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Electronic Supporting information

Enhanced Efficiency and Stability of Non-Fullerene Ternary Polymer Solar Cells Based on Spontaneously Assembled Active Layer: The Role of a High Mobility Small Molecular Electron Acceptor

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Experimental Section

All manipulations involving air-sensitive reagents were performed under an inert atmosphere of dry nitrogen. Compounds 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*c*][1,2,5]-thiadiazole (**1**),[1] 5-(2-ethylhexyl)-1-iodo-thieno[3,4-c]pyrrole-4,6(5*H*)-dione (**2**)[2] and (5-(1,3-dioxolan-2-yl)-3-octylthiophen-2-yl)tributylstannane (**5**)[3] were synthesized according to the methods in the literature. All the other starting materials, unless otherwise specified, were purchased commercially and used as received without further purification.

Synthesis of (benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(5-(2-ethylhexyl)-thieno[3,4-c]pyrrole-4,6(5H)-dione) (**3**)

Compound 3 was synthesized using a modified procedure from the literature.[2] $Pd_2(dba)_3$ (28 mg, 0.0306 mmol) and P(*o*-tolyl)$_3$ (74 mg, 0.2448 mmol) were added to a mixture of 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*c*][1,2,5]thiadiazole (**1**) (180 mg, 0.46 mmol), 5-(2-ethylhexyl)-1-iodo-4*H*-thieno[3,4-c]pyrrole-4,6(5H)-dione (**2**) (400 mg, 1.02 mmol) and KOAc (451 mg, 4.6 mmol) in THF (15 mL) and H_2O (2 mL) under N_2. The reaction was heated at 100 °C overnight. After being cooled to room temperature, the mixture was poured into water and extracted with CH_2Cl_2. The organic layer was separated, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was subjected to column chromatography over silica gel using petroleum ether/CH_2Cl_2 as eluent to afford an orange red solid. Yield: 210 mg (69%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 9.43 (s, 2H), 7.99 (s, 2H), 3.60 (d, J = 7.1 Hz, 4H), 1.86 (m, 2H), 1.41-1.33 (m, 16H), 0.948 (t, J = 7.25 Hz, 6H), 0.907 (t, J = 6.45 Hz, 6H). MS (APCI) m/z (M + H^+): calcd for $C_{34}H_{39}N_4O_4S_3$, 663.2; found, 663.8 (100%).

Synthesis of (benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(3-bromo-5-(2-ethylhexyl)-thieno[3,4-c]pyrrole-4,6(5H)-dione) **(4)**

N-bromosuccinimide (201 mg，1.131 mmol) was added in one portion to a solution of compound **3** (250 mg, 0.377 mmol) in chloroform (30 mL) and trifluoroacetic acid (4 mL) and concentrated sulfuric acid (2 mL). The reaction was stirred at room temperature for 2 h in the dark. And then aqueous sodium hydroxide solution was added by adjusting the pH = 7. The resulting mixture was poured into water and extracted with CH_2Cl_2. The organic layer was separated, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was subjected to column chromatography over silica gel using petroleum ether/CH_2Cl_2 as eluent to afford a red solid. Yield: 300 mg (96.7%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 9.38 (s, 2H), 3.60 (d, J = 7.3 Hz, 4H), 1.88-1.83 (m, 2H), 1.42-1.32 (m, 16H), 0.96 (t, J = 7.45 Hz, 6H), 0.92 (t, J = 6.8 Hz, 6H), MS (APCI) m/z (M + H^+): calcd for $C_{34}H_{37}Br_2N_4O_4S_3$, 821.03; found, 821.5 (100%).

Synthesis of (benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(3-(5-formyl-3-octylthiophen-2-yl)-5-(2-ethylhexyl)thieno[3,4-c]pyrrole-4,6(5H)-dione) **(7)**

$Pd_2(dba)_3$ (13.35 mg, 0.0146 mmol) and P(*o*-tolyl)$_3$ (35.5 mg, 0.1168 mmol) were added quickly to a mixture of compound **4** (200 mg, 0.243mmol) and (5-(1,3-dioxolan-2-yl)-3-octyl- thiophen-2-yl)tributylstannane (**5**) (407.5 mg, 0.73 mmol) in toluene (30 mL) under N_2. The reaction was heated at 110 °C for 24 h. After being cooled to room temperature, 50 mL of 2 mol/L KF solution was added and then the resulting mixture continued stirring for 20 min. After being filtered, the filtrate was treated with water and extracted with CH_2Cl_2. The organic layer was separated, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was subjected to column chromatography over silica gel using petroleum ether/CH_2Cl_2 as eluent to afford (benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(3-(5-(1,3-dioxolan-2-yl)-3-octylthiophen-2-yl)-5-(2-ethylhexyl)thieno[3,4-c]pyrrole-4,6(5*H*)-dione) (**6**) as a dark red solid, which was directly used for the next reaction.

