Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supporting Information

A new two-dimensional oligothiophene end-capped with alkyl cyanoacetate groups for highly efficient solution-processed organic solar cells

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Experimental details

General

Solvents were dried and distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification. All reagents for the chemical syntheses were purchased from Aldrich or Acros Organics. NMR spectra were measured in $CDCl_3$ on a Bruker AV 400 MHz FT-NMR spectrometer and chemical shifts are quoted relative to tetramethylsilane for ^{1}H and ^{13}C nuclei. The matrix-assisted laser desorption ionization time of flight (MALDI-TOF) mass spectra were recorded on a Autoflex Bruker MALDI-TOF system. UV/Vis spectra were obtained on an HP-8453 diode array spectrophotometer. The CV measurements were carried out on the CH Instrument work station with the films on glassy carbon electrode in 0.1 mol/L acetonitrile solution of Bu_4NPF_6 at a scan rate of 100 mV s^{-1} using a platinum counter electrode and a Ag/AgCl reference electrode.

Device Fabrication

Photovoltaic devices were fabricated by doctor-blading on indium-tin oxide (ITO)-covered glass substrates (from Osram). These substrates were cleaned in toluene, water, acetone, and isopropyl alcohol. After drying, the substrates were bladed with 50 nm PEDOT:PSS (HC Starck, PEDOT PH-4083). Photovoltaic layers, consisting of **DCA3T(VT)BDT** and $PC_{70}BM$ in different weight ratios, were dissolved at the concentration of 2% (20 mg/mL) in chlorobenzene (CB) and bladed on top of the PEDOT:PSS layer. Finally, a calcium/silver top electrode of 15/80 nm

thickness was evaporated. The typical active area of the investigated devices was 10.4 mm^2. The current-voltage characteristics of the solar cells were measured under AM 1.5G irradiation on an OrielSol 1A Solar simulator (100 mW cm^{-2}). The external quantum efficiencies (EQE) was detected with Cary 500 Scan UV-Vis-NIR spectrophotometer under monochromatic illumination, which was calibrated with a mono-crystalline silicon diode. The characterization of the current density-voltage (*J*–*V*) curve was done in an inert nitrogen atmosphere and the EQEs of the devices without encapsulation were measured in air.

Hole Mobility Measurements

Single carrier devices were fabricated and the dark current-voltage characteristics measured and analyzed in the space charge limited (SCL) regime following the procedure as described in the reference.[1] The structure of hole only devices was glass/ITO/PEDOT:PSS/active layer/PEDOT:PSS/Ag (100 nm). The reported mobility data are average values over the two cells (with each cell containing six separate devices) of each sample at a given film composition.

