Cyano-terminated dithienyldiketopyrrolopyrrole dimer as a solution processible ambipolar semiconductor in ambient conditions

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Contents

1. Materials and general methods.

All reactions were carried out under argon atmosphere with the use of standard Schlenk techniques. Solvents were exactly purified according to the < Purification of Laboratory Chemicals-5th Edition > edited by Willey. Other reagents were obtained from commercial resources and used without further purification unless otherwise stated. 2,5-Bis(2-ethylhexyl)-3-(5-bromo-thiophene-2-yl)-6-(thiophene-2-yl) pyrrolo [3,4-c]pyrrole-1,4-dione (**1**) was synthesized following the reported method with a moderate yield of 55%.[1] ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400-MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard. Elemental analysis was carried out on a FlashEA1112 elemental analyzer. Cyclic voltammetry (CV) was performed on a CHI660a electrochemical analyzer with a three-electrode cell in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) solution of CH_2Cl_2 (with a concentration of 10^{-3} M) at a scan rate of 100 mV/s. A Pt disk (2-mm diameter) was used as working electrode with a Pt wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The redox potential was calibrated by the ferrocene/ferrocenium (Fc/Fc^{+}). The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels were estimated by the equations: HOMO = $-(4.80+E^{ox}_{onset})$ eV, LUMO = $-(4.80-E^{re}_{onset})$ eV.[2] UV-vis absorption spectra were obtained on a PerkinElmer Lambda35 UV/Vis Spectrometer. The bandgap was calculated according to the onset absorption of UV-vis spectrum (E_g= $1240/\lambda_{onset}$ eV). Molecular mass was measured by means of MALDI-TOF on Autoflex III mass spectrometer (Bruker Daltonics Inc.) with 2-[(2E)-3-(4-tert-buthyl phenyl)-2-methylprop-2-enylidene] malononitrile (DCTB) as the matrix. Out-of-plane X-ray diffraction (XRD) was recorded on Bruker D8 Discover thin-film diffractometer with Cu Kα radiation (λ = 1.54056 Å) operated at 40 keV and 40 mA. In-plane XRD of the thin films were measured with a Rigaku SmartLab with Cu Kα source (λ = 1.54056 Å) in the air. Atomic force microscopy (AFM) measurements were performed in tapping mode on a SPA400HV instrument with a SPI 3800 controller (Seiko Instruments Inc., Japan). For the transmission electron microscope (TEM) measurement, the oligomer films were spin-coated from their chloroform solution of 0.3% (w/w) on ODTS modified Si/SiO_2 substrates. Then the films were separated from the Si/SiO_2 substrates by floating from 10% HF solution, and transferred to a copper grid for measurement. TEM was performed on a JEOL JEM-1011 transmission electron microscope operated at an acceleration voltage of 100 kV with cameral length of 160 cm and Au (111) diffraction as the external standard. The two dimensional grazing incidence X-ray diffraction (GIXD) was measured at Beijing Synchrotron Radiation Facility on beam line 1W1A ($\lambda = 0.154$ nm) with a Huber diffractometer and a Mar 345 detector.

2. Synthetic details

2,5-Bis(2-ethylhexyl)-3-(5-cynao-thiophene-2-yl)-6-(thiophene-2-yl)pyrrolo[3,4-c] pyrrole-1,4-dione (**2**)

A mixture of 2,5-bis(2-ethylhexyl)-3-(5-bromo-thiophene-2-yl)-6-(thiophene-2-yl) pyrrolo[3,4-c]pyrrole-1,4-dione (**1**, 400 mg, 0.66 mmol) and copper(I)cyanide (1.5 g, 16.6 mmol) in dry DMF was heated under argon for 8 h at 130 °C. After cooling to the room temperature, the mixture was poured into icy water and then extracted with $CHCl_3$, washed with water for three times, $MgSO_4$ was added to dry the organic phase. Evaporation off the solvent, the residue was purified by chromatography on silica gel (chloroform) to give a dark red solid of **2** (260 mg, 72%). ^{1}H NMR(400 MHz, $CDCl_3$) δ= 9.03 (d, J = 4 Hz , 1H), 8.74 (d, J = 4 Hz, 1H), 7.71 (t, J = 5.6 Hz 2H), 7.31 (t, J = 4.4 Hz 1H), 3.96-3.99 (m, 4H), 1.78-1.84 (m, 2H), 1.26 (m, 16H), 0.87-0.91(m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.81, 161.09, 143.21, 137.68, 136.60, 135.81, 133.32, 132.19, 129.38, 128.78, 113.57, 112.22, 110.74, 107.70, 48.93, 46.05, 39.37, 39.06, 30.17, 28.30, 23.52, 23.04, 23.02, 13.98, 10.42. Anal. Calcd. for $C_{31}H_{39}N_3O_2S_2$: C, 67.72; H, 7.15. Found: C, 67.68; H, 7.40. MALDI-TOF-MS m/z: 549.2, calcd for $C_{31}H_{39}N_3O_2S_2$: 549.25 (100.0%).

