Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2020

Supporting information

Rational design of pyrrolopyrrole-aza-BODIPY-based acceptor-donor-acceptor triad for organic

photovoltaics application

Ru Feng, Narumi Sato, Takuma Yasuda, Hiroyuki Furuta and Soji Shimizu

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i. Instrumentation and measurements

Electronic absorption spectra were recorded on a JASCO V-770 spectrophotometer. Fluorescence spectra were recorded on a SPEX Fluorolog-3-NIR spectrometer (HORIBA) with a NIR-PMT R5509 photomultiplier tube (Hamamatsu). Absolute fluorescence quantum yields were measured using a Hamamatsu Photonics C9920-03G calibrated integrating sphere system with self-absorption correction. ¹H NMR spectra were recorded on a JEOL JNM-ECX500 spectrometer (operating at 495 MHz for ¹H) using a residual solvent as an internal reference for ¹H (δ = 5.32 ppm for CD₂Cl₂ and δ = 7.26 ppm for CDCl₃). High resolution mass spectrometry was performed on a JEOL LMS-HX-110 spectrometer (FAB mode with 3-nitrobenzyl alcohol (NBA) as the matrix). Cyclic voltammograms and differential pulse voltammograms were recorded on a CH Instrument Model 620B (ALS) under an argon atmosphere in dichloromethane solution with 0.1 M tetra-n-butylammonium hexafluorophosphate ($nBu_4N \cdot PF_6$) as the supporting electrolyte. Measurements were made with a glassy carbon electrode, an Ag/AgCl reference electrode, and a Pt-wire counter electrode. The concentration of the solution was fixed at 0.5 mM and the sweep rates were set to 100 mV s⁻¹. The ferrocenium/ferrocene (Fc⁺/Fc) couple was used as the internal standard. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F₂₅₄ (MERCK). Preparative separations were performed using silica gel column chromatography (KANTO Silica Gel 60 N, spherical, neutral, 40-50 μm). Transmission electron microscopy (TEM) images were obtained using a JEM-2010 transmission electron microscope (JEOL) at an accelerating voltage of 120 keV. The spin-coated thin films on mica were peeled from substrates by soaking in water and then transferred onto copper grids for the TEM observations. All reagents and solvents used for reactions were of commercial reagent grade and were used without further purification unless noted otherwise. All solvents used in optical measurements were of commercial spectroscopic grade.

ii. OPV device fabrication and evaluation

Prepatterned ITO-coated glass substrates were ultrasonic cleaned sequentially by in detergent solution (15 min), deionized water (10 min × 2) and acetone (10 min), kept in isopropyl alcohol overnight, and then subjected to UV/ozone treatment for 30 min. A thin layer (~30 nm) of ZnO was prepared by spin-coating (at 5000 rpm for 30 s) a precursor solution of zinc acetate (1.00 g) and ethanolamine (0.28 g) in 2-methoxyethanol (10 mL) through a 0.20 µm polyethylene membrane filter, followed by baking at 200 °C for 10 min under air. The photoactive layer was then deposited by spin-coating from a chloroform solution containing a donor (5 mg mL⁻¹ or 7 mg mL⁻¹) and PC₇₁BM (10 mg mL⁻¹ or 7 mg mL⁻¹) after passing through a 0.45 µm poly(tetrafluoroethylene) membrane filter. The thickness of the photoactive layer was ca. 70-110 nm, measured with a profilometer. The thin films were then loaded into an E-200 vacuum evaporation system (ALS Technology). Finally, 10-nm-thick MoO₃ and 100-nm-thick Ag layers were sequentially vacuumdeposited on top of the photoactive layer under high vacuum ($<5.0 \times 10^{-4}$ Pa) through a shadow mask, defining an active area of 0.04 cm^2 for each device. The current density-voltage (J-V) characteristics and EQE spectra of the fabricated OPVs were measured with a computer-controlled Keithley 2400 source measure unit in air, under simulated AM 1.5G solar illumination at 100 mW cm⁻² (1 sun) conditions, using a Xe lamp-based SRO-25GD solar simulator and IPCE measurement system (Bunko Keiki). The light intensity was calibrated using a certified silicon photovoltaic reference cell.

iii. Computational methods

The Gaussian16^{S1} software package was used to carry out DFT and TDDFT calculations using the B3LYP functional with the 6-31G(d) basis set. Structural optimizations were performed on model compounds, in which alkyl substituents were replaced with methyl groups for simplicity.

iv. Synthesis



CPDT-2Br: **CPDT** (200 mg, 0.50 mmol) was dissolved in a dry DMF (4 mL) under nitrogen atmosphere. Then *N*-bromosuccinimide (NBS) (206 mg, 2.30 eq) in DMF (2 mL) was added dropwise. The resulting mixture was stirred at room temperature under dark for 12 h. The reaction was quenched with water (30 mL). The organic layer was extracted with diethyl ether (3 × 10 mL), washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The crude product was purified by silica gel column chromatography with hexane to give **CPDT-2Br**^{S2} as a pale yellow oil (275 mg, 98%).