A solution of compound **6** in HCl (10%):THF (1:2) was heated to 80 °C under an inert atmosphere for 12 h. After being cooled to room temperature, the mixture was poured into water and extracted with CH_2Cl_2. The organic layer was separated, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was subjected to column chromatography over silica gel using petroleum ether/CH_2Cl_2 as eluent to afford a dark red solid. Yield: 150 mg (55.6%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 9.93 (s, 2H), 9.55 (s, 2H), 7.72 (s, 2H), 3.62 (d, J = 7.2 Hz, 4H), 2.89 (t, J = 7.75 Hz, 4H), 1.87-1.84 (m, 2H), 1.74-1.67 (m, 4H), 1.42-1.22 (m, 36H), 0.94 (t, J = 7.45 Hz, 6H), 0.90 (t, J = 6.8 Hz, 6H), 0.83 (t, J = 6.75 Hz, 6H). MS (MALDI-TOF) m/z ($M + Na^+$): calcd: 1129.41; found: 1130.2212 (100%).

Synthesis of 2,2'-((5E,5'E)-(((benzo[c][1,2,5]thiadiazole-4,7-diylbis(5-(2-ethylhexyl)-4,6-dioxo-5,6-dihydro-4H-thieno[3,4-c]pyrrole-3,1-diyl))bis(4-octylthiophene-5,2-diyl))bis(methylene))bis(3-ethyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile **(BPTCN)**

3-Ethyl-rhodanine (65.4 mg, 0.338 mmol) and CH_3COONH_4 (31.21 mg, 0.405 mmol), CH_3COOH (3 mL) were added to a solution of compound **7** (150 mg, 0.135 mmol) in $C_2H_4Cl_2$. The mixture was stirred at 85 °C for 24 h. After being cooled to room temperature, the mixture was poured into water and extracted with CH_2Cl_2. The organic layer was washed with water and then dried over $MgSO_4$. After removal of solvent, the crude product was purified on a silica-gel column chromatography using CH_2Cl_2 as the eluent. **BPTCN** was obtained as a purple black solid. Yield: 150 mg (76.5%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.58 (s, 2H), 8.03 (s, 2H), 7.39 (s, 2H), 4.34 (q, J = 7.2 Hz, 4H), 3.64 (d, J = 7.2 Hz, 4H), 2.87 (t, J = 7.76 Hz, 4H), 1.89-1.86 (m, 2H), 1.73-1.66 (m, 4H), 1.42 (t, J = 7.08 Hz, 6H), 1.41-1.23 (m, 36H). 0.95 (t, J = 7.36 Hz, 6H), 0.91 (t, J = 6.76 Hz, 6H), 0.83 (t, *J* = 6.8 Hz, 6H). MS (MALDI-TOF): m/z 1479.5319 (100%) [M + Na$^+$] (calcd. 1457.99). Anal. Calcd. for $C_{76}H_{84}N_{10}O_6S_7$: C, 62.61; H, 5.81; N, 9.61; S, 15.39. Found: C, 62.50; H, 5.78; N, 9.55; S, 15.15.

General Measurement and Characterization: ^{1}H NMR spectra was recorded on Bruker Avance 400 and 500 spetrameters, respectively. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF) was obtained on a Bruker Agilent1290/maXis impact analyzer. Thermogravimetric analysis (TGA) was performed on a Netzsch TG 209 at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements of BPTCN were performed on a Netzsch DSC 204 under nitrogen at a heating rate of 10 °C min^{-1}.

UV-Vis-NIR absorption spectra were recorded on a Shimadzu UV-3600 UV-Vis-NIR spectrometer. The photoluminescence experiments (PL) were performed on the fluorescence spectrometer Jobin−Yvon Triax320 spectrometer equipped with xenon lamp as the excitation source and with a Hamamatsu R5108 photomultiplier tube. The neat PTB7-Th (D), CO*i*8DFIC (A1), **BPTCN** (A2) and binary D:A1, D:A2, A1:A2 and ternary D:A1:A2 blend films were spin-cast on quartz glass from 10 mg mL^{-1} $CHCl_3$ solution (total concentration) at a speed of 2000 rpm. Specifically, for PTB7-Th:CO*i*8DFIC and PTB7-Th:CO*i*8DFIC:**BPTCN**, both the D:A1 and D:(A1 + A2) ratios were set as 1:1.5 wt/wt, while the D:A2 ratio was set as 1:1.8 wt/wt for the PTB7-Th:**BPTCN** blend. The concentration of PTB7-Th was 4 mg mL^{-1} in the ternary blend.

Cyclic voltammetry (CV) was measured on a CHI630E Electrochemical Workstation equipped with a glass carbon working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode. The measurements were carried out in dry dichloromethane with tetrabutylammonium hexafluorophosphate (0.1 mol L^{-1}) as the supporting electrolyte under a nitrogen atmosphere at a scan rate of 100 mV s^{-1}. The potential of Ag/AgCl reference electrode was internally calibrated by using the ferrocene/ferrocenium redox couple (Fc/Fc^+).