2,5-Bis(2-ethylhexyl)-3-(5-cynao-thiophene-2-yl)-6-(5-bromo-thiophene-2-yl)pyrrolo [3,4-c]pyrrole-1,4-dione (**3**)

A solution of **2** (352 mg, 0.64 mmol) in 40 ml dry chloroform was cooled to 0 °C for 20 minutes. NBS (450 mg, 2.50 mmol) was added in one portion. Then the mixture was allowed to warm to the room temperature and stirred for 12 h. The mixture was then poured into water, extracted with chloroform and then dried with $MgSO_4$.

Evaporation off the solvent, the residue was purified by chromatography on silica gel ($CHCl_3$) to give a dark red solid of **3** (306 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.78 (d, *J* = 4 Hz, 1H), 8.75 (d, *J* = 4 Hz, 1H), 7.70 (d, *J* = 4 Hz, 1H), 3.92-3.99 (m, 4H), 1.78-1.84 (m, 2H), 1.26 (m, 16H), 0.87-0.91(m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.54, 160.98, 141.71, 137.69, 137.60, 136.77, 135.67, 133.52, 131.76, 130.75, 120.68, 113.50, 112.49, 110.58, 107.85, 46.14, 46.10, 39.35, 39.10, 30.15, 28.28, 23.53, 23.01, 13.99, 10.42. Anal. Calcd. for $C_{31}H_{38}BrN_3O_2S_2$: C, 59.22; H, 6.09. Found: C, 59.53; H, 6.11. MALDI-TOF-MS m/z: 627.2, calcd for $C_{31}H_{38}BrN_3O_2S_2$: 627.16 (100.0%).

Traditional Yamamoto reaction was followed for the syntheses of the two final compounds. A mixture of $Ni(COD)_2$, COD, and bipyridine was added into a 100 ml Schleck Tube with a ratio of 1.2:1.2:1.2, 4 ml DMF was added and then the mixture was heated to 80 °C for 20 min. Then the monobrominated intermediates **1** or **3** in 15 ml toluene (0.02 M) was added in one portion. The reaction was carried out for 36 hours. After cooling to the room temperature, the mixture was poured into water and then extracted with $CHCl_3$, wash with water for three times. $MgSO_4$ was added to dry the organic layer. Evaporation off the solvent, the crude products was then purified by chromatography.

For **DPP2**, $CHCl_3$ was used as the eluant. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.95 (d, *J* = 4 Hz, 2H), 8.92 (d, *J* = 4 Hz, 2H), 7.64 (d, *J* = 4 Hz, 2H), 7.43 (d, *J* = 4 Hz, 2H), 7.28 (t, *J* = 4.4 Hz 2H), 4.03-4.06 (m, 8H), 1.78-1.90 (m, 4H), 1.25-1.33 (m, 32H), 0.87- 0.91(m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.61, 140.88, 140.53, 139.17, 136.67, 135.57, 130.78, 129.82, 129.70, 128.50, 126.01, 108.84, 108.18, 45.97, 39.33, 39.10, 30.33, 30.22, 28.48, 28.35 23.68, 23.57, 23.07, 14.06, 14.01, 10.57, 10.50. Anal. Calcd. for $C_{60}H_{78}N_4O_4S_4$: C, 68.79; H, 7.51. Found: C, 68.80; H, 7.49. MALDI-TOF-MS m/z: 1046.5, calcd for $C_{60}H_{78}N_4O_4S_4$: 1046.5 (100.0%).