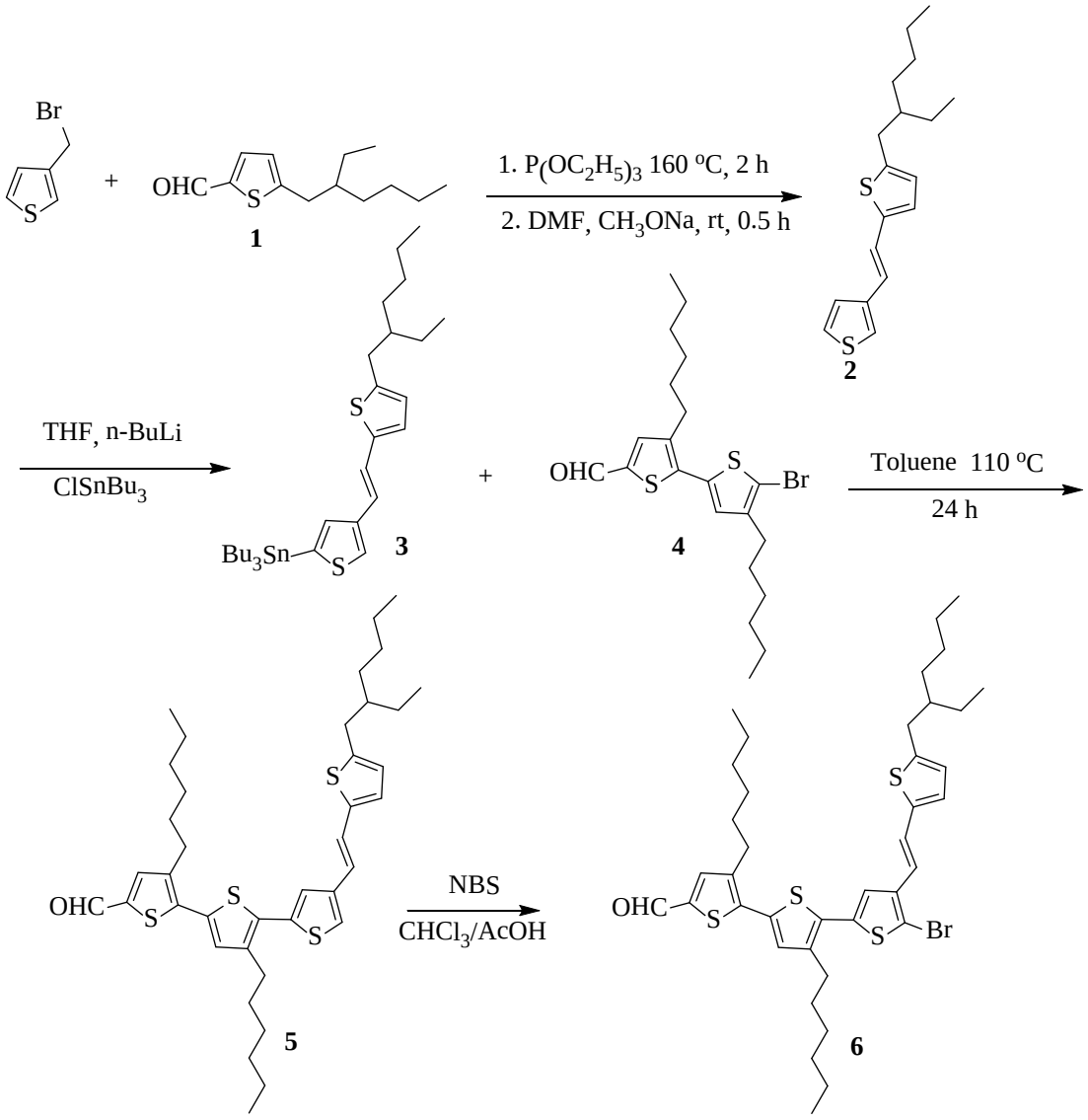
DFT Calculations

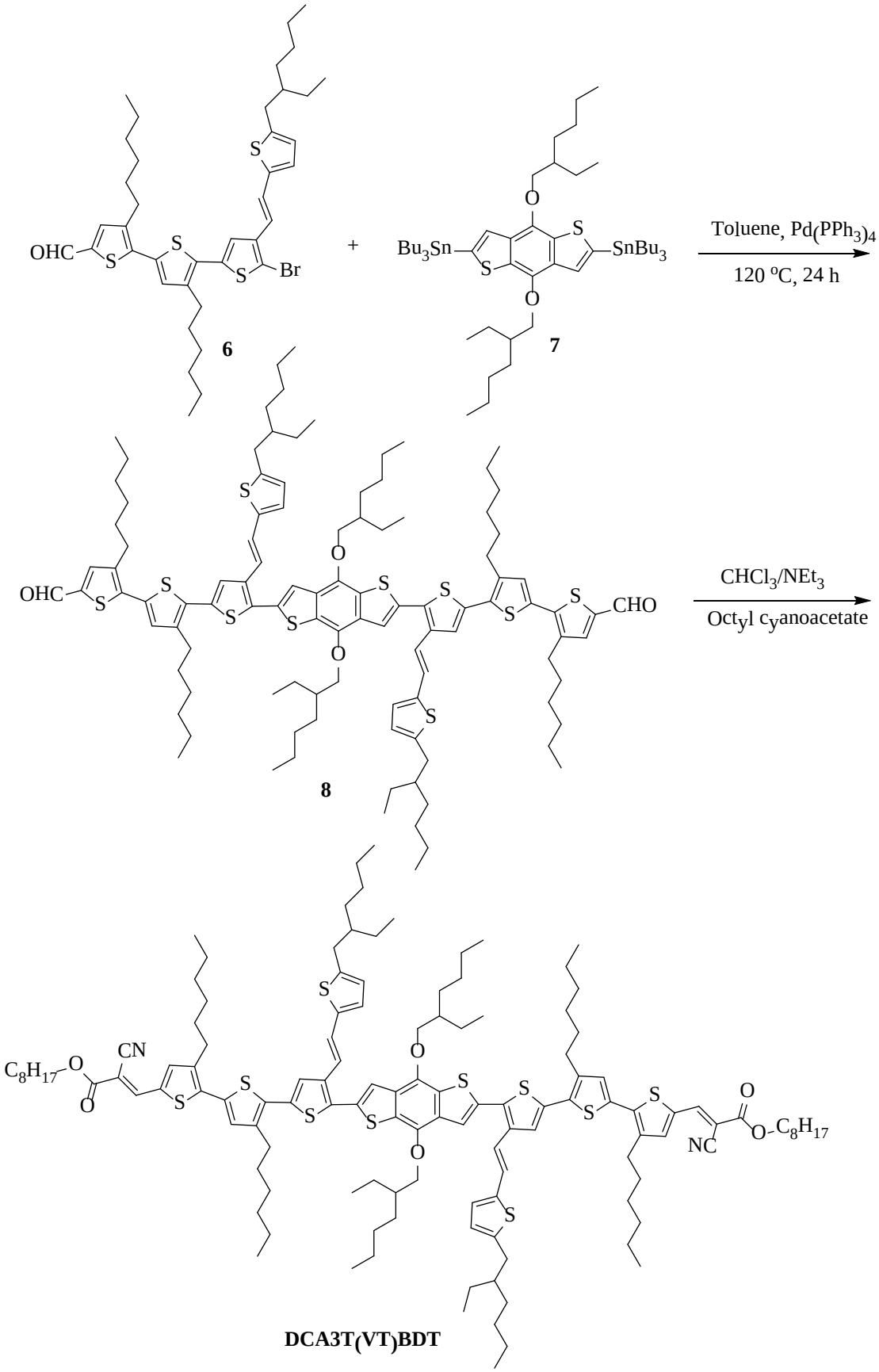
The geometries of the compounds were optimized using density functional theory (DFT) with B3LYP functional and 6-31G(d) basis set. Time-dependent DFT (TDDFT) was used for the calculation of the electronic spectra of the compounds. The steady state UV-vis absorption of the organic dyes were calculated with the optimized S_0

state geometry. All these calculations were performed with Gaussian 09W.[2]

Synthesis

(4,8-Bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b*']dithiophene-2,6-diyl)bis(tributylstannane)[3] (**7**), 5-(2-ethylhexyl)thiophene-2-carbaldehyde[4] (**1**) and 5'-bromo-3,4'-dihexyl-[2,2'-bithiophene]-5-carbaldehyde[5] (**4**) were synthesized according to the procedures reported in the literature. The synthetic route of the **DCA3T(VT)BDT** is shown in Scheme S1.





Scheme S1. Synthetic route of **DCA3T(VT)BDT**.

(*E*)-2-(2-Ethylhexyl)-5-(2-(thiophen-3-yl)vinyl)thiophene (2)