Atomic force microscopy (AFM) measurements were carried out using a Bruker MultiMode8 microscope in ScanAsyst in air mode. The samples of PTB7-Th:**BPTCN**, PTB7-Th:CO*i*8DFIC and the ternary blends were prepared by spin-casting on a ZnO substrate. GIXD was carried out at the Advanced Light Source on beamline 7.3.3, Lawrence Berkeley National Lab (LBNL). The samples were prepared on Si wafers. The scattering signals were recorded on a 2D detector (Pilatus 2M) with a pixel size of 0.172 × 0.172 mm. The incidence angle was 0.16°, which gave the optimized signal-to-background ratio. RSoXS was performed at beamline 11.0.1.2 Advanced Light Source, LBNL, using optimized photon energy (284.2eV). The samples were floated onto Si3N4 substrates. The scattering signals were collected in vacuum using Princeton Instrument PI-MTE CCD camera in transmission mode. The pure films of PTB7-Th, CO*i*8DFIC and **BPTCN** were spin-cast from 10 mg mL^{-1} $CHCl_3$ solution at a speed of 2000 rpm. The samples comprising PTB7-Th:**BPTCN**, PTB7-Th:CO*i*8DFIC and PTB7-Th:CO*i*8DFIC:**BPTCN** were spin-cast from chloroform at 3000 rpm for 30 s in a dry box. For the binary and ternary blends, the total concentration was 16 mg mL^{-1}. Specifically, for PTB7-Th:CO*i*8DFIC and PTB7-Th(D):CO*i*8DFIC(A1):**BPTCN**(A2), both the D:A1 and D:(A1 + A2) ratios were set as 1:1.5 wt/wt, while the D:A2 ratio was set as 1:1.8 wt/wt for the PTB7-Th:**BPTCN** blend. In the ternary blends, the concentration of PTB7-Th was 6.4 mg mL^{-1}.

Fabrication of organic solar cells: All devices were fabricated based on inverted structure: ITO/ZnO/active layer/MoO_3/Al. ITO-coated glass substrates were cleaned by sonification in acetone, detergent, deionized water, and isopropyl alcohol and dried in a nitrogen stream. A ZnO cathode interfacial layer (ca. 40 nm, via the sol-gel process)[4] was spin-cast at 3000 rpm onto the ITO-coated glass substrate which was pretreated by oxygen plasma for 2 min and then thermally annealed at 200 °C on a hotplate for 1 h under ambient conditions. The active layer was prepared by spin-casting chloroform solution at 3100 rpm for 30 s in a dry box. The total concentration was 16 mg mL^{-1}. The thickness is approximately 100 nm as measured by the profilometer. Finally, the vacuum-deposited molybdenum trioxide (MoO_3) layer (10 nm) and the aluminum cathode layer (100 nm) were thermally evaporated onto the active layer under high vacuum ($< 2 \times 10^{-4}$ Pa) through a shadow mask defining an active device area of 0.056 cm^2. The current density–voltage (J–V) curves were measured using Keithley 2400 source meter under 1 sun (AM 1.5 G spectrum) generated from a class solar simulator (Japan, SAN-EI, XES-40S1). The external quantum efficiency (EQE) spectra were measured using a Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech Co., Ltd.). The light intensity at each wavelength was calibrated using a standard single crystal Si photovoltaic cell.

Fabrication of single-carrier devices: Single-carrier device (ITO/PEDOT:PSS(40 nm)/active layer(130 nm)/MoO_3(10 nm)/Al) and (ITO/ZnO(40 nm)/[4]active layer(150 nm)/PFN-Br/Al) were fabricated to measure hole and electron mobility of the binary PTB7-Th:CO*i*8DFIC and ternary blend films PTB7-Th:CO*i*8DFIC:**BPTCN**, respectively. In the electron-only devices, PFN-Br[5] was used as an electron-injection layer at the cathode, spin-cast from methanol solution (0.25 mg mL^{-1}) at 2000 rpm for 30 s in a dry box.

The thickness for the binary film PTB7-Th:**BPTCN** was ca. 90 nm, while the as-cast pure film of **BPTCN** was ca. 80 nm from chloroform solution (12 mg mL^{-1}).

The mobility μ was derived from the SCLC model which is described by the equation $J = (9/8)\varepsilon_0\varepsilon_r\mu(V^2/d^3)$,[6] where J is the current, ε_0 the permittivity of free space, ε_r the relative permittivity of the material, d the thickness of the active layers, and V the effective voltage.

Table S1. Summary of the photovoltaic data.

Active layer	D/A ratio (wt/wt)	J_{sc} (mA cm^{-2})	V_{oc} (V)	*FF* (%)	PCE (%)
PTB7-Th:**BPTCN**	1:1.6	14.66	0.81	51.91	6.16
	1:1.8	14.68	0.81	54.04	6.42
	1:2	14.95	0.81	43.41	5.26

Table S2. Hole and electron mobility in single-carrier devices based on the PTB7-Th (D):CO*i*8DFIC (A1):**BPTCN** (A2) blends.

D:A1:A2 (wt/wt/wt)	A2/[A1 +A2] (wt%)	μ_h ($cm^2\ V^{-1}\ s^{-1}$)	μ_e ($cm^2\ V^{-1}\ s^{-1}$)	μ_h / μ_e ratio
1:1.5:0	0	3.47×10^{-4}	7.08×10^{-6}	52.8
1:1.2:0.3	20	3.80×10^{-4}	1.13×10^{-5}	33.6
1:1.05:0.45	30	8.31×10^{-4}	2.77×10^{-5}	30.0
1:0.9:0.6	40	6.93×10^{-4}	2.01×10^{-5}	34.5
1:0.6:0.9	60	3.61×10^{-4}	1.03×10^{-5}	35.1
1:0:1.8	100	6.26×10^{-4}	1.03×10^{-4}	6.07

Table S3. GIXD test performance parameters of the PTB7-Th, CO*i*8DFIC and **BPTCN** pure films and the related blends.