For **DPP2-CN**, $CHCl_3$: acetone (50:1, v/v) was used as the eluant. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.08 (d, *J* = 4 Hz, 2H), 8.78 (d, *J* = 4 Hz, 2H), 7.71 (d, *J* = 4 Hz, 2H), 7.48 (d, *J* = 4 Hz, 2H), 4.00-4.06 (m, 8H), 1.81-1.90 (m, 4H), 1.25-1.33 (m, 32H), 0.87-0.91 (m, 24H). ^{13}C NMR was failed to got due to the limit solubility of the product in chloroform. IR (pellet KBr): ν/cm^{-1} 2213 for cyano-group. Anal. Calcd. for $C_{62}H_{76}N_6O_4S_4$: C, 67.85; H, 6.98. Found: C, 67.93; H, 7.01. MALDI-TOF-MS m/z:

1096.5, calcd for $C_{62}H_{76}N_{6}O_{4}S_{4}$: 1096.48 (100.0%).

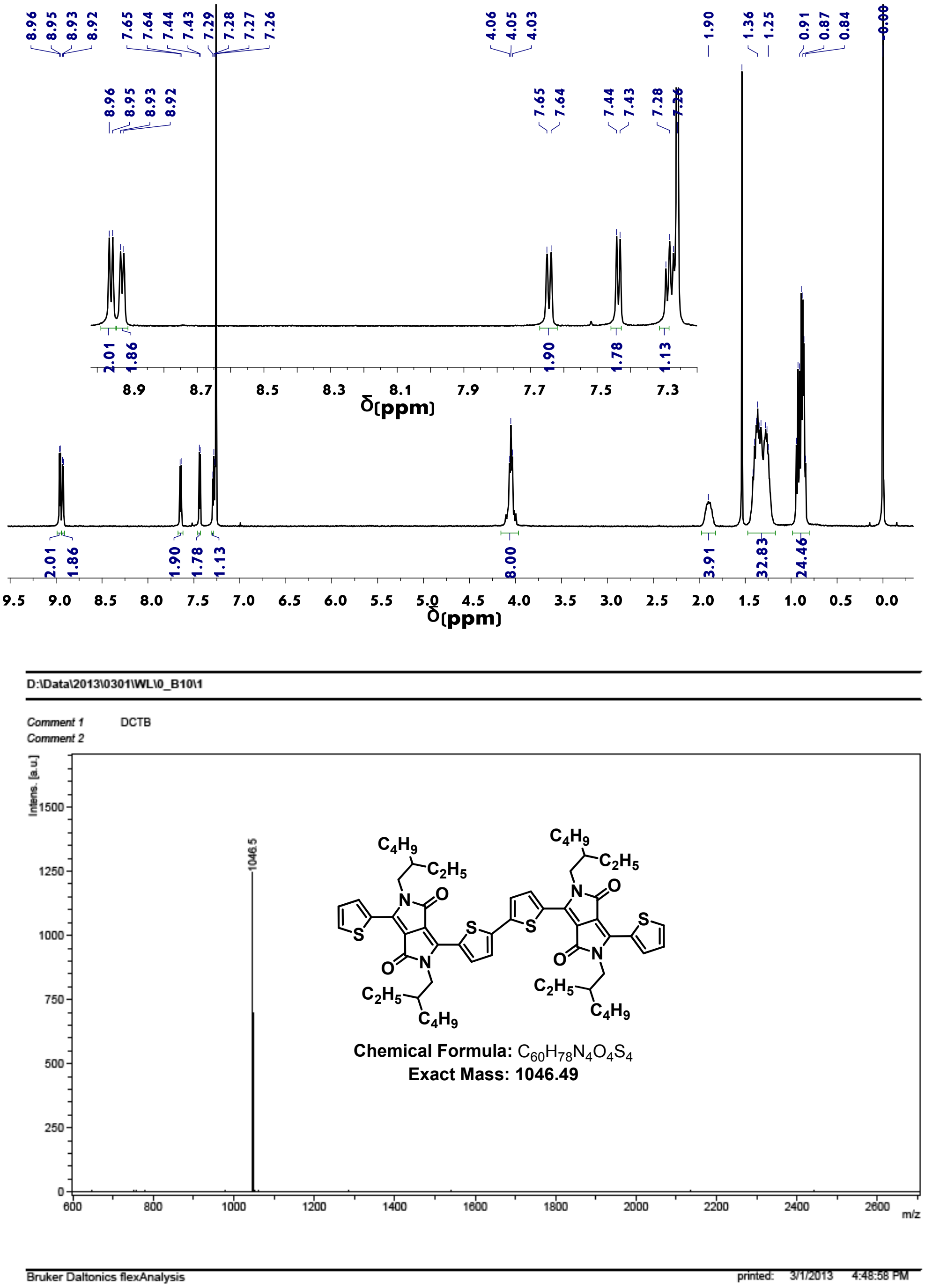

Figure S1 ^{1}H NMR (top) and MALDI-TOF MS (bottom) spectra of **DPP2**.

