Supporting Information

One-Pot [1+1+1] Synthesis of Dithieno[2,3-b:3',2'-d]thiophene (DTT) and Their Fuctionalized Derivatives for Organic Thin-Film Transistors

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Materials and Methods.

All chemicals and solvents were of reagent grade obtained from Aldrich, Arco, or TCI Chemical Co. Solvents (toluene, benzene, ether, THF, and hexanes) were distilled under nitrogen from Na/benzophenone ketyl, and halogenated solvents were distilled from CaH_2. Compound **1** and **2** were prepared according to literature procedures.[1,2] ^1H and ^{13}C NMR spectra were recorded on Bruker 500, 300, or Bruker DRX-200 instrument. Chemical shifts for ^1H and ^{13}C spectra were referenced to solvent peaks. ^{19}F NMR spectra were referenced to external $CFCl_3$. DSC thermographs were carried out on a Mettler DSC 822 and calibrated with a pure indium sample with a scan rate of 10.0 °C/min. Thermogravimetric analysis (TGA) was performed with a Perkin Elmer TGA-7 thermal analysis system using dry nitrogen as a carrier gas at a flow rate of 40 ml/min. The UV–vis absorption and fluorescence spectra were obtained using a JASCO V-530 and a Hitachi F-4500 spectrometers, and all spectra were measured in specified solvent at room temperature. The IR spectra were obtained using a JASCO FT/IR-4100 spectrometer. Differential Pulse Voltammetry experiments were performed with a CH Instruments model CHI621C Electrochemical Analyzer. All measurements were carried out at specified temperature with a conventional three-electrode configuration consisting of a platinum disk working electrode, an auxiliary platinum wire electrode, and a nonaqueous Ag reference electrode, and the supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in specified dry solvent. All potentials reported are referenced to an Fc^+/Fc internal standard. Elemental analyses were performed on a Heraeus CHN-O-Rapid elemental analyzer. Mass data was performed on JMS-700 HRMS instrument. Prime grade silicon wafers (p^+-Si) with ~ 300 nm (±5%) thermally grown oxide (from Montco Silicon) were used as device substrates.

One-pot [1+1+1] synthesis of dithieno[2,3-b:3’,2’-d]thiophene (DTT).

Under nitrogen at -78°C, 2.5 M *n*-BuLi (24 mL in hexanes, 0.06 mol) was slowly added into an ether solution (24 mL) of 3-bromothiophene (6 mL, 0.06 mol) and the mixture was stirred for 40 min at this temperature. This solution was then warmed to 0°C to vacuum remove C_4H_9Br and ether (24 mL) was reloaded. (Note: without remove C_4H_9Br, 3-Butyl-S-Thiophene will be generated as major side product after the S addition in the next step). At -78 °C, sulfur (1.92 g, 0.06 mol) was added into this ether solution, stirred for 30min, then warmed to 0°C and stirred for another 30 min. p-Toluenesulfonyl chloride (TsCl, 11.42 g, 0.06 mol) was added into this solution at 0°C, stirred for 30 min, then warmed up to 40°C for 4 hours. The second portion of 3-Li-thiophene (1.2 eq.) was prepared as above procedure from 2.5 M *n*-BuLi (28.8 mL in hexanes, 0.072 mol) with 3-bromo-thiophene (6.7 mL, 0.072 mol). Again, this solution was warmed to 0°C to vacuum remove C_4H_9Br and ether was reloaded. At -78 °C, the second portion of 3-Li-thiophene ether solution was added into the first reaction mixture, stirred for 1 hour, then warmed to room temperature and stirred for overnight. The next day at 0°C, 2.5 M *n*-BuLi (52.8 mL in hexanes, 0.132 mol) was slowly added into this mixture, stirred for 30 min, and then refluxed for 1 hour. $CuCl_2$ (18.32 g, 0.138 mol) was added into this mixture at 0°C, stirred for 1 hour, then warmed to room temperature and stirred for overnight. Solids were filtered out and the organic ether portion was collected which was then subjected to chromatography (silica gel; n-hexanes as the eluent). **DTT** was recrystallized from hexanes (~ four times) as light-yellow powder to give a total of 3.56 g, yield, 30.3%. ^{1}H NMR (300Hz; $CDCl_3$): δ 7.36 (d, *J*=5.4 Hz, 2H, 2,6-*CH*), 7.29 (d, *J* = 5.1 Hz, 2H, 3,5-*CH*).

One-pot [1+1+2] synthesis of tetrathienoacene (TTA).

Follow the above one-pot [1+1+1] synthetic procedure, 3-bromo-thienothiophene[3] was employed in the second 3-Li-thiophene portion addition, instead of 3-bromo-thiophene. Similar reaction condition and work up steps were carried out and **TTA** was recrystallized from hexanes (~ four times) as yellow-orange powder in 27.1% yield.[3] ^{1}H NMR (200Hz; $CDCl_3$): δ 7.38 (d, *J*=5.4 Hz, 2H, *CH*), 7.32 (d, *J* = 5.4 Hz, 2H, *CH*).

One-pot [1+1+1] synthesis of asymmetric DS-DTT.

Follow the above one-pot [1+1+1] synthetic procedure, 4-bromo-2,3-di(methylthio)thiophene[4] was employed in the second 3-Li-thiophene portion addition, instead of 3-bromo-thiophene. Similar reaction condition and work up steps were carried out and the organic ether portion was subjected to chromatography (silica gel; n-hexanes as the eluent). The asymmetric **DS-DTT** derivative was recrystallized from cold hexanes as light yellow powder in 24.3% yield. ^{1}H NMR (300Hz; $CDCl_3$): δ 7.38 (d, *J*=5.4 Hz, 1H, *CH*), 7.30 (d, *J* = 5.1 Hz, 1H, *CH*), 2.56 (s, 3H, S-CH_3), 2.53 (s, 3H, S-CH_3). ^{13}C NMR (300Hz; $CDCl_3$): δ144.5, 140.6, 138.3, 131,3 129.7, 128.9, 126.4, 120.8, 21.4, 17.8. MS (FAB) *m*/z) calcd for $C_{10}H_8S_5$: 288(M^+). Found: 288.

Three synthetic routes to DFB-DTT (3).

