Electronic Supplementary Information for

An asymmetric conjugated oligomer based on thienoacene for solution processed single crystal organic thin-film transistors

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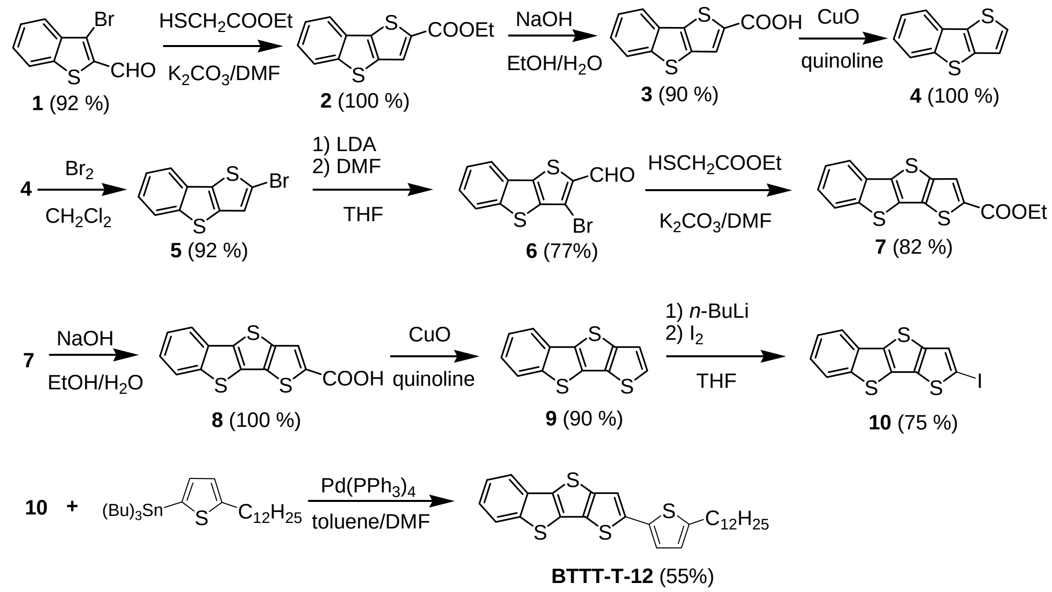
1. Synthesis and characterization of BTTT-T-12

General Information. Toluene was distilled over sodium/benzophenone. *N*, *N*-dimethyl formamide (DMF) was distilled over CaH_2 under reduced pressure. Quinoline was distilled over zinc powder and Na_2SO_4. 3-Bromobenzothiophene-2-carbaldehyde [1] (**1**) and 5-dodecyl-2-tributylstannythiophene [2] were synthesized as reported in the literatures. Other reagents were obtained from commercial resources and used without further purification. ^1H NMR spectra were recorded on Bruker AV 300-MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. Elemental analysis was carried out on a FlashEA1112 elemental analyzer. GC/MS were recorded on an Agilent 5975/6890N gas chromatography-mass spectrometer. MALDI-TOF mass spectra were recorded on Kratos AXIMA-CFR Kompact MALDI Mass Spectrometer with anthracene-1,8,9-triol as the matrix. Optical micrographs were collected on a Zeiss Axio Imager A2m equipped with polarizer and analyzer Thin-film XRD were recorded on a Bruker D8 Discover thin-film diffractometer with Cu Kα radiation (λ = 1.54056 Å) operated at 40 keV and 40 mA. Film morphology was imaged by a SPI 3800/SPA 300HV AFM (Seiko Instruments Inc., Japan) with tapping mode. A 150 μm scanner and a commercially available SiN_4-cantilevel with a spring constant of 2 N/m were used. For the transmission electron microscope measurements, a carbon thin films which were used as support layer were deposited on the film of **BTTT-T-C12**. Then, the films were separated from the Si/SiO_2 substrate by floating from 10% HF solution, and then transferred to a copper grid for measurements. The selected area electron diffraction was performed by JEOL JEM-1011 transmission electron microscope operated at 100 kV. In order to provide weaker-intensity beam and high contrast, dark field was used.



Scheme S1. Synthesis route of **BTTT-T-C12**.