3-Bromomethylthiophene (1.77 g, 10 mmol) and phosphorous acid triethyl ester (1.66 g 10 mmol) were charged in a flask and heated up to 160 ^{o}C for 2 h. After cooling down to room temperature, this product was dissolved in 20 mL dry DMF. Under an ice-water bath, $NaOCH_3$ (0.6 g in 10 mL DMF) was added into the solution. Then 5-(2-ethylhexyl)thiophene-2-carbaldehyde (**1**) was added dropwisely. After 0.5 h, the solution was poured into cold water and extracted with ether. The organic layer was washed with water and then dried over Na_2SO_4. After the removal of solvent, purification was carried out by silica gel column chromatography using hexane as the eluent and compound **2** (2.1 g, yield 70%) was obtained as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.32–7.27 (m, 2H), 7.18 (s, 1H, Ar), 7.02–6.98 (d, 1H, Ar), 6.84–6.80 (m, 2H, CH=CH), 6.65–6.64 (d, 1H, Ar), 2.63–2.38 (m, 2H, alkyl), 1.86–1.71 (m, 1H, alkyl), 1.55–1.25 (m, 8H, alkyl), 0.91–0.86 (m, 6H, alkyl). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 145.18 (Ar), 140.52, 140.02 (C=C), 126.19, 125.97, 124.89, 124.70, 122.43, 121.78, 121.55 (Ar), 43.80, 35.60, 33.24, 30.69, 29.56, 25.46, 14.65, 11.45 (alkyl). FAB-MS: *m/z* 304.1 $[M]^+$.

(*E*)-Tributyl(4-(2-(5-(2-ethylhexyl)thiophen-2-yl)vinyl)thiophen-2-yl)stannane (3)

Compound **2** (2.1 g, 6.9 mmol) and 60 mL of dry THF were added into a flask under nitrogen protection. The solution was cooled to –78 ^{o}C and 3 mL of *n*-butyllithium (7.2 mmol, 2.4 M in *n*-hexane) was added dropwise. After stirring at –78 ^{o}C for 1 h, the reaction mixture was then warmed to room temperature for another 1 h.

Tributyltin chloride (7.6 mmol, 2 mL) was added in one portion at –78 ^{o}C and the mixture was stirred at ambient temperature for 24 h. After that, the reaction mixture was poured into water and extracted with ether. The organic layer was washed with water three times and then dried over Na_2SO_4. After the removal of solvent, the crude product was used for next step without any purification.

(*E*)-4''-(2-(5-(2-Ethylhexyl)thiophen-2-yl)vinyl)-3,3'-dihexyl-[2,2':5',2''-terthiophene]-5-carbaldehyde (5)

5'-Bromo-3,4'-dihexyl-[2,2'-bithiophene]-5-carbaldehyde (**4**) (3 g, 6.7 mmol) and (*E*)-tributyl(4-(2-(5-(2-ethylhexyl)thiophen-2-yl)vinyl)thiophen-2-yl)stannane (**3**) (4 g, 6.7 mmol) were charged into a flask with 50 mL toluene, and the solution was flushed with nitrogen for 10 min, and then 380 mg of $Pd(PPh_3)_4$ was added. The solution was flushed again for another 10 min and stirred at 110 ^{o}C for 24 h under nitrogen. Then, the reaction mixture was poured into water (100 mL) and extracted with ether. The organic layer was washed with water and dried over Na_2SO_4. After the removal of solvent, the crude product was purified by column chromatography on silica gel using a mixture of hexane and dichloromethane (5:1, v/v) as eluent to afford compound **5** (2.6 g, yield: 60%) as a red oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.84 (s, 1H, CHO), 7.60 (s, 1H, Ar), 7.35 (s, 1H, Ar), 7.21 (s, 1H, Ar), 7.11–7.06 (d, 1H, Ar), 7.02–7.01 (d, 1H, Ar), 6.84–6.67 (m, 2H, CH=CH), 6.62 (s, 1H, Ar), 2.86–2.53 (m, 6H, alkyl), 1.71–1.52 (m, 1H, alkyl), 1.43–1.20 (m, 24H, alkyl), 0.90–0.80 (m, 12H, alkyl). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 182.40 (CHO), 148.11, 147.92, 143.70, 140.12, 139.57, 138.67, 138.12, 138.03, 137.51, 137.21 (Ar), 136.40 (C=C), 135.60,

135.03 (Ar), 133.34 (C=C), 126.32, 124.85, 122.13. 119.74 (Ar), 41.78, 35.38, 32.65, 32.08, 31.87, 29.03, 28.95, 25.60, 23.14, 22.78, 14.21, 11.90 (alkyl). FAB-MS: *m/z* 664.3 $[M]^+$.

