345 g, 0.100 mmol), IDTT-Br (0.1166 g, 0.099 mmol), $Pd_2(dba)_3$ (0.0018 g, 0.002 mmol), and tri(*o*-tolyl)phosphine (0.0024 g, 0.008 mmol) was subjected to 5 vacuum/nitrogen backfill cycles. SB$_R$S (0.0374 g, 0.025 mmol) was dissolved in dry toluene (25 mL) and from that solution 1 mL (0.0015 g, 0.001 mmol) was transferred to the reaction mixture. Dry toluene (14 mL) was added (total 15 mL) and the mixture was stirred at 100 °C for 2 h. The polymer was end-capped with 2-(tributylstannyl)thiophene (0.0448 g, 0.120 mmol) and 2-bromothiophene (0.0228 g, 0.140 mmol) and purified following the procedure described for PIDTT. Finally, PIDTT-SB$_R$S (0.076 g, 37%) was collected as red solid. GPC: M_n = 207.1 kg mol^{-1}, PDI = 2.6.

2. DFT Calculations

Table S1. DFT-calculated and measured properties of the isolated DAD guest segments.

DAD	E_g^{DFT} (eV)	Torsion (°)	E_g^{CV} (eV)	E_g^{OPT} (eV)	PL peak (nm)
TBT	2.74	0.1	2.34	2.42	554
TB$_R$T	2.80	7.9	2.50	2.51	540
EBE	2.60	3.6	2.32	2.25	590
EB$_R$E	3.06	46.7	2.53	2.62	547
SBS	2.19	3.8	2.11	2.01	646
SB$_R$S	2.25	8.2	2.35	2.09	624