PTB7-Th:CO*i*8DFIC:**BPTCN**	**in plane (IP)**				**out of plane (OOP)**			
	Position (Å^{-1})	D-spacing Å	FWHM Å	CCL Å	**Position** (Å^{-1})	D-spacing Å	FWHM Å	CCL Å
1:0:0	0.263	23.83	0.109	51.49	1.616	3.88	0.572	9.87
0:1:0	0.356	17.62	0.214	26.37	1.661	3.78	0.313	18.02
0:0:1	0.315	19.90	0.135	41.76	1.741	3.60	0.624	9.05
1:1.5:0	0.281	22.34	0.075	75.00	1.710	3.67	0.339	16.64
1:1.2:0.3	0.278	22.58	0.096	58.88	1.718	3.65	0.335	16.84
1:1.05:0.45	0.278	22.59	0.050	100.6	1.723	3.64	0.329	17.15
1:0.9:0.6	0.283	22.17	0.107	52.51	1.701	3.69	0.395	14.31
1:0.6:0.9	0.290	21.63	0.139	40.50	1.680	3.73	0.434	13.02
1:0:1.8	0.294	21.35	0.128	44.05	1.659	3.78	0.453	12.46
0:0.7:0.3	0.330	19.01	0.212	26.65	1.684	3.72	0.510	11.07

Fig. S1-1. ^{1}H NMR spectrum of **BPTCN** ($CDCl_3$, 400 MHz).

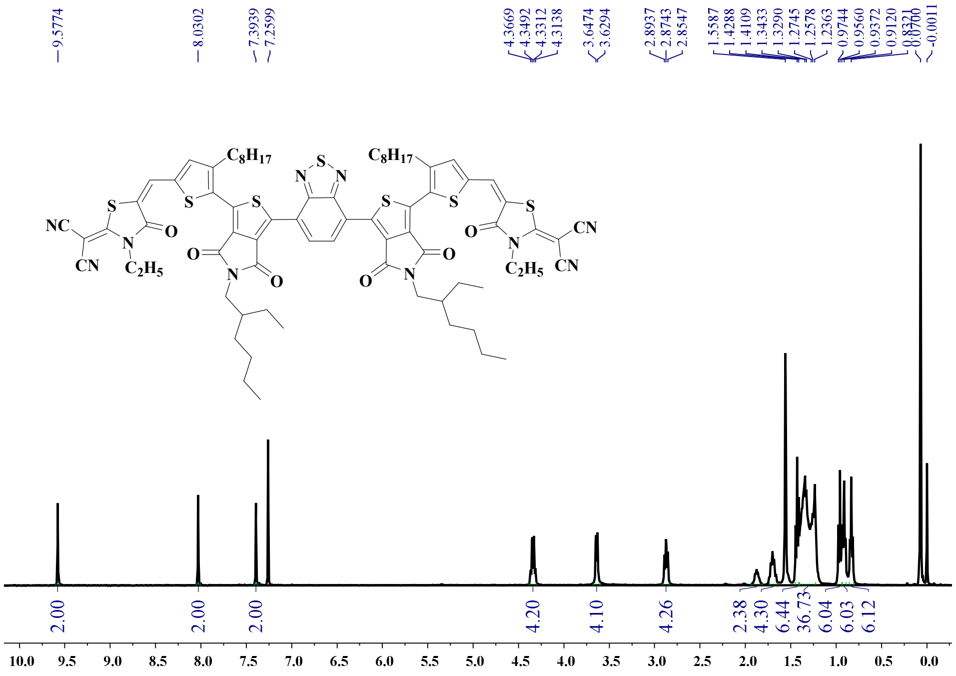


Fig. S1-2. MALDI-TOF of **BPTCN**.