Route I: Under nitrogen at 0°C, 2.5 M *n*-BuLi (0.5 mL in hexanes, 1.23 mmol) was slowly added into a 40 mL THF solution of **DTT** (105 mg, 0.53 mmol) and the mixture was stirred for 1 hour at this temperature. At -78 °C, pentafluorobenzoyl chloride (0.2 mL, 1.34 mmol) was added into the solution, stirred for 2 hours, then warm to room temperature and stirred for overnight. Water was added and the desired product was extracted with CH_2Cl_2, which was then subjected to chromatography (silica gel; CH_2Cl_2:n-hexanes = 3:7 as the eluent). The product was purified by gradient sublimation at pressures of $< 10^{-4}$ Torr, giving a bright-yellow solid, 113 mg; yield, 36%. ^{1}H NMR (300Hz; $CDCl_3$): δ 7.77 (s, 2H). ^{19}F NMR (300Hz; $CDCl_3$): δ -139, -148. -158. ^{13}C NMR (500Hz; $CDCl_3$): δ 176, 145.7, 145.4, 144.8, 144, 141, 138.8, 138.3, 136.7, 113. Anal. Calcd for $C_{22}H_2F_{10}O_2S_3$: C, 45.21; H, 0.34; S, 16.46. Found: C, 45.31; H, 0.34; S, 16.25. MS (FAB) *m*/z) calcd for $C_{22}H_2F_{10}O_2S_3$: 584(M^+). Found: 584. Orange crystals of the title compound suitable for X-ray diffraction were obtained by slow diffusion of hexanes into CH_2Cl_2 solution. The crystal structure of **3** has been confirmed by X-ray diffraction, perspective ORTEP drawing of molecular structure **3** is shown in Figure S1, and detailed crystal structure packing information are shown in Figure S4. (cif file of **3** are attached).

Route II: Under nitrogen, a CH_2Cl_2 (or CS_2) solution of **DTT** (105 mg, 0.53 mmol) and pentafluorobenzoyl chloride (0.2 mL, 1.34 mmol) was added $AlCl_3$ (10 eq) and stirred at 35°C for one week. Water was added to quench the reaction and the desired product was extracted with CH_2Cl_2. Black oily residue was normally obtained, which was then subjected to chromatography as the work up procedure in route I. Yield: 20~ 30%. Note: Mono-acylated product (**FB-DTT**; characterized by ^{1}H NMR) could also be isolated as the major side product (20~30%) from this route, which was subjected to the next acylation without further purification, see synthesis of **FBB-DTT (4).**

Route III: Under nitrogen at -78°C, a THF solution of **DTT**-$(COCl)_2$ (generated in situ from **DTT**-$(COOH)_2$ with $SOCl_2$)[5] was added 2.2 eq. of pentafluorophenyl lithium (generated in situ from pentafluorophenyl bromide with n-BuLi at -78°C) and stirred at room tempertaure (reaction turned black right away) for one day. Water was added to quench the reaction and the desired product was extracted with CH_2Cl_2, which was then subjected to chromatography as the work up procedure in route I. Yield: ~ 10%.

Synthesis of FBB-DTT (4).

Under nitrogen, a 140 mL CH_2Cl_2 solution of **FB-DTT** (0.20 g, 0.51 mmol) and benzoyl chloride (0.1 mL, 0.71 mmol) was added $AlCl_3$ (0.7 g, 5.12 mmol) and stirred at room tempertaure for one day. Water was added to quench the reaction and product was extracted with CH_2Cl_2. Solvent was removed and the solid product was washed with ether and then purified by gradient sublimation at pressures of $< 10^{-4}$ Torr, giving a bright-yellow solid, 145 mg; yield, 57%. ^{1}H NMR (300Hz; $CDCl_3$): δ 7.90~7.87 (m, 3H), 7.76 (s, 1H), 7.65~7.62 (m, 1H), 7.55~7.52 (m, 2H). ^{13}C NMR (500Hz; $CDCl_3$): δ 188, 176, 147, 145, 144.7, 144.2, 143, 142, 141, 138.9, 138.7, 137, 136.3, 132, 129.2, 128, 127. Anal. Calcd for $C_{22}H_7O_2S_3F_5$: C, 53.44; H, 1.43; S, 19.45. Found: C, 53.71; H, 0.92; S, 19.63. Orange crystals of the title compound suitable for X-ray diffraction were obtained by slow diffusion of hexanes into CH_2Cl_2 solution. The crystal structure of **4** has been confirmed by X-ray diffraction, perspective ORTEP drawing of molecular structure **4** is shown in Figure S2, and detailed crystal structure packing information are shown in Figure S5. (cif file of **4** are attached).

Synthesis of DB-DTT (5).

Under nitrogen, a 140 mL CH_2Cl_2 solution of **DTT** (0.60 g, 3.06 mmol) and benzoyl chloride (0.8 mL, 6.71 mmol) was added $AlCl_3$ (4.1 g, 30.6 mmol) and stirred at room tempertaure for one day. Water was added to quench the reaction and product was extracted with CH_2Cl_2. Solvent was removed and the solid product was washed with ether and then purified by gradient sublimation at pressures of $< 10^{-4}$ Torr, giving a bright-yellow solid, 0.77 g; yield, 63%. ^{1}H NMR (500Hz; $CDCl_3$): δ 7.91 (d, *J* = 7.2 Hz, 4H), 7.88 (s, 2H), 7.64~7.60 (m, 2H), 7.56~7.53 (m, 4H). ^{13}C NMR (500Hz; $C_2D_2Cl_4$): δ 188, 146, 144, 137, 136, 129, 128.8, 128.7. Anal. Calcd for $C_{22}H_{12}O_2S_3$: C, 65.32; H, 2.99; S, 23.78. Found: C, 65.21; H, 3.05; S, 24.25. MS (FAB) *m*/z) calcd for $C_{22}H_{12}O_2S_3$: 404(M^+). Found: 404. Orange crystals of the title compound suitable for X-ray diffraction were obtained by slow diffusion of hexanes into CH_2Cl_2 solution. The crystal structure of **5** has been confirmed by X-ray diffraction, perspective ORTEP drawing of molecular structure **5** is shown in Figure S3, and detailed crystal structure packing information are shown in Figure S6. (cif file of **5** are attached).

Synthesis of DT-DTT (6).

Under nitrogen, a 70 mL CH_2Cl_2 solution of **DTT** (0.30 g, 1.53 mmol) and 2-thiophenecarbonyl chloride (0.5 g, 3.36 mmol) was added $AlCl_3$ (2.1 g, 15.3 mmol, 10 eq） and stirred at room tempertaure for one day. Water was added to quench the reaction and the solid product was collected and washed with CH_2Cl_2. The product was purified by gradient sublimation at pressures of < 10^{-4} Torr, giving a bright-yellow solid, 0.26 g; yield, 41%. ^1H NMR (500Hz; $C_2D_2Cl_4$): δ 8.18 (s, 2H), 7.98 (m, 2H), 7.80 (m, 2H), 7.26 (m, 2H), as shown in Figure S8. ^{13}C NMR can only be obtained partially since this product with very low solubility even in $C_2D_2Cl_4$ at 70°C. Anal. Calcd for $C_{18}H_8O_2S_5$: C, 51.90; H, 1.94; S, 38.49. Found: C, 51.74; H, 1.92; S, 38.56. MS (EI) *m*/z) calcd for $C_{18}H_8O_2S_5$: 416(M^+). Found: 416.

Synthesis of DB-TT (7).