Thieno[3,2-*b*]benzo[*b*]thiophene-2-ethyl-carboxylates (**2**). A mixture of **1** (15.8 g, 65.5 mmol), ethyl mercaptoacetate (8.50 mL, 76.6 mmol) and K_2CO_3 (18.1 g, 131 mmol) in DMF (130 ml) was stirred at room temperature for 50 h, and then poured into a large amount of water for extraction with CH_2Cl_2. The organic extracts were separated and washed with brine for drying with anhydrous $MgSO_4$. The solvent was removed to afford **2** in a yield of 100% (17.2 g). mp: 125-126 ^{o}C (lit[3]. 124 ^{o}C). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.06 (s, 1H), 7.95-7.78 (m, 2H), 7.55-7.32 (m, 2H), 4.41 (q, $J = 6.0$ Hz, 2H), 1.42 (t, $J = 6.0$ Hz, 3H).

Thieno[3,2-*b*]benzo[*b*]thiophene-2-carboxylic acid (**3**). A mixture of **2** (17.2 g, 65.5 mmol), NaOH (9.82 g, 196 mmol), EtOH (280 mL) and water (40 mL) was stirred in reflux for 4 h and then poured into a mixture of ice and hydrochloric acid. The precipitate was filtered off, washed with water and dried in vacuum to afford **3** in a yield of 90% (13.8 g). mp: 263-265 ^{o}C (lit[3]. 259 ^{o}C). ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) 13.49 (s, 1H), 8.25 (s, 1H), 8.16-8.13 (m, 2H), 7.56-7.53 (m, 2H).

Thieno[3,2-*b*]benzo[*b*]thiophene (**4**). A mixture of **3** (13.8 g, 58.9 mmol), CuO powder (0.60 g, 7.50 mmol) and freshly distilled quinoline (130 mL) was heated to reflux and stirred for 5 h. After cooling to room temperature, the mixture was poured into a mixture of ice water and hydrochloric acid, and then extracted with $CHCl_3$. The organic extracts were washed with brine and dried with anhydrous $MgSO_4$. After the solvent had been removed, the residue was purified by column chromatography on silica gel with petroleum ether as eluent to afford **4** in a yield of 100% (10.1 g). mp: 90-92 ^oC (lit[3]. 91 ^oC). ^1H NMR（300 MHz, $CDCl_3$）δ (ppm) 7.87-7.84 (m, 2H), 7.51 (d, *J* = 5.1 Hz, 1H), 7.45-7.35 (m, 2H), 7.32 (d, *J* = 5.1 Hz, 1H). Anal. Calcd. for $C_{10}H_6S_2$: C 63.12; H 3.18. Found: C 63.08, H 3.37.

2-Bromothieno[3,2-*b*]benzo[*b*]thiophene (**5**). A solution of bromine (0.30 mL, 5.83 mmol) in dichloromethane (3.2 mL) was added dropwise to a vigorously stirred solution of **4** (1.11 g，5.83 mmol) in dichloromethane (15 mL) at -35 ^oC. The mixture was stirred at this temperature for 4 h, then warmed to room temperature and stirred overnight. Water was added and the mixture was extracted with dichloromethane. The combined organic extracts were washed with brine and dried with anhydrous $MgSO_4$. After the solvent had been removed, the residue was purified by column chromatography on silica gel with petroleum ether (PE) as eluent to afford **5** as a white solid in a yield of 92% (1.44 g). mp: 101 ^oC. (lit[3]. 98 ^oC) ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.86- 7.83 (m, 1H), 7.78-7.75 (m, 1H), 7.44-7.33 (m, 2H), 7.32 (s, 1H). Anal. Calcd. for $C_{10}H_5BrS_2$: C, 44.62; H, 1.87. Found: C, 44.51; H, 2.17.