(*E*)-5''-Bromo-4''-(2-(5-(2-ethylhexyl)thiophen-2-yl)vinyl)-3,3'-dihexyl-[2,2':5',2'' -terthiophene]-5-carbaldehyde (6)

A solution of compound **5** (2.6 g, 3.9 mmol) in THF was stirred at 0 ^oC, and N-bromosuccinimide (0.76 g, 4.3 mmol) was added in small portions. After being stirred for 12 h at room temperature, the reaction mixture was poured into water and extracted with ether. The organic layer was washed with water three times and dried over Na_2SO_4. After the removal of solvent, the crude product was purified by column chromatography on silica gel using hexane as eluent to afford compound **6** (2.4 g, yield: 83%) as a dark red oil. ^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.84 (s, 1H, CHO), 7.59 (s, 1H, Ar), 7.21–7.17 (d, 1H, Ar), 7.11–7.08 (d, 1H, Ar), 7.06–7.02 (d, 1H, Ar), 6.91 (s, 1H, Ar), 6.84–6.61 (m, 2H, CH=CH), 2.87–2.63 (m, 6H, alkyl), 1.71–1.51 (m, 1H, alkyl), 1.46–1.21 (m, 24H, alkyl), 0.90–0.81 (m, 12H, alkyl). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 182.41 (CHO), 148.17, 147.95, 143.73, 141.32, 140.22, 139.67, 138.67, 138.22, 138.08, 137.61 (Ar), 136.40 (C=C), 135.60, 135.03 (Ar), 133.54 (C=C), 126.35, 124.85, 122.23, 109.74 (Ar), 41.77, 35.34, 32.65, 32.10, 31.89, 29.03, 28.96, 25.60, 23.14, 22.79, 14.21, 11.90 (alkyl). FAB-MS: *m/z* 744.2 $[M]^+$.

Compound 8

Compounds **6** (1 g, 1.3 mmol) and **7** (0.64 g, 0.6 mmol) were charged into a flask containing 50 mL toluene. The solution was flushed with nitrogen for 10 min, and then 75 mg of $Pd(PPh_3)_4$ was added. The solution was flushed again for another 10 min. After being stirred at 110 ^oC for 24 h under nitrogen, the reaction mixture was poured into water (100 mL) and extracted with ether. The organic layer was washed with water and dried over Na_2SO_4. After the removal of solvent, the crude product was purified by column chromatography on silica gel using a mixture of hexane and dichloromethane (1:1, v/v) as eluent to afford compound **8** (0.72 g, yield: 68%) as a red solid. ^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.84 (s, 2H, CHO), 7.61 (s, 2H, Ar), 7.56 (s, 2H, Ar), 7.38 (s, 2H, Ar), 7.23–7.15 (m, 4H, Ar), 6.93–6.92 (d, 2H, Ar), 6.68–6.67 (d, 4H, CH=CH), 2.87–2.83 (m, 4H, alkyl), 2.73–2.71 (m, 12H, alkyl), 1.72–1.58 (m, 20H, alkyl), 1.46–1.19 (m, 48H, alkyl), 0.90–0.80 (m, 36H, alkyl). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 182.52 (CHO), 147.21, 145.04, 144.26, 141.02, 140.97, 140.48, 140.39, 140.22, 139.05, 138.12, 137.20 (Ar), 136.41 (C=C), 135.12, 134.96, 133.41 (Ar), 133.22 (C=C), 132.14, 130.46, 126.65, 125.83, 125.01, 119.71. 119.54 (Ar), 41.40, 40.76, 34.58, 32.39, 31.69, 31.66, 30.56, 30.28, 29.49, 29.44, 29.27, 29.23, 29.19, 28.85, 25.48, 23.97, 23.13, 23.06, 22.66, 22.64, 14.19, 14.15, 11.46, 10.77 (alkyl). FAB-MS: *m/z* 1771.8 $[M]^+$. Anal. calcd. for $C_{104}H_{138}O_4S_{10}$: C, 70.46; H, 7.85; N; found: C, 70.67; H, 7.98.