Under nitrogen, a 120 mL CH_2Cl_2 solution of thieno[3,2-*b*]thiophene (**TT**; 0.67 g, 4.78 mmol) benzoyl chloride (1.34 g, 9.56 mmol) was added $AlCl_3$ (2.59 g, 19.11 mmol) and stirred at room tempertaure for one day. Water was added to quench the reaction and product was extracted with CH_2Cl_2. The yellow product was washed with ether and purified by gradient sublimation at pressures of < 10^{-4} Torr, giving a bright-yellow solid, 1.1 g; yield, 66%. ^1H NMR (500Hz; $CDCl_3$): δ 7.90 (d, *J* = 7.3 Hz, 2H), 7.86 (s, 1H), 7.64~7.60 (m, 2H), 7.65~7.53 (m, 3H). ^{13}C NMR (200Hz; $CDCl_3$): δ 188, 149, 143, 137, 132, 129, 127, 118. Anal. Calcd for $C_{20}H_{12}O_2S_2$: C, 68.94; H, 3.47; S, 18.41. Found: C, 68.92; H, 3.54; S, 18.49. MS (FAB) *m*/z) calcd for $C_{20}H_{12}O_2S_2$: 348(M^+). Found: 348.

Synthesis of DT-TT (8).

Under nitrogen, a 120 mL CH_2Cl_2 solution of **TT** (0.65 g, 4.64 mmol) and 2-thiophenecarbonyl chloride (1.39 g, 9.27 mmol) was added $AlCl_3$ (6.27 g, 46.4 mmol) and stirred at room tempertaure for one day. Water was added to quench the reaction and product was collected as solid and washed with CH_2Cl_2. The product was purified by gradient sublimation at pressures of < 10^{-4} Torr, giving a bright-yellow solid, 0.95 g; yield, 57%. ^{1}H NMR (500Hz; $C_2D_2Cl_4$): δ 8.14 (s, 2H), 7.97 (d, *J* = 3.38 Hz, 2H), 7.81 (d, *J* = 4.75 Hz, 2H), 7.26 (*t*, 2H). ^{13}C NMR (500Hz; $C_2D_2Cl_4$): δ 178, 148, 143, 142, 134, 133, 128, 125. Anal. Calcd for $C_{16}H_8O_2S_4$: C, 53.21; H, 2.24; S, 35.58. Found: C, 53.01; H, 2.37; S, 35.61. MS (EI) *m*/z) calcd for $C_{16}H_8O_2S_4$: 360(M^+). Found: 360.

X-ray Crystal Structure Determinations of 3, 4, and 5.

Crystals of the title complexes suitable for X-ray diffraction were obtained as described above by slow diffusion of hexanes into CH_2Cl_2 solution at 0°C. The crystals were placed on a glass slide and covered with dry Infineum V8512 oil. A suitable crystal was chosen and mounted on a glass fiber for X-ray analysis. Data collection of compound **DFB-DTT (3)** was carried out on a Bruker SMART Apex CCD area detector diffractometer with Mo radiation (λ = 0.71073 Å) at 150(2) K. The compound of **FBB-DTT** (**4**) and **DB-DTT (5)** were transferred to a NONIUS Kappa CCD area detector diffractometer for data collection with Mo radiation (λ = 0.71073 Å) at 200 (2) K and 150 (2) K, respectively. After data collection, the frames were integrated, the initial crystal structure was solved by direct methods, the structure solution was expanded through successive least-squares cycles, absorption corrections were applied, and the final solution was determined. Crystal data, data collection, and refinement parameters are summarized in Table S2~S4.

Differential scanning calorimetry (DSC) measurements and thermo gravimetric analysis (TGA).

The differential scanning calorimetry (DSC) measurements of **3-8** were carried out under nitrogen as shown in Figure S7 and Table S1. The thermo gravimetric analyses (TGA) of **3-8** were performed under nitrogen as shown in Figure S8.

Table S1. Physical Properties of Compounds **3** - **8**.

	DSC	TGA	UV-Vis[a]	ΔE_{gap} (eV)	
	T_m (°C)	(°C; 5%)	λ_{max} (nm)	(UV)	(DPV)[b]
3	214	241	403,383	2.86	2.97
4	239	265	399,382	2.88	3.07
5	262	298	395,378	2.93	3.08
6	320	342	406,391	2.82	2.99
7	194	275	343	3.10	3.30
8	263	297	362	3.05	3.15

[a] in *o*-$C_6H_4Cl_2$. [b] in *o*-$C_6H_4Cl_2$ at 25°C.

UV-Vis spectroscopy.

As shown in Figure S9, the UV-Vis absorption spectra of **1-8** were collected in *o*-$C_6H_4Cl_2$ at room temperature. The photooxidative stability of **3-8** were investigated by monitoring the absorbance decay at λ_{max} of aerated *o*-$C_6H_4Cl_2$ solutions of **3**–**8** exposed to white light (fluorescent lamp) at room temperature.

Differential pulse voltametry.

Differential pulse voltammogram (DPV) of **3-8** were recorded in *o*-$C_6H_4Cl_2$ at 25°C and the DPV plots are shown in Figure S10. The electrochemically derived HOMO and LUMO energy of compounds **3** – **8** was shown in Figure 2.

Film Deposition and Characterization.

All p^+-Si/SiO_2 substrates were cleaned by sonication in absolute ethanol for 3 min and then by oxygen plasma treatment for 5 min (20 W). For the SiO_2 coating layer, -$SiMe_3$ groups were introduced using hexamethyldisilazane (HMDS), deposited by placing the SiO_2 substrates in an N_2-filled chamber saturated with HMDS vapor for 48 h. All of the semiconducting materials were vacuum deposited at 5×10^{-6} Torr (~500Å thickness, 0.2 Å/s growth rate) at preset substrate temperatures. For FET device fabrication, top-contact electrodes (~70 nm) were deposited by evaporating gold ($< 1 \times 10^{-6}$ Torr) through a shadow mask with the channel length (L) and width (W) defined as 100 μm and 5000 μm, respectively.

Electrical Measurements.

The capacitance of the bilayer dielectrics was measured on MIS structures using an HP4192A Impedance Analyzer. All OTFT measurements were carried out under vacuum (1×10^{-5} Torr) using a Keithly 6430 subfemtoammeter and a Keithly 2400 source meter, operated by a local Labview program and GPIB communication. Mobilities (μ) were calculated in the saturation regime using the relationship[6] : $\mu_{sat} = (2I_{DS}L)/[WC_i(V_G - V_T)^2]$, where I_{DS} is the source-drain saturation current; C_i is the gate dielectric capacitance (per area), V_G is the gate voltage, and V_T is the threshold voltage. The latter can be estimated as the x intercept of the linear section of the plot of V_G vs $(I_{DS})^{1/2}$.

Field-Effect Transistor Performance.

Top-contact OTFTs were fabricated by vapor-depositing **3 - 8** films on bare or hexamethyldisilazane (HMDS)-treated SiO_2/p^+-Si substrates, followed by Au deposition through a shadow mask to define the source and drain electrodes. The substrate temperature during semiconductor film deposition was controlled with a thermocouple. OTFT characterization was preformed under vacuum and the OTFT data are summarized in Table 1 and as shown in Figure S11~S16 for **3~8**, respectively.