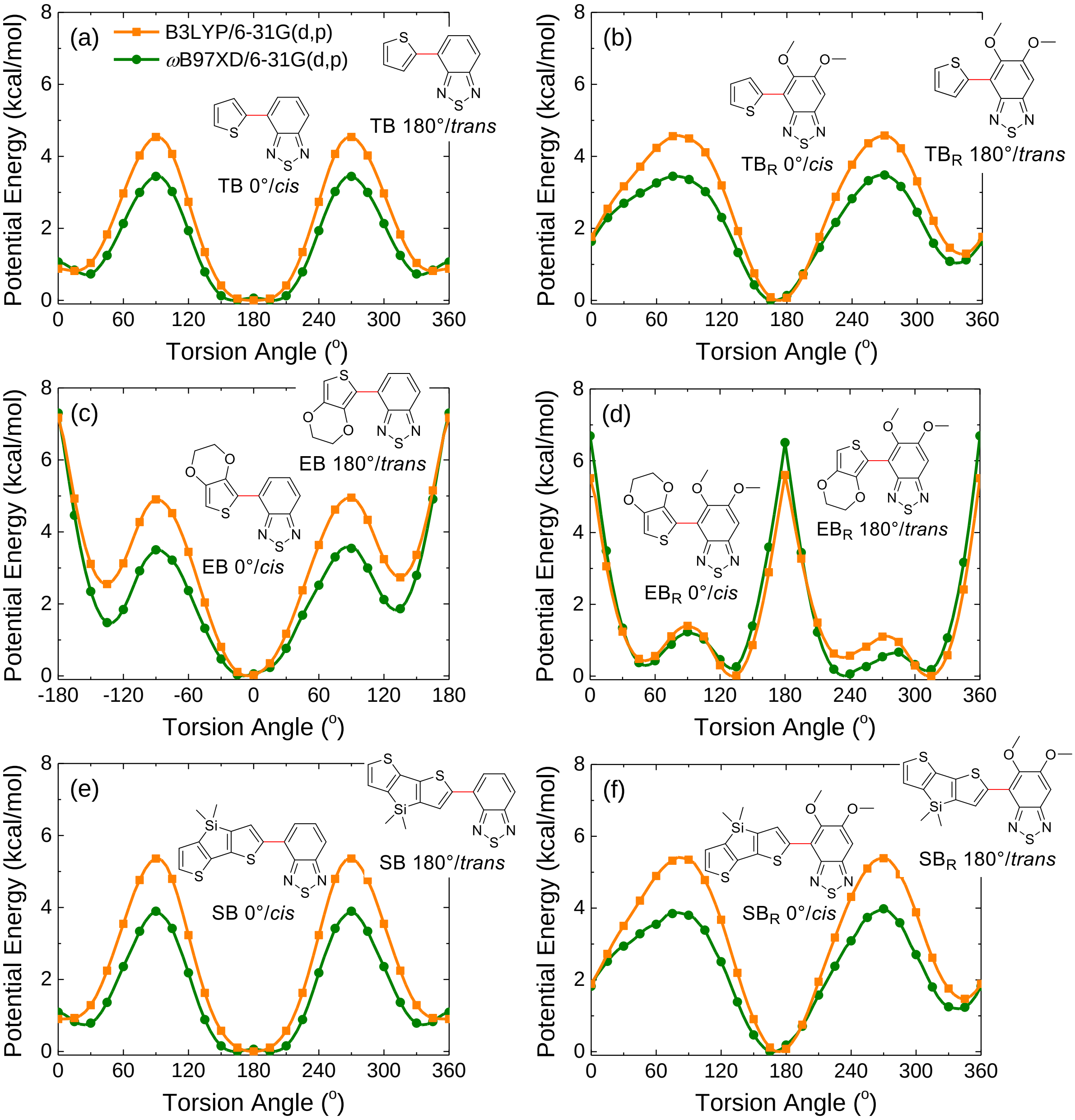


Figure S1. The DFT-calculated potential energy as a function of torsion angle for the donor–acceptor units: (a) TB, (b) TB$_R$, (c) EB, (d) EB$_R$, (e) SB, (f) SB$_R$. The DFT calculation used the 6-31G(d,p) basis set and either the B3LYP or the *ω*B97XD functional, as specified in the inset in (a).

The density functional theory (DFT) calculations were carried out on the compound under study in gas phase with the Gaussian 09 package,[2] and using the B3LYP hybrid functional and the 6-31G(d,p) basis set,[3-6] unless otherwise noted. The graphical visualization was performed with the Visual Molecular Dynamics (VMD) software.[7] In order to facilitate the DFT calculations, the IDTT host was modeled by a three repeat-unit structure with the hexyl side chains replaced by shorter methyl groups, while the 2-ethylhexyl side chains on the S donor and the dodecyloxy side chains on the B_R acceptor were replaced by shorter methyl and methoxy groups, respectively.

The potential energy of the donor–acceptor structures were calculated by changing the torsion angle of the single bond between the donor and acceptor (colored red in the insets of Figure S1) in steps of 5° over 360°, and allowing the other geometric parameters to relax to their energy minimum for each torsion angle. The torsion angle data presented in Figure S1 were also calculated with the long-range corrected ωB97XD functional[8] to confirm the validity of the minimum-energy conformations calculated with the B3LYP functional, as the former is reported to better account for the non-covalent interactions.[9-13] We found that both functionals gave qualitatively similar results.

Figure S1 reveals that the most stable conformation for the TBT (a), TB_RT (b), SBS (e), and SB_RS (f) DAD segments is *trans-trans*, while the *cis-cis* conformer is most stable for the EBE segment (c). For the EB_RE DAD segment (Figure S1d), the energy difference between several conformers is comparatively small (<0.5 kcal/mol), which implies that different conformations can co-exist at room temperature.