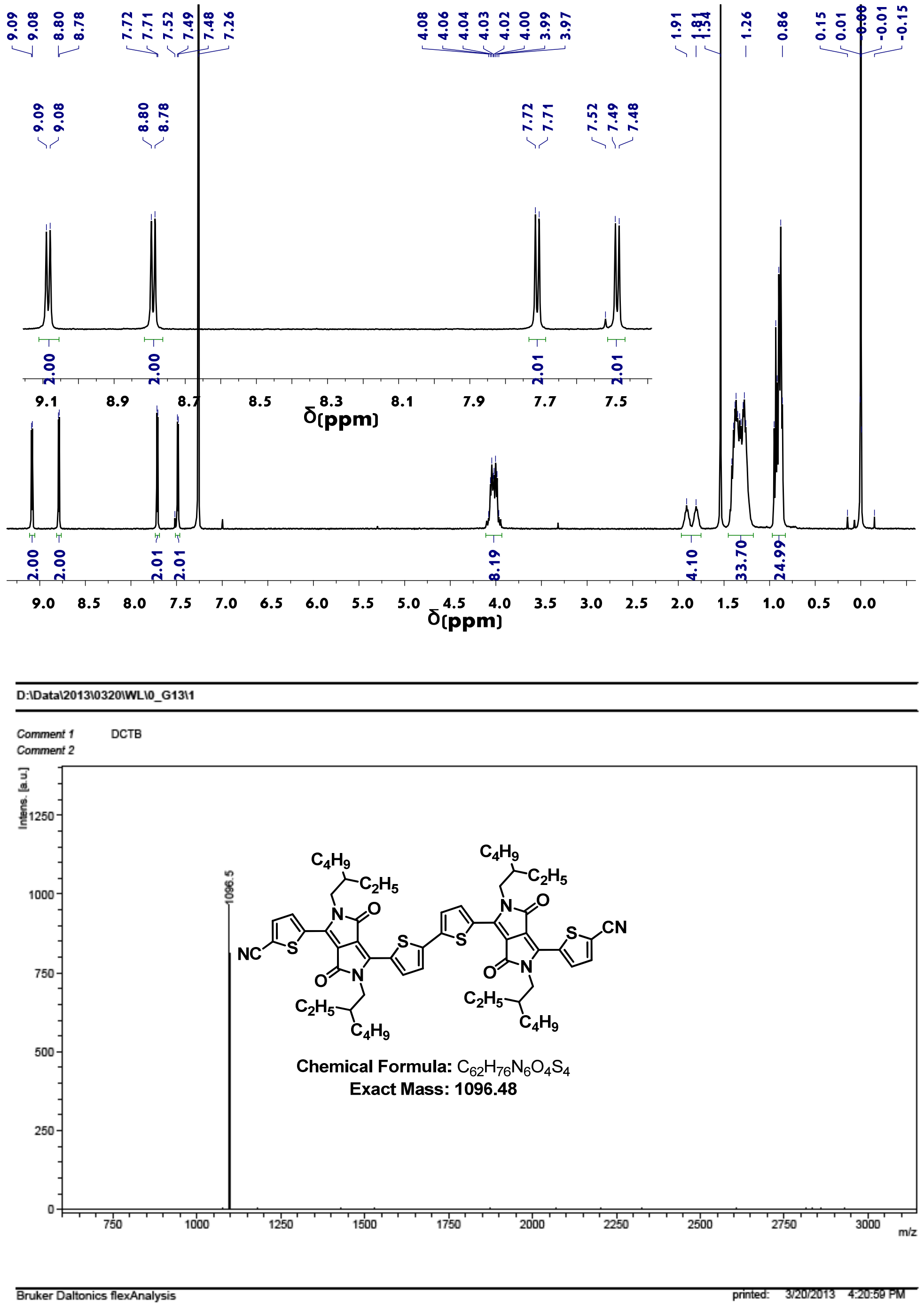

Figure S2 ^{1}H NMR (top) and MALDI-TOF MS (bottom) spectra of **DPP2-CN**

3. Thermal, optical, electrochemical properties and DFT calculations of the two oligomers

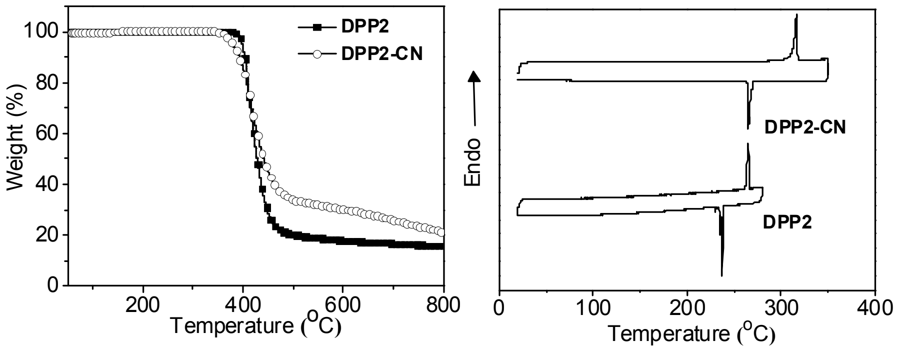

Figure S3 TGA (left) and DSC (right) curves of the oligomers

Table S1 Thermal, optical, electrochemical properties and DFT calculations of the two oligomers

	Thermal [a]		UV-vis [b]			CV		DFT [c]	
Compound	T_d	T_m	λ_{max}^{sol}	λ_{max}^{film}	E_{gap}	HOMO	LUMO	HOMO	LUMO
	(°C)	(°C)	(nm)	(nm)	(eV)	(eV)	(eV)	(eV)	(eV)
DPP2	398	265	623	643	1.55	-5.18	-3.46	-4.82	-2.97
DPP2-CN	380	316	648	684	1.48	-5.45	-3.74	-5.28	-3.52

[a] T_d referred to 5% mass loss temperature for TGA measurement, [b] E_{gap} was calculated from the onset of thin film absorption spectrum, [c] DFT calculation was based on B3LYP/6-31G.

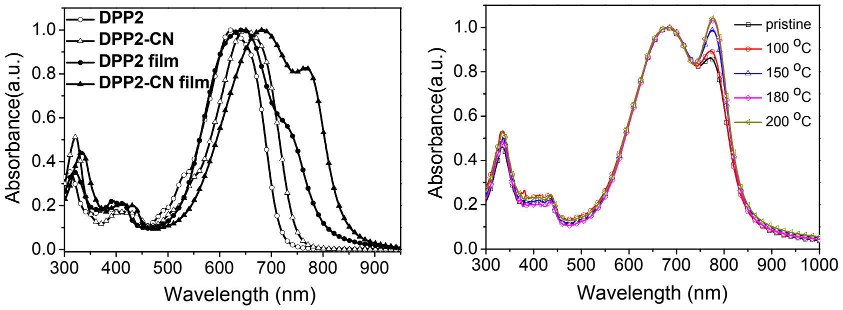

Figure S4 Solution ($CHCl_3$, 10^{-5} mol L^{-1}) and pristine film absorption spectra of **DPP2** and **DPP2-CN** (left), thin film absorption spectra of **DPP2-CN** upon thermal annealing at different temperature (right).

4. OTFT fabrication and characterization

OTFTs were fabricated in a bottom-gate/top-contact configuration on heavily doped *n*-type Si wafers covered with 300 nm thick thermally grown SiO_2 (C_i = 10 nF cm^{-2}). The Si/SiO_2 substrates were carefully cleaned according to the literature procedure and then treated with octadecyltrichlorosilane (ODTS) to form a self-assembled monolayer (SAM).[3] Thin films of **DPP-2CN** were spin-coated from $CHCl_3$ solution with a concentration of 0.3% (w/w) at various spin rates ranging from 3000 to 700 rpm in ambient condition. The thicknesses were in the range of 13-53 nm, determined by both spectroscopic ellipsometry (Horiba Jobin Yvon) or out-of-plane thin-film XRD. Thin films of **DPP2** were spin-coated from $CHCl_3$ solution with a concentration of 0.3% (w/w) at 1000 rpm in ambient condition with the thickness of ~30 nm. Au drain and source electrodes (thickness 40 nm) were deposited in vacuum through a shadow mask. The channel length (L) and width (W) are 100 μm and 3000 μm, respectively. Final OTFTs devices were annealed at different temperature for 20 min in glove box. All the measurements were done in ambient condition with two Keithley 236 measurement units.