3-Bromothieno[3,2-*b*]benzo[*b*]thiophene-2-carbaldehyde (**6**). Into a solution of compound **5** (4.40 g, 16.3 mmol) in THF (50 mL) was added LDA (9.7 mL, 2.0 mol/L, 19.4 mmol) at

-78 °C. After stirred for 16 h at this temperature, DMF (1.55 mL, 1.46 g, 20.0 mmol) was added. Then the mixture was warmed to room temperature and stirred overnight. Water was added and the mixture was extracted with chloroform. The combined organic layers were washed with brine and dried with anhydrous $MgSO_4$. After the solvent had been removed, the residue was purified by column chromatography on silica gel with PE/CH_2Cl_2 (1/1, v/v) as eluent to afford **6** in a yield of 77% (3.70 g). mp: 227-228 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 10.06 (s, 1H), 7.95-7.90 (m, 2H), 7.56-7.44 (m, 2H). GC/MS: 298 (M^+). Anal. Calcd. for $C_{11}H_5BrOS_2$: C, 44.46; H, 1.70. Found: C, 44.19; H, 2.00.

Benzo[*d*,*d′*]thieno[3,2-*b*;4,5-*b′*]dithiophene-2-ethyl-carboxylates (**7**). Into a mixture of **6** (3.46 g, 11.6 mmol) and K_2CO_3 (3.20 g, 23.3 mmol) in DMF (30 mL) was added ethyl mercaptoacetate (1.60 mL, 1.76 g, 14.7 mmol). The mixture was stirred for 72 h at room temperature, and then Et_2O (200 mL) was added. The organic layer was separated and washed with brine and dried with anhydrous $MgSO_4$. After the solvent had been removed, the residue was purified by column chromatography on silica gel with PE and DCM (1/1, v/v) as eluent to afford **7** as a light yellow solid in a yield of 88% (3.28 g). mp: 199-200 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.06 (s, 1 H), 7.95-7.78 (m, 2 H), 7.55-7.32 (m, 2 H), 4.41 (q, J = 7.1 Hz, 2 H), 1.42 (t, J = 7.1 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 162.68, 142.61, 141.00, 140.16, 136.68, 134.83, 133.38, 129.68, 127.18, 125.80, 125.53, 124.40, 121.57, 61.91, 14.76. Anal. Calcd. for $C_{15}H_{10}O_2S_3$: C, 56.58; H, 3.17. Found: C, 56.27; H, 3.46.

Benzo[*d*,*d*’]thieno[3,2-*b*;4,5-*b*’]dithiophenes-2-carboxylic acid (**8**). A mixture of **7** (4.08 g, 12.8 mmol), NaOH (1.5 g, 37.5 mmol), EtOH (56 mL) and water (8 mL) was stirred under reflux for 5 h and then poured onto a mixture of ice and hydrochloric acid. The precipitate was filtered off, washed with water and dried to afford **8** quantitatively (3.70 g) and used directly for the next reaction. mp > 370 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) 13.30 (s, 1H), 8.09-7.99 (brm, 2H), 7.47 (brm, 2H), 3.40-3.12 (m, 3H), 1.16-0.80 (m, 20H). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm) 164.25, 143.65, 143.59, 142.46, 138.62, 133.17, 129.99, 129.54, 126.49, 126.26, 125.23, 121.93, 41.18, 40.90, 40.63, 40.35, 40.07, 39.79, 32.14, 29.85, 29.73, 29.57, 28.99, 22.94, 14.73. Anal. Calcd. for $C_{13}H_6O_2S_3$: C 53.77; H, 2.08. Found: C, 53.47; H, 2.23.

Benzo[*d*,*d′*]thieno[3,2-*b*;4,5-*b′*]dithiophenes (9). A mixture of **8** (3.85 g, 13.3 mmol), CuO powder (138 mg, 1.7 mmol) and freshly distilled quinoline (30 mL) was heated to reflux under stirring for 5 h. After cooling to room temperature, the mixture was poured onto a mixture of ice water and hydrochloric acid, and extracted with CH_2Cl_2. The extracts were washed with brine and dried with anhydrous $MgSO_4$. The residue after evaporation was purified by column chromatography on silica gel with PE as eluent to afford **9** as a white solid in a yield of 100% (3.26 g). mp: 196 – 197 °C. ^{1}H NMR（300 MHz, $CDCl_3$）δ (ppm) 7.89-7.82 (m, 2 H), 7.46-7.41 (m, 2 H), 7.39-7.34 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 142.64, 141.60, 136.69, 133.73, 131.59, 129.73, 126.28, 125.81, 125.29, 122.54, 122.01, 121.63. GC/MS: 246 (M^+) Anal. Calcd. for $C_{12}H_6S_3$: C, 58.50; H, 2.45. Found: C, 58.18; H 2.85.