DCA3T(VT)BDT

Compound **8** (0.2 g, 0.11 mmol) was dissolved in a solution of dry $CHCl_3$ (50 mL) and three drops of triethylamine and octyl cyanoacetate (0.5 ml, 2.2 mmol) were added subsequently and the resulting solution was stirred for 40 h under nitrogen at room temperature. The reaction mixture was then extracted with CH_2Cl_2, washed with water and dried over Na_2SO_4. After the removal of solvent, the mixture was purified on silica gel column using a mixture of dichloromethane and petroleum ether (1:1, v/v) as eluent to afford **DCA3T(VT)BDT** as a dark solid (200 mg, yield: 85%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.22 (s, 2H, C=CH), 7.58–7.56 (d, 4H, Ar), 7.39 (s, 2H, Ar), 7.23–7.20 (m, 4H, Ar), 6.94–6.93 (d, 4H, CH=CH), 6.94–6.93 (d, 2H, CH=CH), 4.43–4.27 (m, 8H, alkyl), 2.88–2.71 (m, 12H, alkyl), 1.76–1.55 (m, 12H, alkyl), 1.42–1.29 (m, 80H, alkyl), 1.02–0.87 (m, 42H, alkyl). ^{13}C NMR (100 MHz, $CHCl_3$): δ 163.12 (O–C=O), 146.01 (C=C), 145.06, 144.31, 143.32, 142.67, 141.22, 141.05, 140.83, 140.64, 140.40 (Ar), 137.28 (C=C), 135.12, 134.97 (Ar), 133.00 (C=C), 132.90, 132.64, 132.39, 132.16, 130.83, 130.26, 126.63, 125.82, 125.13, 119.61 (Ar), 115.98 (C≡N), 97.87 (C=C), 66.57, 41.41, 40.78, 34.59, 32.42, 31.77, 31.63, 31.61, 30.56, 30.14, 29.45, 29.34, 29.26, 29.17, 29.14, 28.85, 14.11, 14.07, 11.41, 10.76 (alkyl). MALDI-TOF: *m/z* 2130.05 $[M]^+$. Anal. calcd. for $C_{126}H_{172}N_2O_6S_{10}$: C, 71.01; H, 8.13; N, 1.31; found: C, 71.32; H, 8.43; N, 1.55.

Further discussion of the DCA3T(VT)BDT-based OSC performance

It is known that the existence of charge recombination in the active layer and

contact resistance at the interface are the major reasons that give rise to the drop in shunt resistance (R_{shunt}) and the increase in series resistance (R_s), respectively.[6, 7] The R_{shunt} and R_s of the **DCA3T(VT)BDT**-based OSCs were independently calculated from the inverse of the slope of the dark *J-V* curves of the devices (Figure S3).[6] The lower performance of 1:0.75, 1:1 and 1:2 combination as compared to 1:0.5 could be explained as follows: As shown in Table S2, when the concentration of $PC_{70}BM$ was increased from 0.5 to 2 as compared to **DCA3T(VT)BDT**, the R_{shunt} decreased from 837.91 kΩ cm^2 to 30.02 kΩ cm^2, and the R_s increased from 3.18 Ω cm^2 to 10.53 Ω cm^2, suggesting that the high concentration of $PC_{70}BM$ can generate a large amount of leakage current in the active layer. The increased R_s and decreased R_{shunt} resulted in lower performance of the OSCs by reducing the FF and J_{sc}.