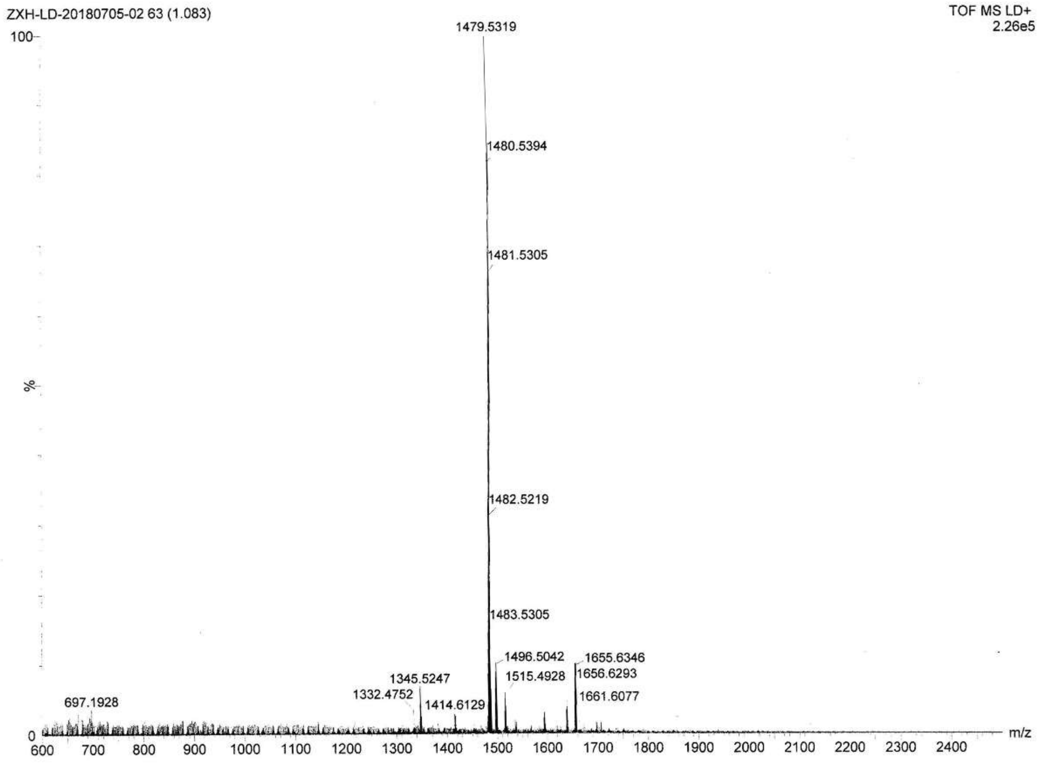
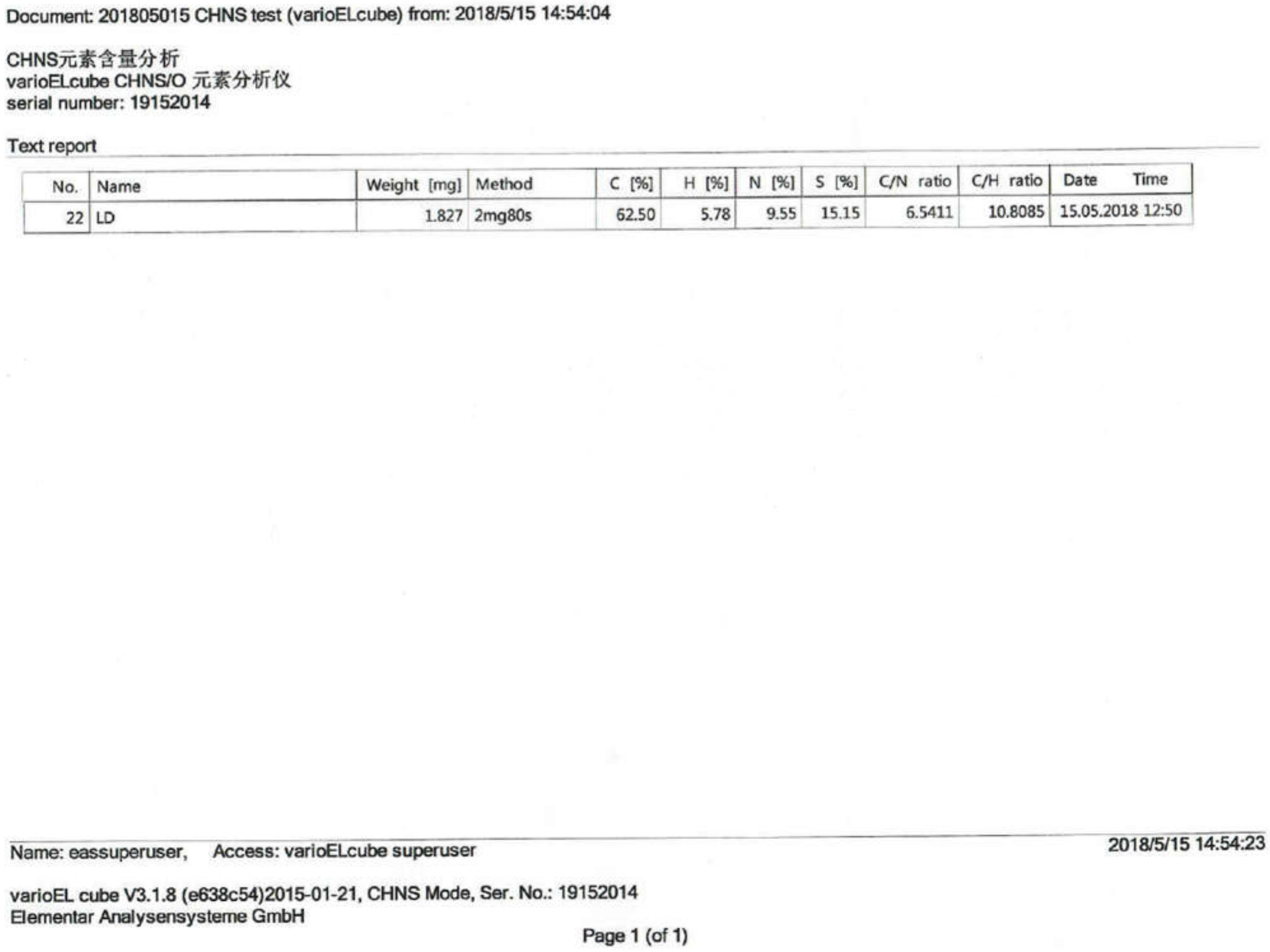


Fig. S1-3. Microanalysis data of compound **BPTCN,** provided by the Instrumental Analysis & Research Center, Sun Yat-Sen University, Guangzhou, China.



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No.	Name	Weight [mg]	Method	C [%]	H [%]	N [%]	S [%]	C/N ratio	C/H ratio	Date Time
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Fig. S2. (a) Spatial structure models, (b) HOMO/LUMO levels and (c) representative dihedral angles of **BPTCN** calculated by Gaussian 09 with density function theory (DFT) at the level of B3LYP/6-31G. The alkyl chains were replaced with methyl groups.