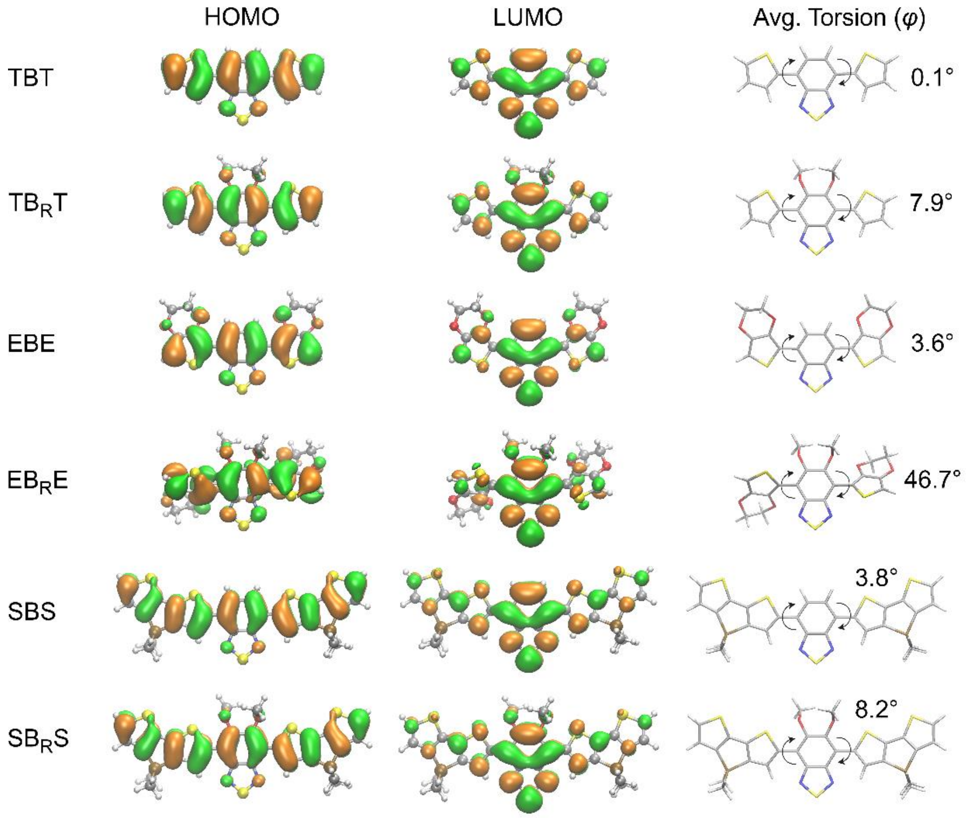


Figure S2. The DFT-calculated HOMO hole density, LUMO electron density, and backbone torsion of the geometry-optimized DAD units.

Figure S2 shows that the HOMO hole density is delocalized over the entire donor–acceptor–donor conjugated backbone, whereas the LUMO electron density is more confined to the central acceptor site. Five of the six DAD segments feature a flat structure with the exception being $\mathrm{EB_RE}$, which exhibits an average donor–acceptor torsion angle of 46.7°. Table S1 shows that the DFT-calculated energy gap of the isolated DAD segments varies between 2.19 and 3.06 eV, with the highest value for $\mathrm{EB_RE}$ and the smallest for SBS; and the general trend being that the introduction of alkyloxy side chains to the acceptor ($\mathrm{B} \rightarrow \mathrm{B_R}$) increases E_g^{DFT}.

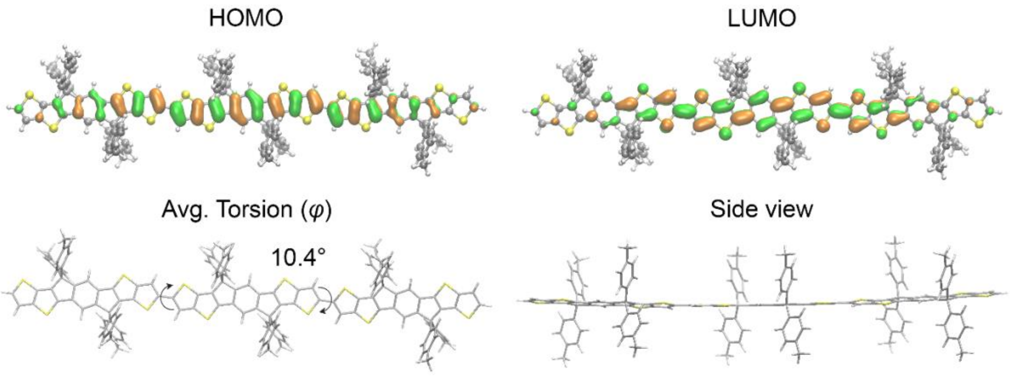


Figure S3. The DFT-calculated HOMO hole density, LUMO electron density, and backbone torsion of PIDTT in its geometry-optimized conformation.