References

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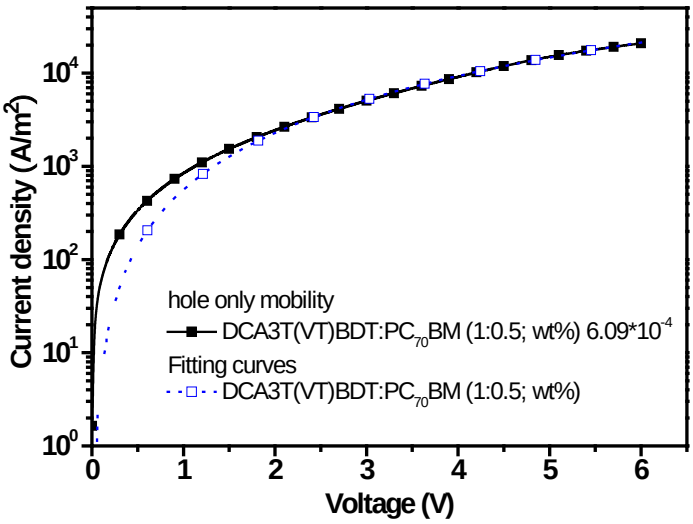

Fig. S1 Field dependence of the current for the hole-only device.

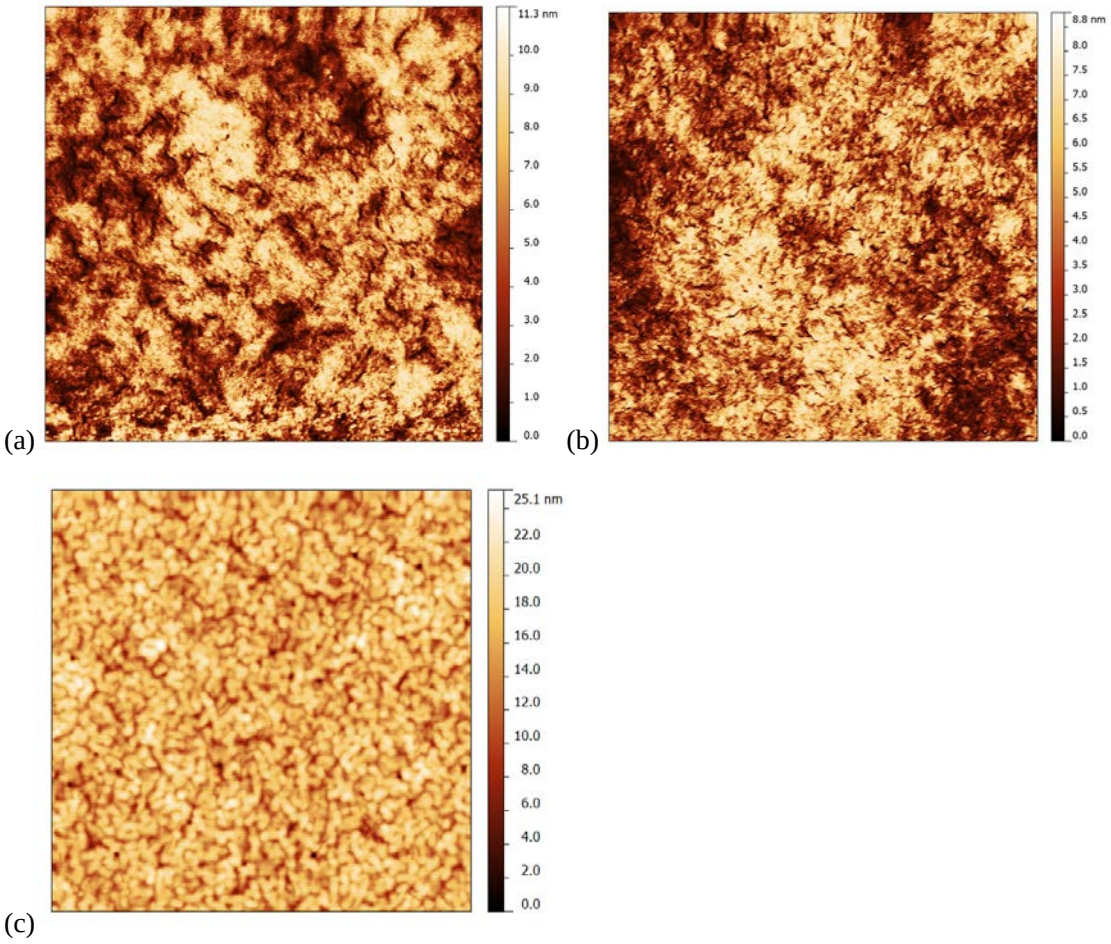

Fig. S2 AFM phase image of the **DCA3T(VT)BDT**:$PC_{70}BM$ blend with the blend ratio of: (a) 1:0.5 w/w, root-mean-square (RMS) roughness is 0.85 nm, (b) 1:1 w/w, RMS roughness is 0.61 nm, and (c) 1:2 w/w, RMS roughness is 2.81 nm.

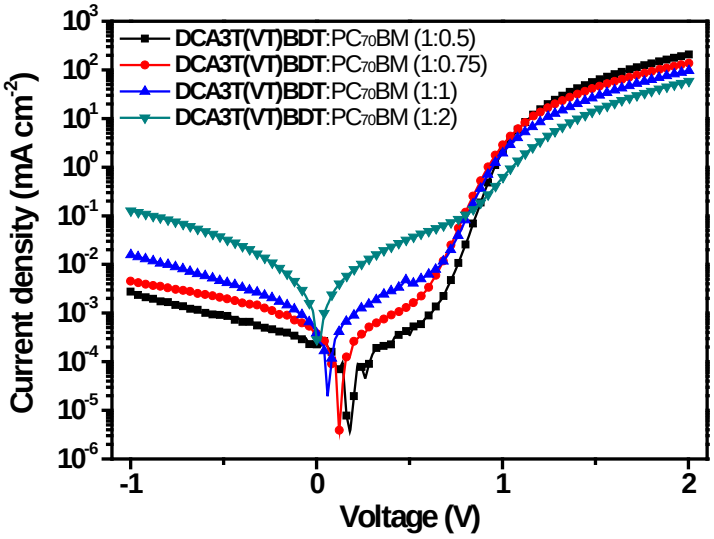

Fig. S3 *J*-*V* curves of the OSCs in the dark and under the illumination of AM 1.5G at 100 mW cm^{-2}

Table S1. TDDFT calculation results

Compound		Electronic transition	TDDFT//B3LYP/6-31G(d)			
			Energy[b]	*f* [c]	Composition [d]	CI [e]
DCA3T(VT)BDT	Singlet (UV-vis)	$S_0 \rightarrow S_1$	1.91 eV	1.5625	HOMO→LUMO	0.6838
			648 nm		HOMO→LUMO+1	0.1299
		$S_0 \rightarrow S_5$	2.47 eV	1.2069	HOMO→LUMO+2	0.6067