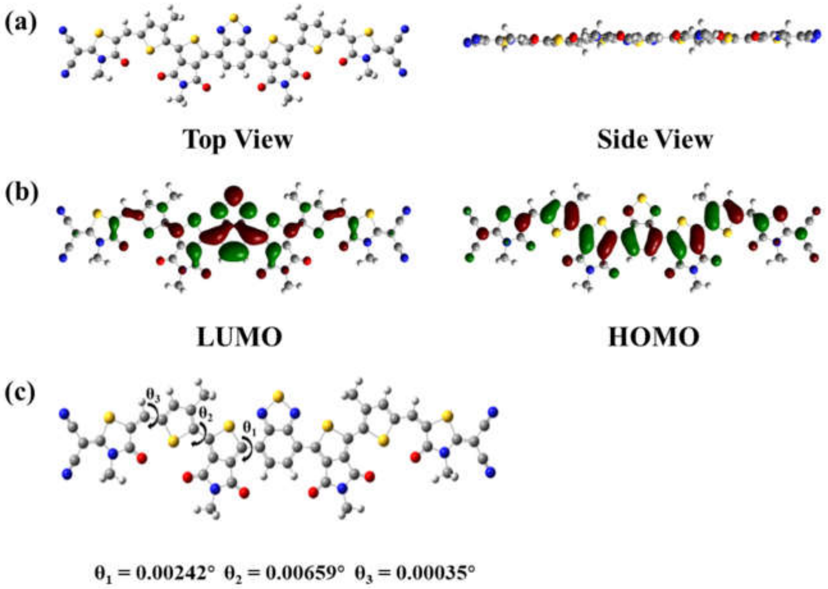


Fig. S3. TGA (a) and DSC (b) diagrams of **BPTCN.**

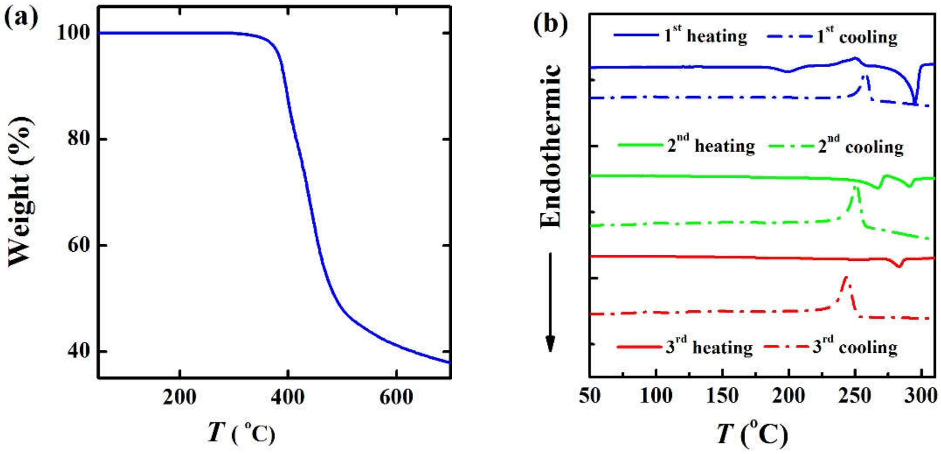


Fig. S4. Normalized UV-vis absorption spectra of **BPTCN** in solution and as-cast film.

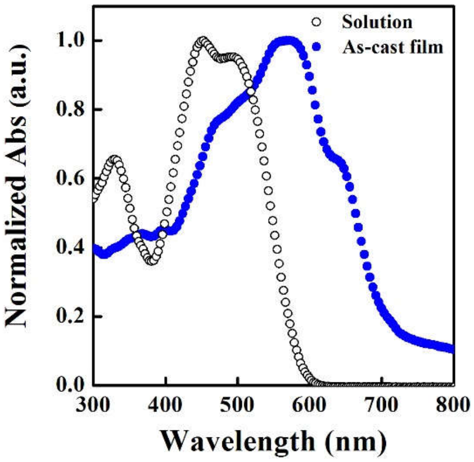


Fig. S5. Cyclovoltammetry curves of (a) **BPTCN** and $PC_{71}BM$.

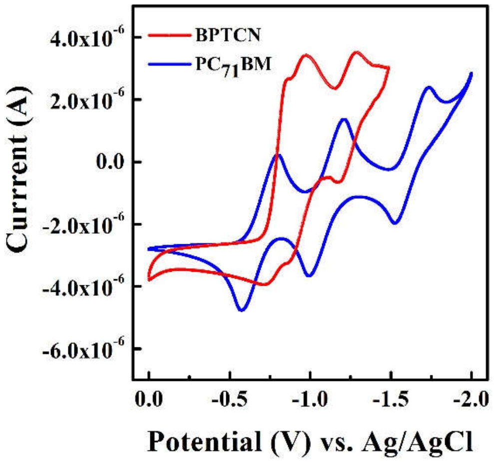


Fig. S6. (a) Normalized PL spectrum of the neat film **BPTCN** and normalized absorption spectrum of the neat film CO*i*8DFIC, (b) PL spectra of the CO*i*8DFIC:**BPTCN** blend films at various weight ratios under 576 nm light excitation.