2-Iodo-benzo[*d*,*d′*]thieno[3,2-*b*;4,5-*b′*]dithiophenes (10). Into a solution of **9** (1.59 g, 6.45 mmol) in dry THF (35 mL) was added *n*-BuLi (2.7 mL, 2.5 M in *n*-hexane, 6.78 mmol) dropwise at -78 °C. The mixture was stirred for 1 h at room temperature. Then iodine (2.00 g, 8.55 mmol) in THF (13 mL) was added at -78 °C. The mixture was warmed to room temperature and stirred overnight. Saturated aqueous sodium thiosulfate solution was added, and the resulting precipitate was collected by filtration and wash with water and acetone. The crude product was purified by recrystallization from THF and give **10** as a brown solid in a yield of 75 % (1.8 g). mp: 207-208 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.88-7.81 (m, 2 H), 7.50 (s, 1 H), 7.47-7.43 (m, 1 H), 7.40-7.34 (m, 1 H). GC/MS: 372 (M^+). Anal. Calcd. for $C_{12}H_5IS_3$: C, 38.72; H, 1.35. Found: C, 38.50; H 1.65.

2-(5-Dodecylthiophen-2-yl)benzo[*d*,*d'*]thieno[3,2-*b*;4,5-*b'*]dithiophene (BTTT-TC12) A mixture of **10** (360 mg, 0.96 mmol), 5-dodecyl-2-tributylstannythiophene (542 mg, 1.00 mmol), $Pd(PPh_3)_4$ (34 mg, 3 mol%), freshly distilled toluene (10 mL) and DMF (2 mL) was heated to 90 °C for 24 h under Ar. After cooled to room temperature, the mixture was poured into CH_3OH. The solid was collected by filtration, dried in vacuum, and purified by twice vacuum sublimation to afford **BTTT-TC12** as a primrose yellow solid in a yield of 55 % (265 mg). ^{1}H NMR (400 MHz, 80 °C, $C_2D_2Cl_4$) δ (ppm) 7.85 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.43-7.39 (m, 1H), 7.35-7.32 (m, 1H), 7.33 (s, 1H), 7.05 (d, J = 3.4 Hz, 1H), 6.71 (d, J = 3.4 Hz, 1H), 2.80 (t, J = 7.6 Hz, 2H), 1.69 (q, J = 7.2 Hz 2H), 1.38-1.26 (m, 18H), 0.87 (t, J = 7.2 Hz, 3H). MALTI-TOF MS: Calcd for $C_{28}H_{32}S_4$: 496.14. Found: 496.1 Anal. Calcd. for $C_{28}H_{32}S_4$: C 67.69; H 6.49. Found: C 67.90; H 6.53.

2. Single crystal structure

The crystal of **BTTT-T-C12** belongs to the triclinic space group P-1 with the unit cell parameters of a = 5.866 Å, b = 7.5451 Å, c = 56.721 Å, α = 91.309°, β = 91.191° and γ = 90.093°, which is little deviate from the orthorhombic crystal system. Two crystallographically independent molecules (Form A and B, Figure S1) were observed in the unit cell of **BTTT-T-C12**. The **BTTT** aromatic moiety is nearly coplanar with the standard deviation of 0.017 Å for Form A (0.019 Å for Form B), while the dihedral angle between the thienyl moiety and the **BTTT** plane is 5.9° for Form A (6.0° for Form B). The dodecyl groups on the thienyl α–position lie outside the plane of conjugated backbone with a dihedral angle of 66.9° for Form A (65.5° for Form B).

The lattice parameters of the single-crystal film were calculated to be *a* = 6.02 Å and *b* = 7.85 Å in a rectangular unit cell from the SAED pattern. Both of them were larger than the length of *a* and *b* axis from single crystal (*a* = 5.866 Å, *b* = 7.5451 Å), indicating a less tight packing in the *ab* plane was formed in the film.