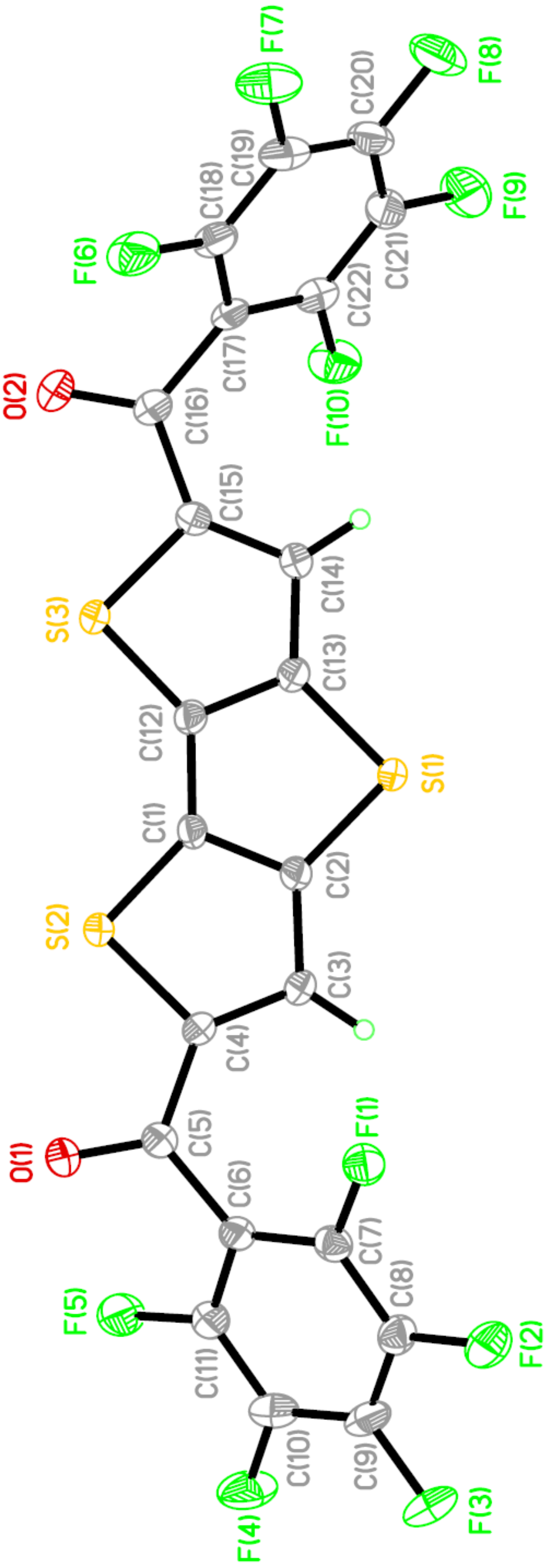

Figure S1. The molecular structure of **3**, thermal ellipsoids drawn at the 30% of probability level.

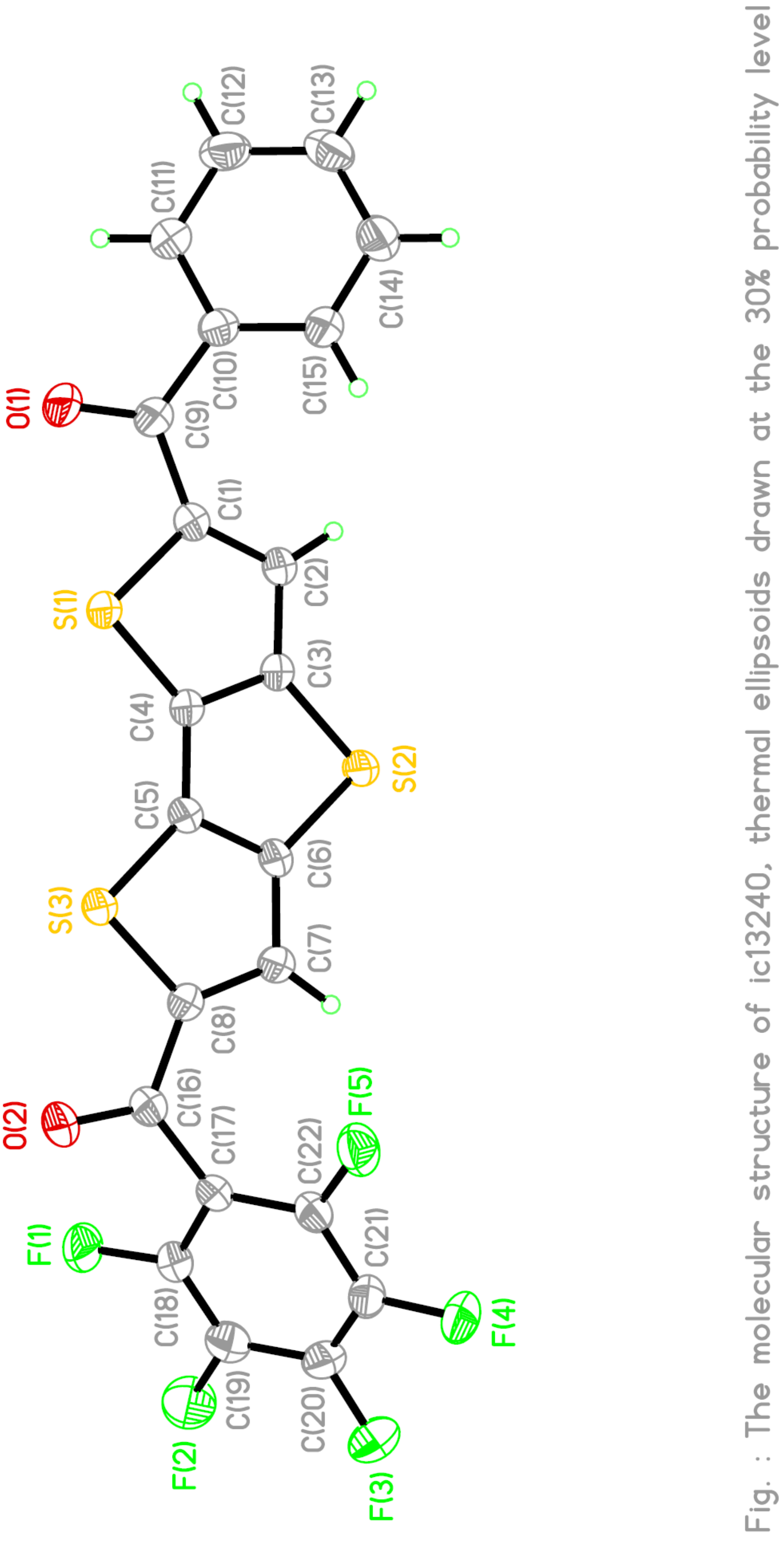

Figure S2. The molecular structure of **4**, thermal ellipsoids drawn at the 30% of probability level.