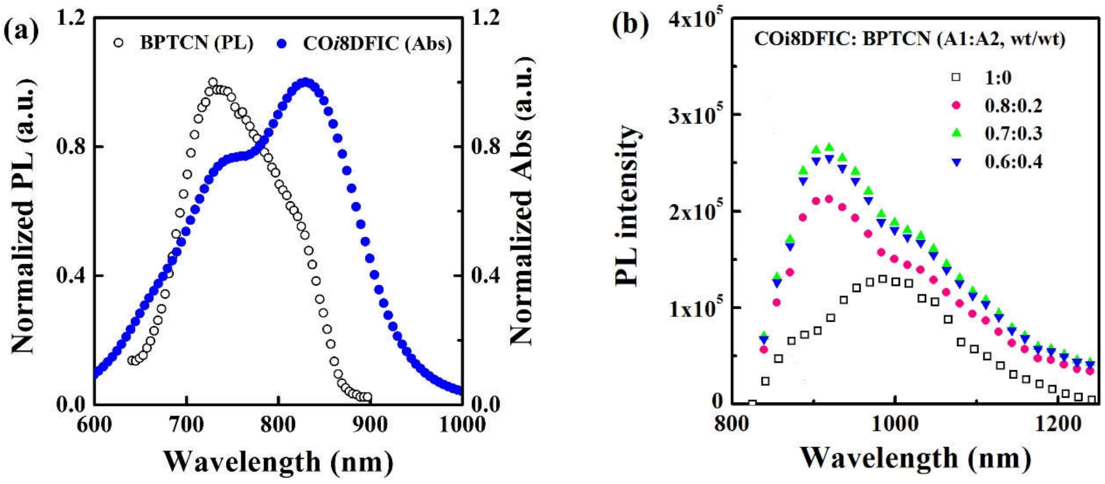


Fig. S7. UV-Vis-NIR absorption spectra of the thin films of COi8DFIC (A1), **BPTCN** (A2) and their blends (wt/wt), spin-cast on quartz glass from 10 mg mL^{-1} CHCl$_3$ solution (total concentration) at a speed of 2000 rpm.

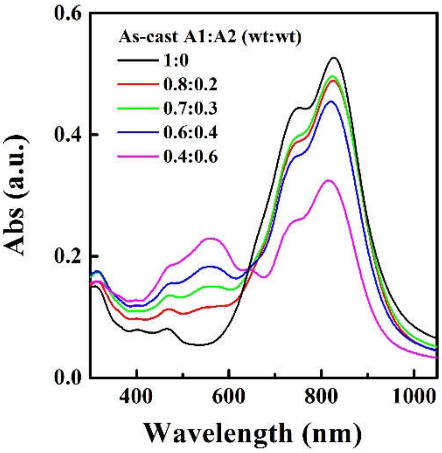


Fig. S8. The $J^{1/2}-V$ characteristics of the hole-only (a) and electron-only (b) devices based on the blend films PTB7-Th (D):CO*i*8DFIC (A1):**BPTCN** (A2), and (c) The $J^{1/2}-V$ characteristic of the electron-only device based on the pure film of **BPTCN**.

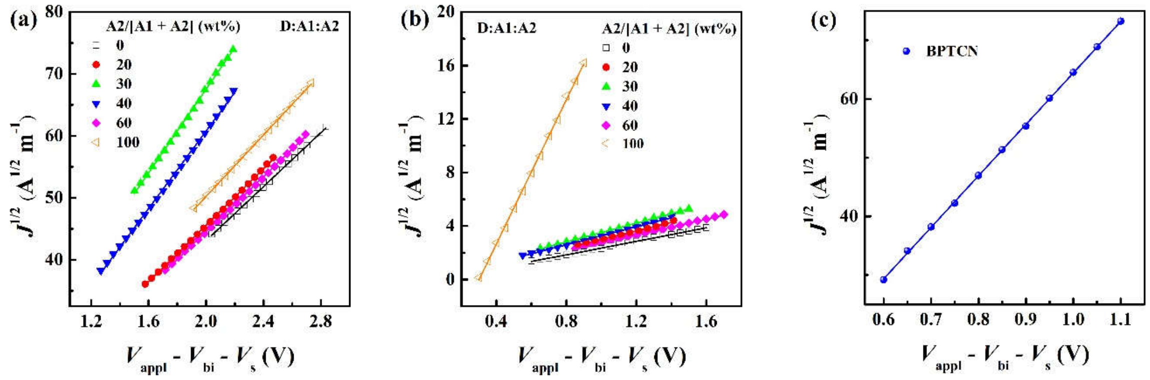


Fig. S9. (a-d) 2D-GIXD patterns and (e) line-cut profiles of the in-plane (dotted line) and out-of-plane (solid line) direction of the neat PTB7-Th, **BPTCN**, CO*i*8DFIC and CO*i*8DFIC (A1):**BPTCN** (A2) blend films (A1:A2 ＝ 0.7:0.3 wt/wt).