Figure S3 shows that the PIDTT homopolymer features hole and electron densities that are well delocalized along the polymer backbone, and that the most stable conformation is *trans-trans*, with an average 10.4° rotation between the repeat units. We further found that the DFT-calculated energy gap of PIDTT was $E_g^{\mathrm{DFT}} = 2.43$ eV.

3. CV Traces

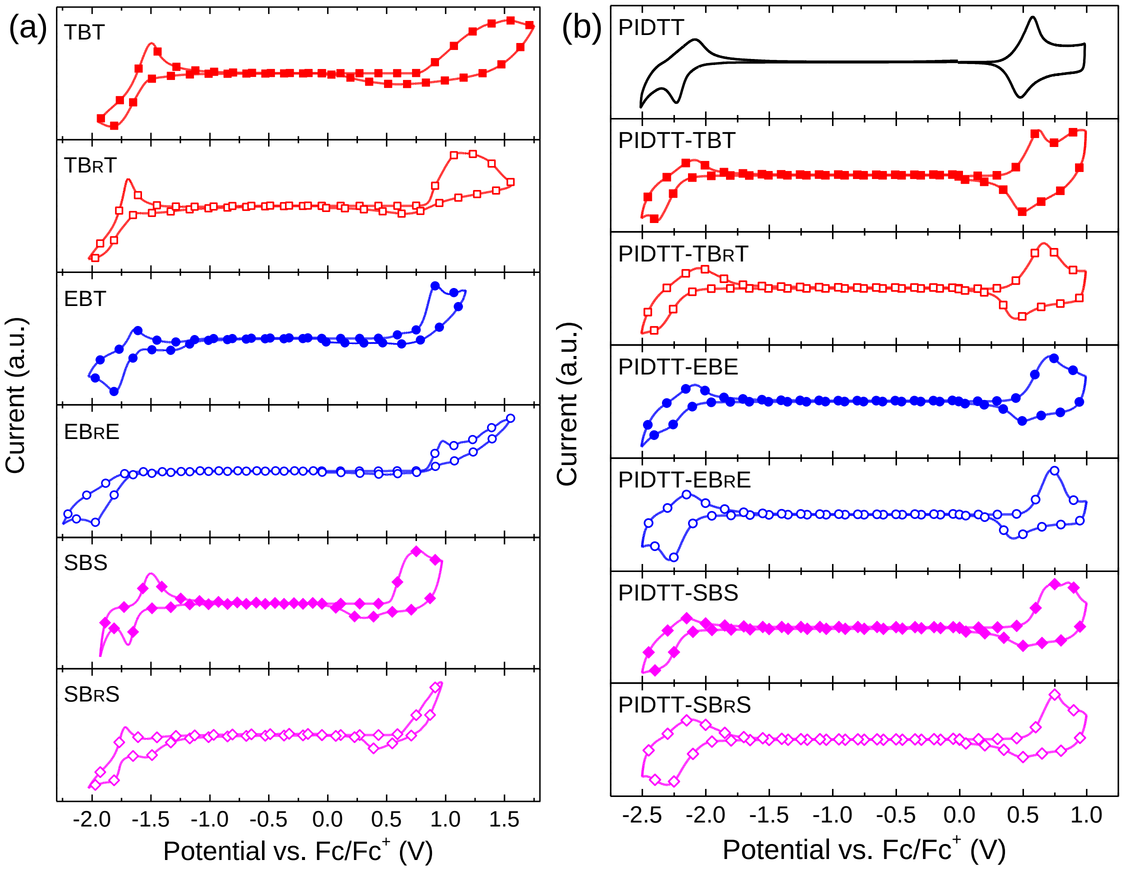


Figure S4. Cyclic voltammetry traces of (a) the six DAD segments and (b) the seven copolymers. The scan rate was 100 mV/s.