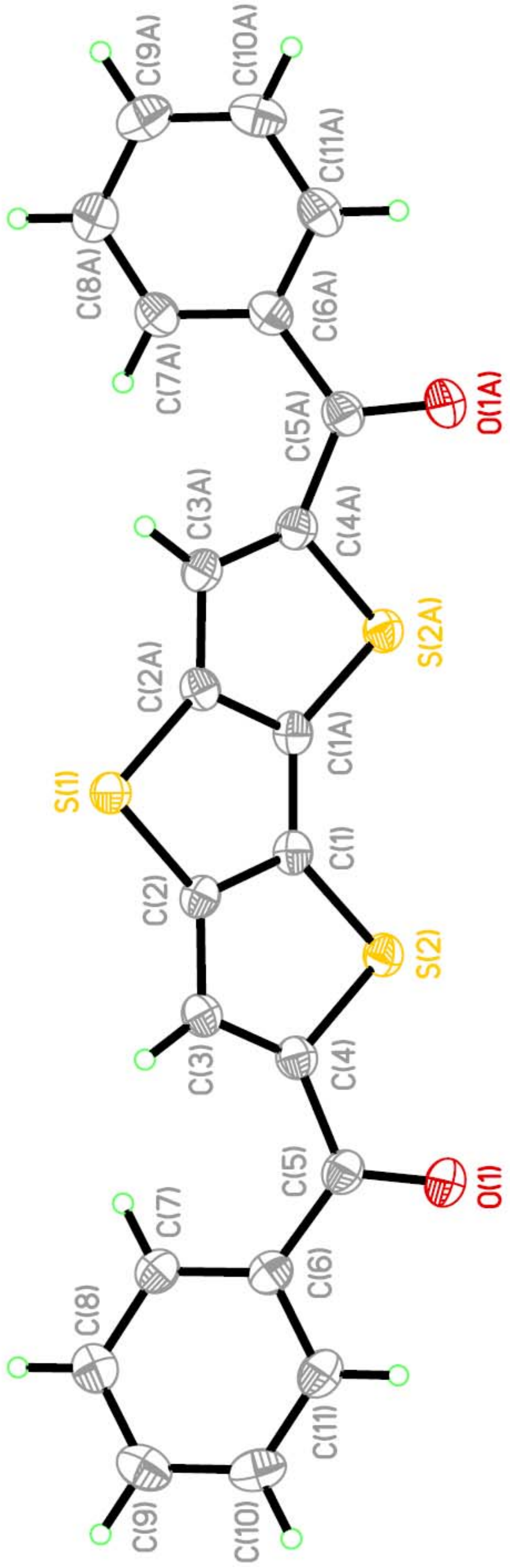

Figure S3. The molecular structure of **5**, thermal ellipsoids drawn at the 30% of probability level.

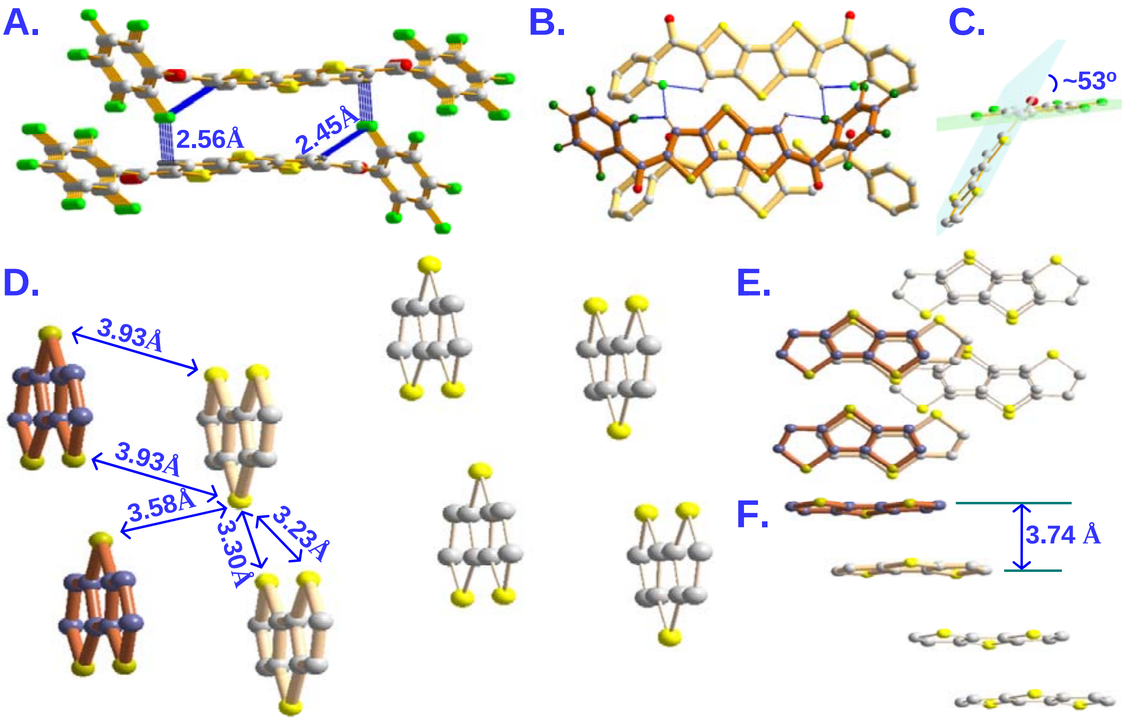

Figure S4. Crystal structures of **3**. A. **DTT** units of **3** with 3.74 Å planar distance. Intramolecular (2.45 Å) and intermolecular (2.56 Å) F-H interactions exist between two non-superimposable **DTT** cores. B. The two **DTT** units are not superimposable when view directly from the top. C. Phenyl and **DTT** with ~53° plane angle. D. Side view of **DTT**s stacking in **3** and S-S distances in **DTT**s (substitutents are omitted for clarity). E. Top view of **DTT**s stacking in **3**. F. Front view of **DTT**s stacking in **3**.