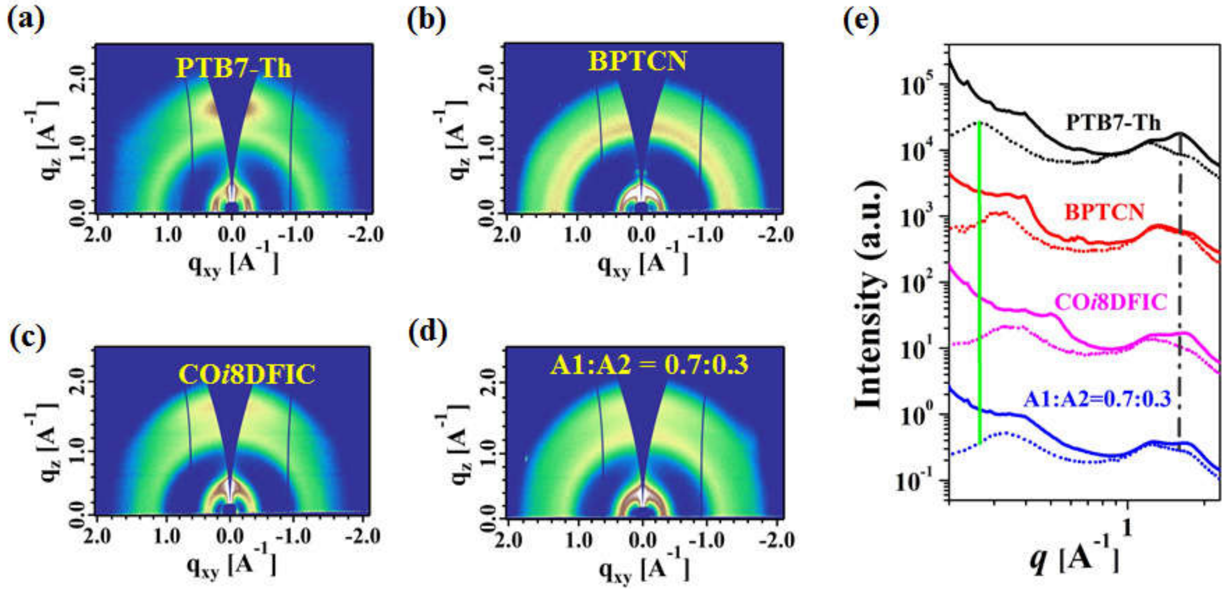


Fig. S10. The AFM images (5 um × 5 um) of the PTB7-Th (D):CO*i*8DFIC (A1):**BPTCN** (A2) blends on the ZnO substrate (ca. 30 nm, via sol-gel process)[4] (A2/[A1 + A2], wt%).

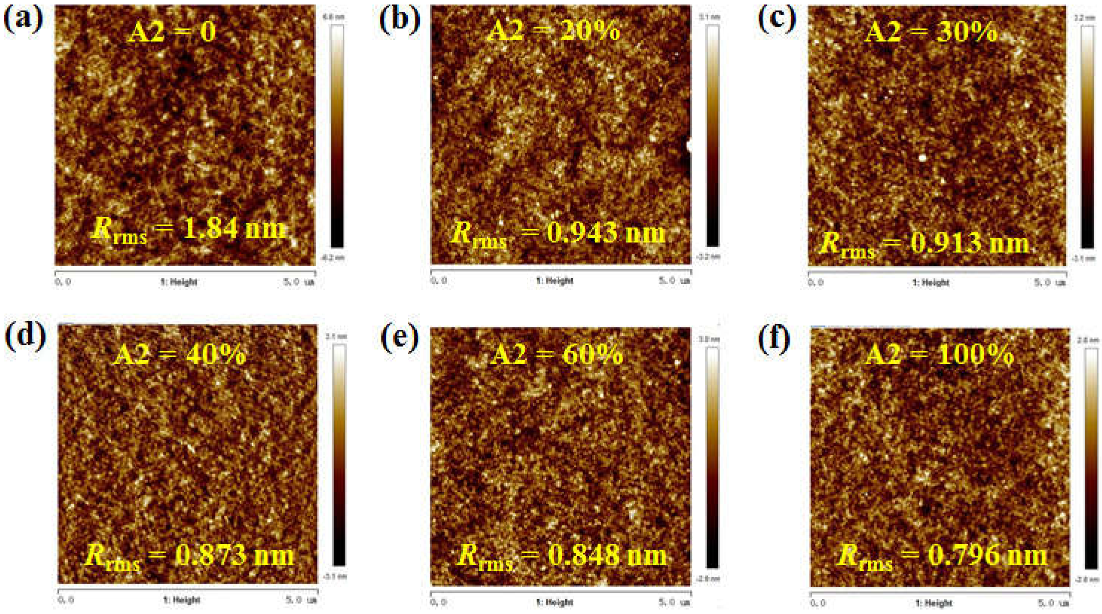
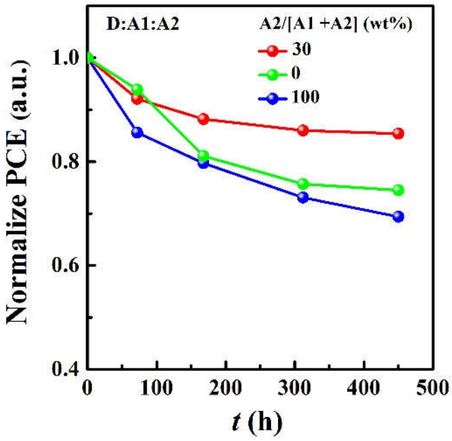


Fig. S11. Stability test of the solar cells (ITO/ZnO/as-cast PTB7-Th (D):CO*i*8DFIC (A1):**BPTCN** (A2)/MoO_3/Al). The devices were continuously aged at 80 °C except breaking for the measurements.



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