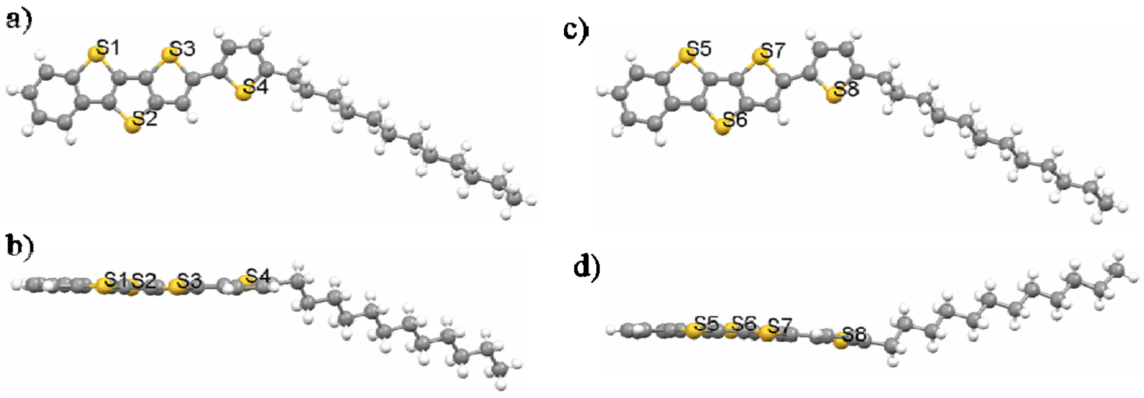
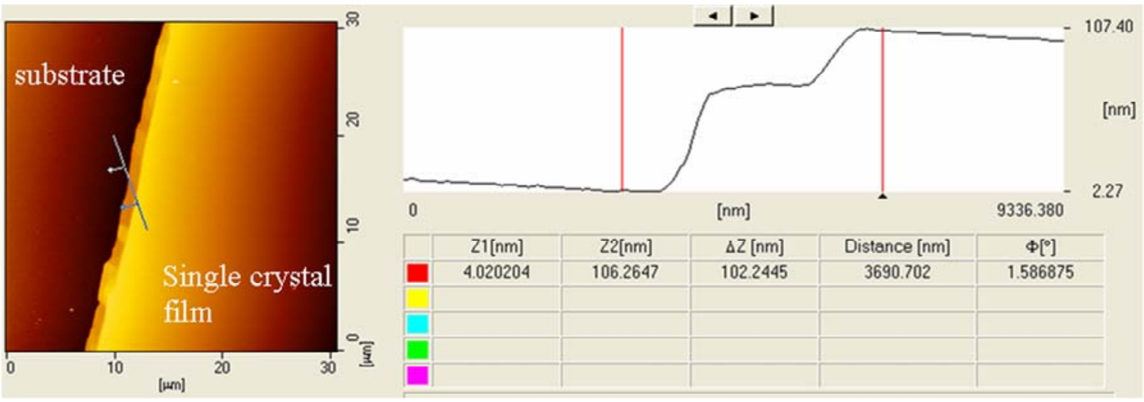
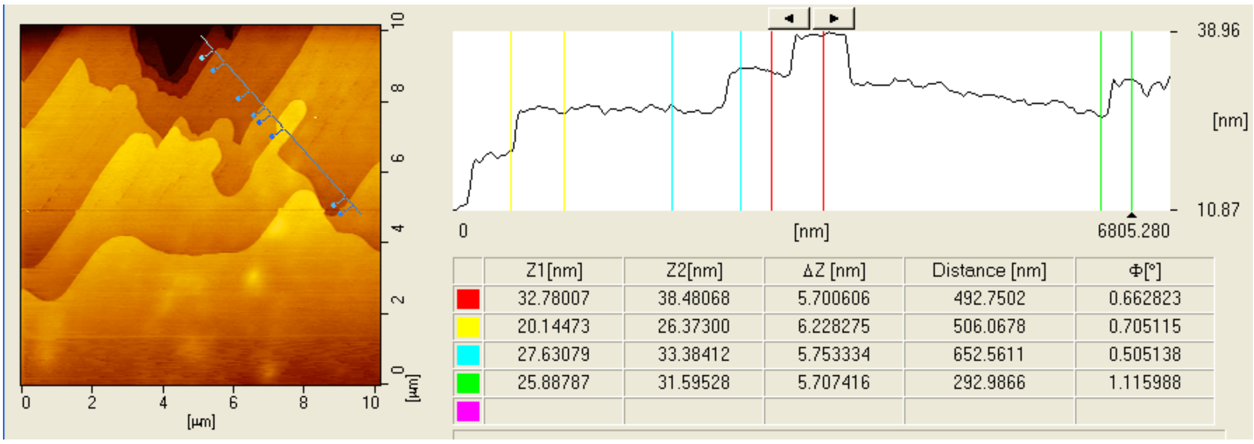