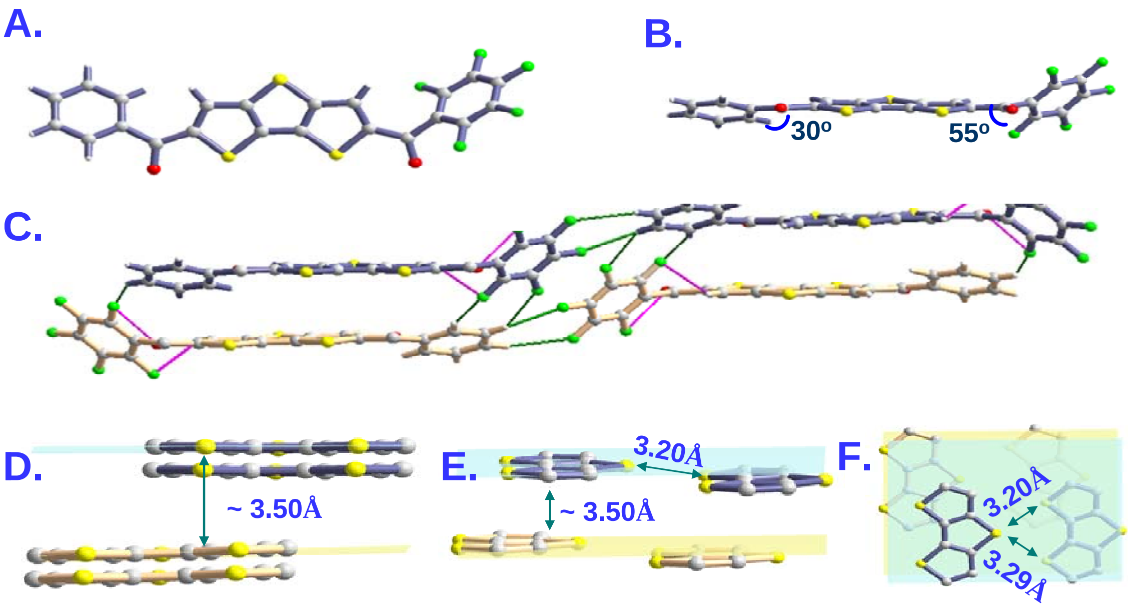

Figure S5. A. Crystal structures of **4**. B. Phenyl and **DTT** as well as perfluorophenyl and **DTT** with 30^o and 55^o plane angle, respectively. C. Intramolecular and intermolecular F-H interactions exist among four non-superimposable tetramer-like **DTT** cores in **4**. D. Front view of **DTT**s stacking in **4. DTT** units with ~3.50 Å planar distance. E. Side view of **DTT**s stacking in **4**. E. Top view of **DTT**s stacking in **4** and S-S distances in **DTT**s.

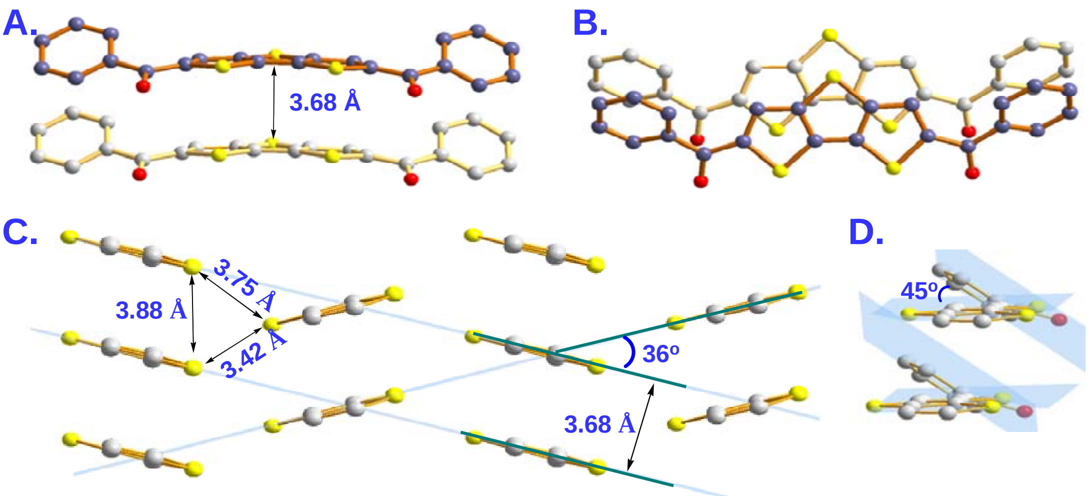

Figure S6. Crystal structures of **5**. A. Two **DTT** units in **5** with 3.68 Å planes distance. B. The two **DTT** units are not superimposable when view directly from the top. C. Side view of **DTT**s stacking in **4** and S-S distances in **DTT**s. **DTT** units in herringbone packing with 36^o planes angle (substitutents are omitted for clarity). D. Phenyl and **DTT** with 45^o plane angle.

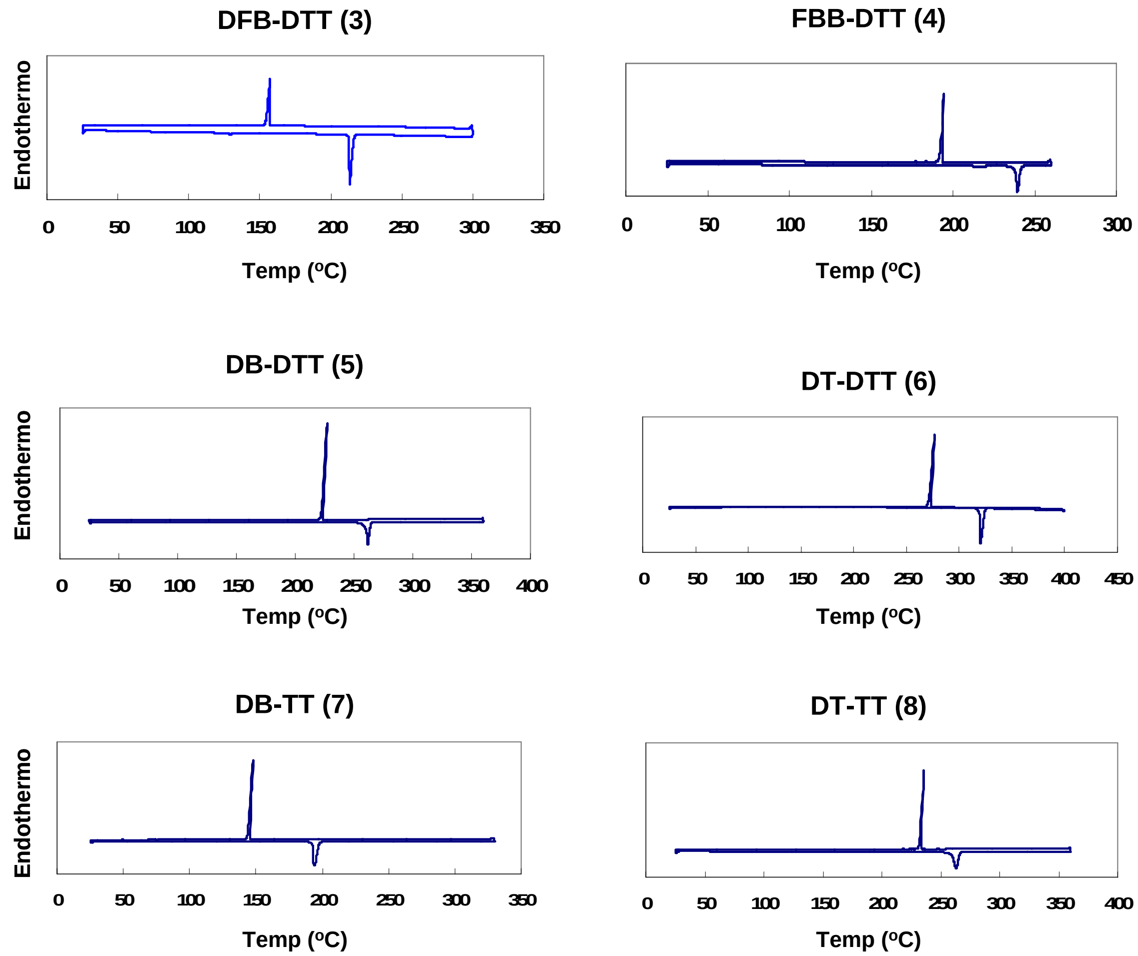

Figure S7. DSC measurements of **3** - **8**.