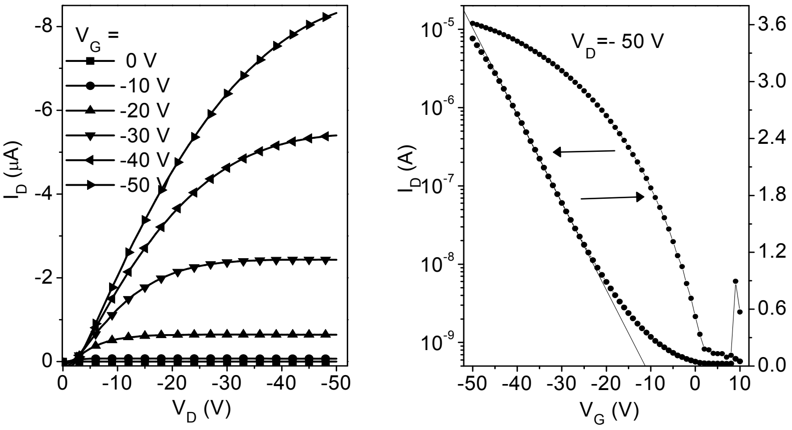

Figure S5 Typical output (left) and transfer (right) characters of the OTFT devices based on **DPP2**

Table S2 OTFT performance for **DPP2** measured in ambient condition

Annealing Temperature (°C)	μ_h(cm^2 V^{-1} s^{-1})	V_T (V)	$I_{on/off}$
pristine	0.05	-8	1.6×10^4
50 °C	0.03	5	6.3×10^4

Table S3 OTFT performance for the **DPP2-CN** at different temperatures measured in ambient condition

Annealing	hole			electron		
Temerature (°C)	μ (cm^2 V^{-1} s^{-1})	V_T (V)	$I_{on/off}$	μ (cm^2 V^{-1} s^{-1})	V_T (V)	$I_{on/off}$
pristine	1.8×10^{-3}	-45	0.6×10^4	1.3×10^{-5}	30	0.6×10^2
100 °C	3.8×10^{-3}	-20	2.3×10^4	3.0×10^{-5}	40	3.3×10^3
150 °C	1.1×10^{-2}	-20	1.2×10^4	1.7×10^{-3}	38	0.3×10^3
180 °C	6.6×10^{-2}	-14	1.2×10^5	3.3×10^{-2}	37	4.7×10^3
200 °C	3.0×10^{-2}	-28	0.4×10^5	2.2×10^{-3}	25	7.0×10^3

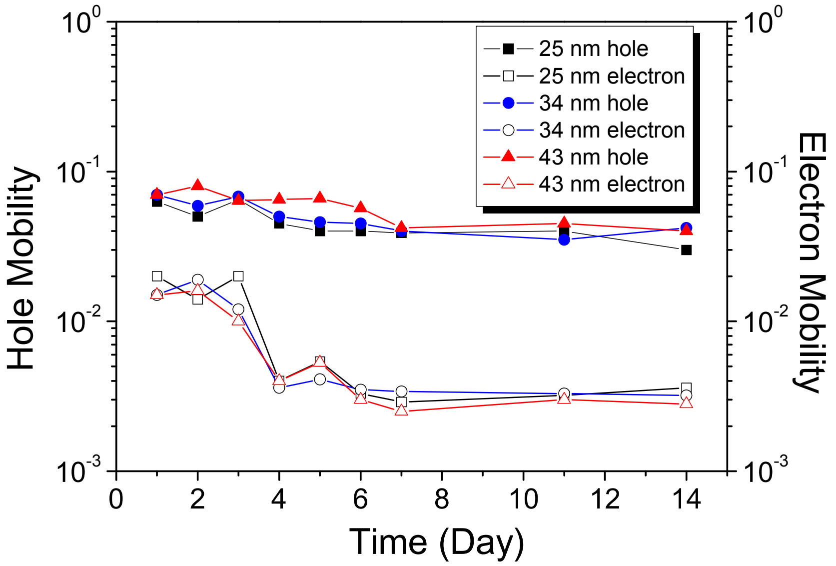

Figure S6. The mobility variation of the devices based on **DPP2-CN** with different film thicknesses stored in ambient conditions during two weeks.