4. Absorption and PL of the DAD Segments

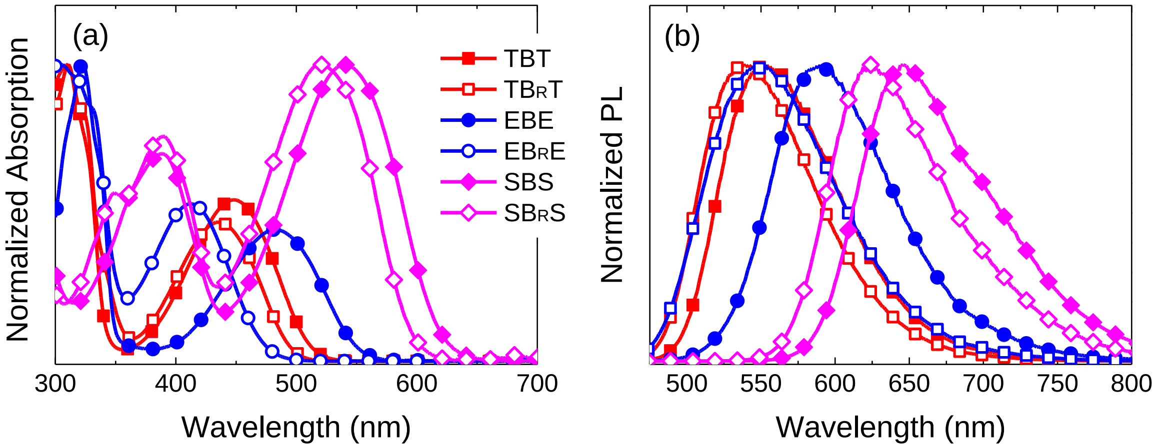


Figure S5. (a) Normalized absorption and (b) PL spectra of the DAD monomers in dilute toluene solution (concentration < 0.001%). The PL spectra were recorded with an excitation beam centered at $\lambda = 410$ nm.

Figure S5 presents the absorption and PL spectra of the DAD monomers in dilute toluene solution. The general trends gleaned from Figure S5(a) are that the absorption onset red-shifts with a change in acceptor from B_R to B, and that the SBS donor–acceptor–donor segment features the lowest-energy absorption. These findings are in qualitative agreement with the DFT and CV data presented in Figures S1–S4 and summarized in Table S1.

The PL spectra were measured at two excitation wavelengths (410 and 510 nm), and both resulted in essentially identical data. Figure S5(b) shows that the SBS segment featured the lowest-energy PL peak at 646 nm in dilute solution, and that the general trend again is that a change in acceptor from B_R to B results in a red-shifted property.