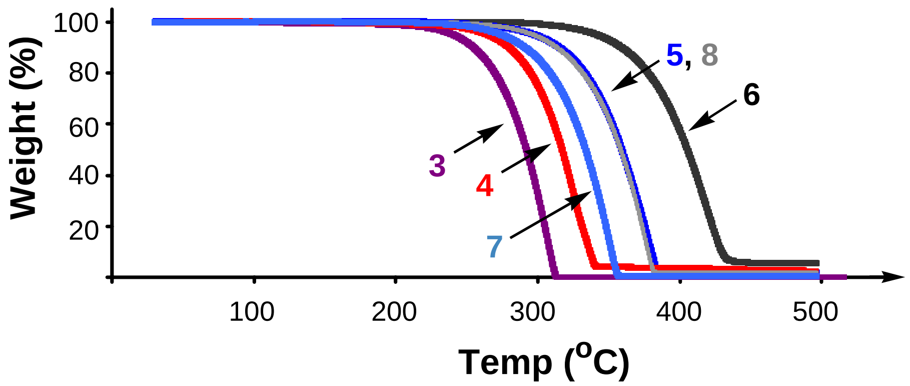

Figure S8. TGA of **3** - **8**.

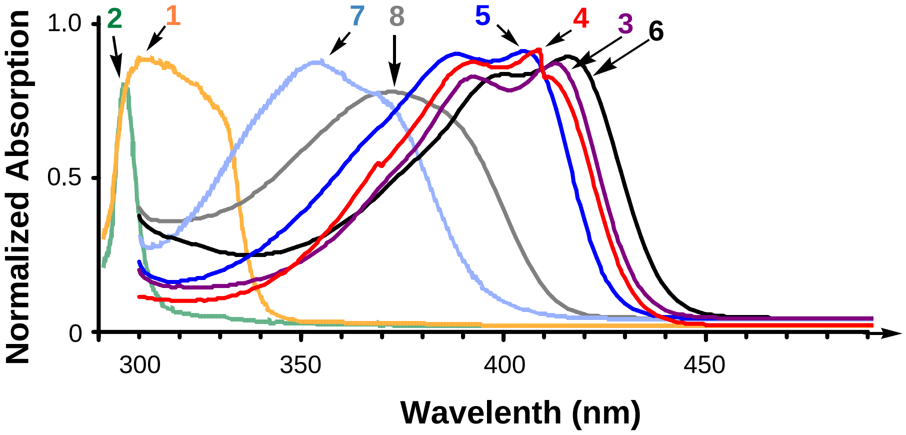

Figure S9. UV-vis spectra of **1** - **8** in *o*-$C_6H_4Cl_2$.

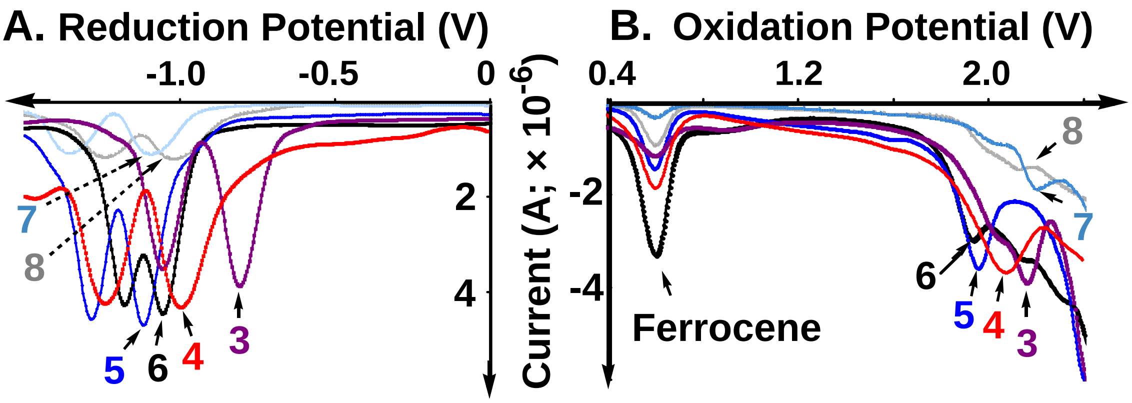

Figure S10. DPV of compounds **3** - **8** in *o*-dichlorobenzene. (A) Reductive and (B) Oxidative scans.

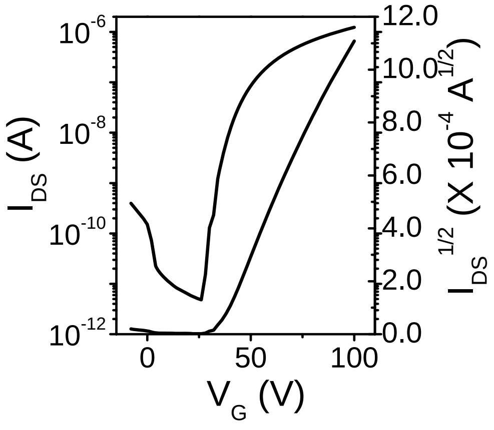

Figure S11. Transfer plots of OFET devices fabricated with **3**, n-type character, film deposited at T_D = 25 °C, treated with HMDS.

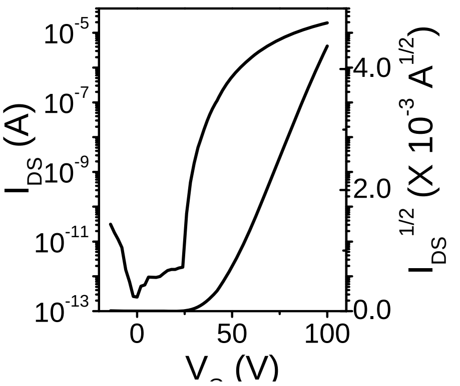

Figure S12. Transfer plot of OFET device fabricated with **4,** n-type character, film deposited at T_D = 70 °C, treated with HMDS.