			501 nm		HOMO-3→LUMO	0.2683
DCA3T(VT)BDT (CH_2Cl_2)	Singlet (UV-vis)	$S_0 \rightarrow S_1$	2.00 eV	1.9972	HOMO→LUMO	0.6885
			667 nm		HOMO-1→LUMO+1	0.1236
		$S_0 \rightarrow S_5$	2.42 eV	1.3404	HOMO→LUMO+2	0.5925
			512 nm		HOMO-2→LUMO	0.2673

[a] Calculated by TDDFT//B3LYP/6-31G(d), based on the DFT//B3LYP/6-31G(d) optimized ground state geometries. [b] Only the low-lying excited states and some allowed transitions were presented.[c] Oscillator strength. [d] Only the main configurations are presented. [e] CI coefficients are in absolute values.

Table S2. The values of shunt resistance (R_{shunt}) and series resistance (R_s) of the **DCA3T(VT)BDT**-based OSCs

Active layer	R_{shunt} (kΩ cm^2)	R_s (Ω cm^2)
DCA3T(VT)BDT:$PC_{70}BM$ (1:0.5)	837.91	3.18
DCA3T(VT)BDT:$PC_{70}BM$ (1:0.75)	329.84	4.36
DCA3T(VT)BDT:$PC_{70}BM$ (1:1)	151.93	6.79
DCA3T(VT)BDT:$PC_{70}BM$ (1:2)	30.02	10.53