Figure S1. Molecular structures from front views (a, c) and side views (b, d) of Form A (a, b) and Form B (c,d)



	Z1[nm]	Z2[nm]	ΔZ [nm]	Distance [nm]	Φ[°]
🟥	4.020204	106.2647	102.2445	3690.702	1.586875
🟨					
🟦					
🟩					
🟪					

Fig. S2 The thickness of the **BTTT-TC12** film prepared by dip-coating as measured by AFM.



	Z1[nm]	Z2[nm]	ΔZ [nm]	Distance [nm]	Φ[°]
🟥	32.78007	38.48068	5.700606	492.7502	0.662823
🟨	20.14473	26.37300	6.228275	506.0678	0.705115
🟦	27.63079	33.38412	5.753334	652.5611	0.505138
🟩	25.88787	31.59528	5.707416	292.9866	1.115988
🟪					

Fig. S3 Step heights of the film on the fringe of the single crystal film as measured by AFM.

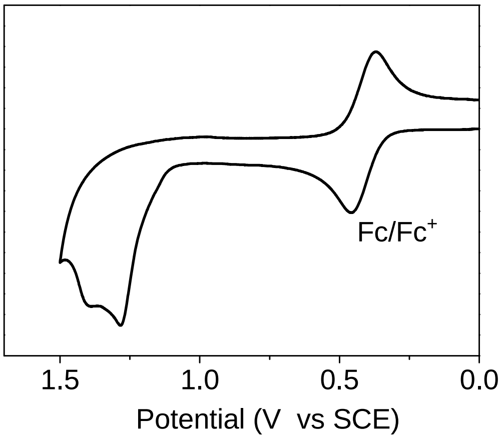


Figure S4. Thin film cyclic voltammogram of **BTTT-T-C12**

3. Cyclic voltammetry (CV) measurement.

Thin-film CV was performed on a CHI660a electrochemical analyzer with a three-electrode cell in a solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile at a scan rate of 100 mV/s. The thin films (~ 50 nm) were prepared by vacuum deposition of **BTTT-T-C12** on a platinum plate electrode (0.6 cm^2) as the working electrode. A Pt wire and a saturated calomel electrode (SCE) were used as the counter electrode, and the reference electrode, respectively. The potential was calibrated against the ferrocene/ferrocenium (Fc/Fc^+) couple. The highest occupied molecular orbital (HOMO) energy levels were estimated by the equations: HOMO = $-(4.80 + E^{onset}{}_{oxi})$ eV.[4]

4. Device Fabrication and Characterization

Top-contact OTFTs were constructed on the heavily n-doped Si substrates with 300 nm SiO_2 layer and a capacitance of 10 nF/cm^2. The SiO_2/Si substrates were modified by the self-assemble monolayer (SAMs) of phenyltrichlorosilane (PTS).[5]. Organic semiconductor layers (~100 nm) were deposited by dip-coating 2 mg/ml solution in toluene and chlorobenzene (6/1 v/v) with a withdrawal speed of 0.01 mm/min under ambient atmosphere through KSV DC (KSV Instruments Ltd). A shadow mask, with a channel width (*W*) of 1500 μm and a channel length (*L*) of 50 μm, was used to deposite a CuPc(3nm) /F_{16}CuPc (3nm) buffer layer with substrate at RT. Finally, Au (40 nm) source and drain electrodes were deposited through the same shadow mask in another chamber. The electrical measurements were performed with two Keithley 236 measurement units at room temperature under ambient conditions.

References

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