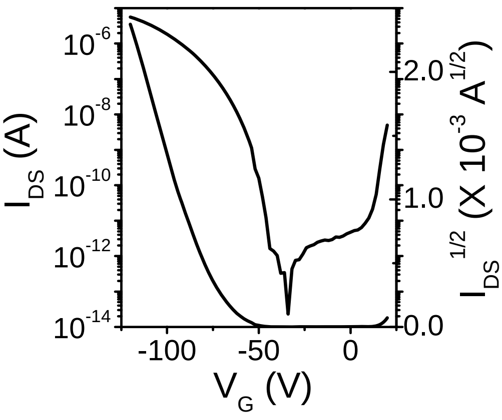

Figure S13. Transfer plot of OFET device fabricated with **5,** p-type character, film deposited at T_D = 90 °C, treated with HMDS.

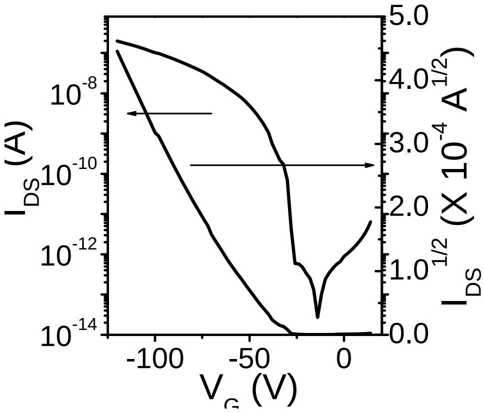

Figure S14. Transfer plots of OFET devices fabricated with **6**, p-type character, film deposited at T_D = 70 °C.

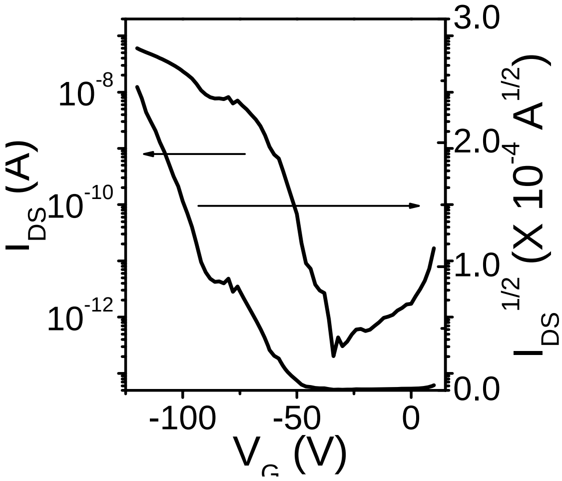

Figure S15. Transfer plot of OFET device fabricated with **7,** p-type character, film deposited at T_D = 25 °C.

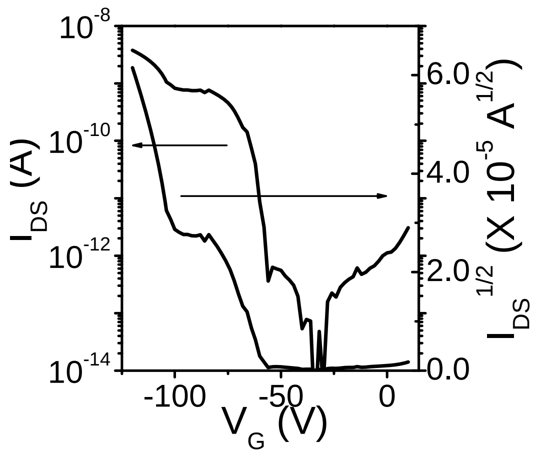

Figure S16. Transfer plot of OFET device fabricated with **8,** p-type character, film deposited at T_D = 60 °C.

Table S2. Crystal data and structure refinement for **DFB-DTT** (**3**).

Identification code	ic12833	
Empirical formula	C22 H2 F10 O2 S3	
Formula weight	584.42	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.1883(3) Å	α= 103.105(1)°.
	b = 9.3340(5) Å	β= 97.954(1)°.
	c = 18.096(1) Å	γ = 93.810(1)°.
Volume	1003.04(9) Å^3	
Z	2	
Density (calculated)	1.935 Mg/m^3	
Absorption coefficient	0.485 mm^{-1}	
F(000)	576	
Crystal size	0.70 x 0.12 x 0.10 mm^3	
Theta range for data collection	1.17 to 27.50°.	
Index ranges	-8<=h<=8, -12<=k<=12, -23<=l<=23	
Reflections collected	13000	
Independent reflections	4567 [R(int) = 0.0335]	
Completeness to theta = 27.50°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9531 and 0.7279	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4567 / 0 / 334	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R1 = 0.0413, wR2 = 0.0884	
R indices (all data)	R1 = 0.0533, wR2 = 0.0931	
Largest diff. peak and hole	0.364 and -0.299 e.Å^{-3}	

Table S3. Crystal data and structure refinement for **FBB-DTT**（**4**）

Identification code	ic13240	
Empirical formula	C22 H7 F5 O2 S3	
Formula weight	494.46	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 6.2481(3) Å	α= 90°.
	b = 40.288(2) Å	β= 107.7950(12)°.
	c = 7.7740(4) Å	γ = 90°.
Volume	1863.27(16) Å^3	
Z	4	
Density (calculated)	1.763 Mg/m^3	
Absorption coefficient	0.467 mm^{-1}	
F(000)	992	
Crystal size	0.60 x 0.16 x 0.10 mm^3	
Theta range for data collection	1.01 to 27.50°.	
Index ranges	-8<=h<=8, -46<=k<=52, -10<=l<=10	
Reflections collected	9650	
Independent reflections	4183 [R(int) = 0.0258]	
Completeness to theta = 27.50°	97.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9548 and 0.7669	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4183 / 0 / 289	
Goodness-of-fit on F^2	1.096	
Final R indices [I>2sigma(I)]	R1 = 0.0400, wR2 = 0.0995	
R indices (all data)	R1 = 0.0547, wR2 = 0.1122	
Largest diff. peak and hole	0.317 and -0.442 e.Å^{-3}	

Table S4. Crystal data and structure refinement for **DB-DTT**（**5**）

Identification code	ic12547	
Empirical formula	C22 H12 O2 S3	
Formula weight	404.50	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell dimensions	a = 11.6446(5) Å	α= 90°.
	b = 38.2970(17) Å	β= 90°.
	c = 3.8808(2) Å	γ = 90°.
Volume	1730.66(14) $Å^3$	
Z	4	
Density (calculated)	1.552 Mg/m^3	
Absorption coefficient	0.444 mm^{-1}	
F(000)	832	
Crystal size	0.30 x 0.15 x 0.01 mm^3	
Theta range for data collection	1.06 to 27.50°.	
Index ranges	-11<=h<=15, -46<=k<=49, -5<=l<=5	
Reflections collected	8272	
Independent reflections	1976 [R(int) = 0.0771]	
Completeness to theta = 27.50°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9956 and 0.8783	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1976 / 0 / 125	
Goodness-of-fit on F^2	1.098	
Final R indices [I>2sigma(I)]	R1 = 0.0460, wR2 = 0.1052	
R indices (all data)	R1 = 0.0817, wR2 = 0.1353	
Extinction coefficient	0.037(3)	
Largest diff. peak and hole	0.497 and -0.538 e.$Å^{-3}$	

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