5. SCLC Mobility

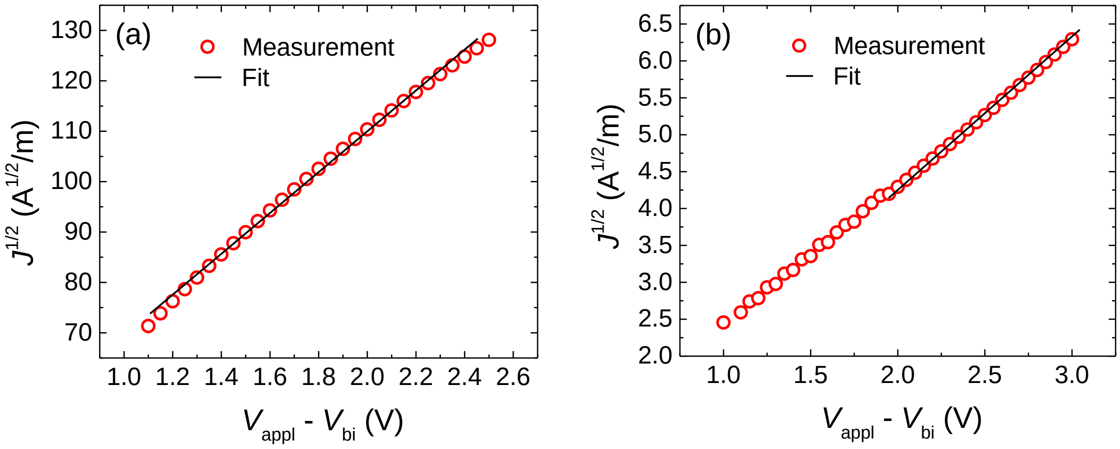


Figure S6. The current as a function of voltage for (a) the ITO/PEDOT:PSS/PIDTT/MoO_3/Al hole-only device, and (b) the ITO/ZnO/PIDTT/LiF/Al electron-only device. The solid line is a fit using the SCLC equation.

The hole mobility was measured in an ITO/PEDOT:PSS/PIDTT/MoO_3/Al hole-only device, while the electron mobility was measured in an ITO/ZnO/PIDTT/LiF/Al electron-only device. The hole-only device was fabricated by sequentially spin-coating PEDOT:PSS (thickness = 40 nm) and PIDTT (100 nm) on an ITO-coated glass substrate, and thereafter sequentially depositing MoO_3 (10 nm) and Al (90 nm) by thermal vacuum evaporation. The electron-only device was fabricated by sequentially spin-coating a ZnO dispersion (40 nm) and PIDTT (100 nm), and thereafter sequentially depositing LiF (6 nm) and Al (90 nm) by thermal vacuum evaporation.

The mobility μ was determined by fitting the equation for the space charge limited current:

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{d^3} \qquad \text{(S1)}$$

to the measured data, where J is the measured current density, ε_0 is the free-space permittivity, ε_r is the relative permittivity of the material, μ is the (hole or electron) mobility at zero field, d

is the thickness of the active layer, and V is the effective voltage being equal to $V_{\mathrm{appl}} - V_{\mathrm{bi}}$, with V_{appl} being the applied voltage and V_{bi} the built-in voltage.

6. Complementary LEC and OLED Device Data

Table S2. LEC performance at 10 mass-% concentration of electrolyte in active material.

Polymer emitter	Current density (mA/cm^2)	EL peak (nm)	Turn-on time (s)[a]	Peak radiance (μW/cm^2)	EQE (%)	Minimum voltage (V)
PIDTT	74.5	580, 620	5	164	0.11	3.8
PIDTT-TBT	74.5	576, 695	34	228	0.17	5.4
PIDTT-TB$_R$T	74.5	694	2	185	0.14	4.2
PIDTT-EBE	74.5	576, 695	–[b]	51	0.04	3.3
PIDTT-EB$_R$E	74.5	578, 621, 672	–[b]	95	0.07	4.2
PIDTT-SBS	74.5	700	2	126	0.10	4.1
PIDTT-SB$_R$S	74.5	622, 680	36	151	0.11	3.9

[a]The turn-on time to a radiance of 100 μW/cm^2. [b]Peak radiance <100 μW/cm^2.

Table S3. Optoelectronic performance of the corresponding OLEDs, comprising a low-work function Ca cathode and with no electrolyte in the active material.[a]

Polymer emitter	Current density (mA/cm^2)	EL peak (nm)	Peak radiance (μW/cm^2)	EQE (%)	Driving voltage (V)
PIDTT-TBT	74.5	696	60	0.05	4.8
PIDTT-TB$_R$T	74.5	692	18	0.01	3.2
PIDTT-EBE	74.5	705	80	0.08	4.4
PIDTT-EB$_R$E	74.5	574, 621	49	0.04	3.9
PIDTT-SBS	74.5	700	23	0.02	3.8
PIDTT-SB$_R$S	74.5	684	61	0.06	3.7

[a]Device structure: ITO/PEDOT:PSS/Polymer/Ca/Al (polymer thickness = 100 nm).

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