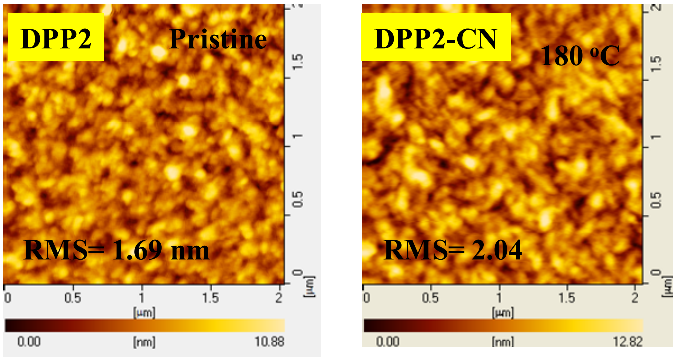

Figure S7 Tapping-mode atomic force microscopy (AFM) images of **DPP2** and **DPP2-CN** films. The film of **DPP2-CN** was thermally annealed at 180 °C for 20 min.

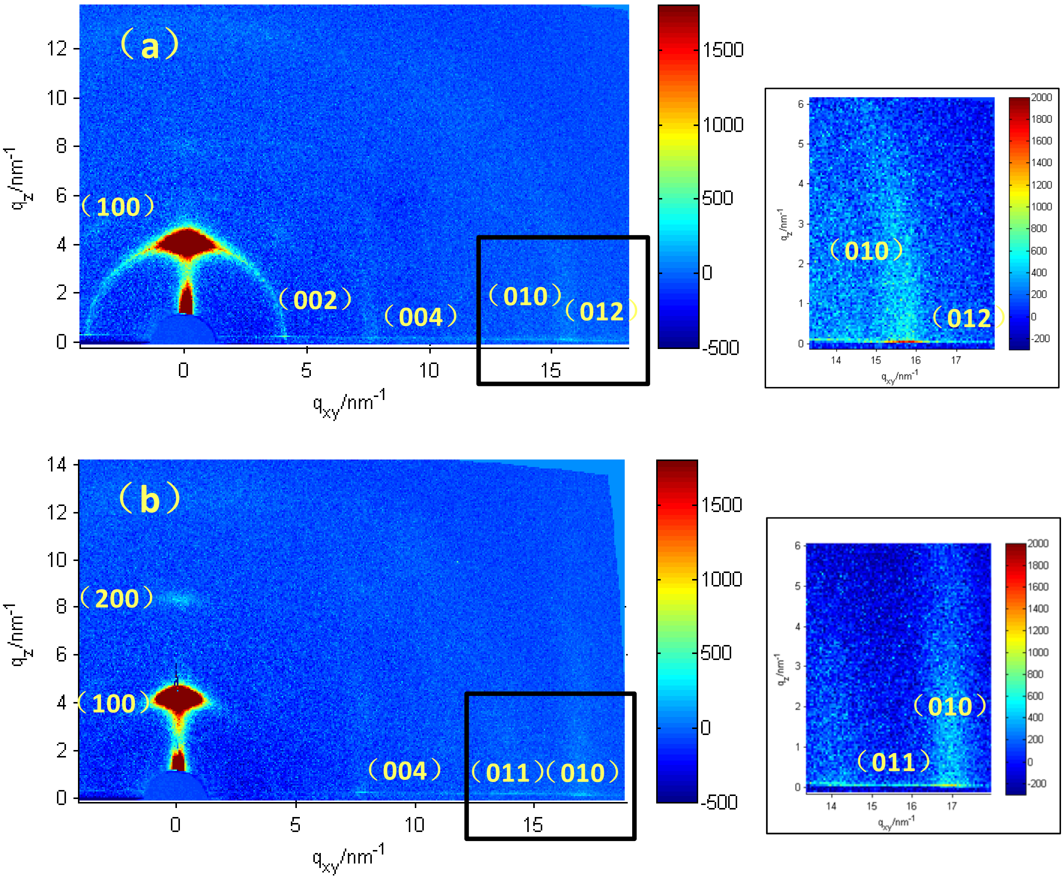

Figure S8 Grazing incident X-ray diffraction (GIXD) patterns for the two molecules.

5. References

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[2] A. J. Bard and L. A. Faulkner, *Electrochemical Methods-Fundamentals and Applications*; Wiley: New York, **1984**.

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