¹H NMR (495 MHz, CDCl₃, 298 K): δ [ppm] = 6.93 (t, *J* = 5.0 Hz, 2H), 1.84–1.75 (m, 4H), 1.03–0.85 (m, 16H), 0.78 (m, 6H), 0.65–0.56 (m, 8H).

CPDT-2SnMe₃: **CPDT-2Br** (258 mg, 0.46 mmol) was dissolved in THF (7 mL) under nitrogen atmosphere. *n*-BuLi (1.57 M in hexane, 1.17 mL, 2.83 mmol) was slowly added dropwise at –78 °C,

and the solution was stirred for 2 h at that temperature. Trimethyltin chloride (1 M in THF, 1.84 mL, 2.83 mmol) was added at –78 °C, and the mixture was stirred at room temperature for 17 h. The reaction was quenched with aqueous NH₄Cl solution and extracted with diethyl ether. The organic layer was washed with brine, dried over anhydrous Na₂SO₄ and evaporated in vacuo. The crude product was purified by GPC-HPLC (CH₂Cl₂) to give **CPDT-2SnMe**₃ as a pale yellow oil (200 mg, 59%). ¹H NMR (495 MHz, CDCl₃, 298 K): δ [ppm] = 6.93 (m, 2H), 1.88–1.78 (m, 4H), 0.99–0.85 (m, 16H), 0.75 (m, 6H), 0.60–0.57 (m, 8H), 0.35 (m, 18H).



DPP-2: DPP-1 (500 mg, 1.66 mmol) and potassium carbonate (810 mg, 5.83 mmol) were dissolved in a dry DMF (10 mL), and the resultant mixture was heated at 120 °C for 1h under nitrogen atmosphere. Then a DMF solution (4 mL) of 1-bromo-2-octyldodecane (1.56 g 4.32 mmol)^{S3} was added over 30 min. After addition, the reaction mixture was stirred and heated at 130 °C for 20 h. The reaction mixture was cooled to room temperature and poured into distilled water (100 mL). The organic layer was extracted with dichloromethane, washed with brine and dried over anhydrous Na₂SO₄. After evaporation of solvent, the residue was purified by column chromatography on silica gel eluting with hexane/dichloromethane (4:1) to afford pure **DPP-2**^{S4} as a red solid (500 mg, 35%).

¹H NMR (495 MHz, CDCl₃, 298 K): δ [ppm] = 8.86 (t, *J* = 4.0 Hz, 1H), 7.61 (d, *J* = 5.0 Hz, 1H), 7.27 (d, *J* = 5.0 Hz, 2H), 4.02 (d, *J* = 9.0 Hz, 4H), 1.90 (m, 2H), 1.29–1.20 (m, 64H), 0.88–0.84 (m, 12H).

DPP-Br: A solution of NBS (44 mg, 0.24 mmol) in chloroform (3 mL) was added to **DPP-2** (200 mg, 0.23 mmol) dissolved in well-degassed chloroform (5 mL) at room temperature under nitrogen atmosphere. The reaction mixture was stirred at 0 °C for 4 h under dark, then allowed to warm to room temperature and stirred overnight. The reaction mixture was poured into water (50 mL), and the mixture was extracted with chloroform (10 mL × 3). The organic layer was separated and dried over anhydrous Na₂SO₄. After the solvent was removed under reduced pressure, the crude product was purified by column chromatography on silica gel with dichloromethane/hexane (4:1) to give pure **DPP-Br** as a red solid (140 mg, 64%).

¹H NMR (495 MHz, CDCl₃, 298 K): δ [ppm] = 8.88 (d, *J* = 4.5 Hz, 1H), 8.60 (d, *J* = 4.5 Hz, 1H), 7.63 (t, *J* = 5.0 Hz, 1H), 7.29 (d, *J* = 10.0 Hz, 1H), 7.21 (d, *J* = 4.5 Hz, 1H), 4.01–3.92 (dd, *J*₁ = 8.0 Hz, *J*₂ = 8.0 Hz, 4H), 1.88 (m, 2H), 1.28–1.21 (m, 64H), 0.88–0.84 (m, 12H).



Scheme S3 Synthesis of PPAB-Br.

PPAB-Br: **PPAB** (200 mg, 0.20 mmol)^{S5} was dissolved in chloroform (10 mL) and stirred at room temperature for 5 min. Then NBS (36 mg, 0.21 mmol) was added to the solution. The reaction mixture was stirred for 1 h and poured to a sodium thiosulfate aqueous solution (100 mL). After extracted with dichloromethane, the organic layer was collected, dried over Na_2SO_4 and concentrated in vacuo. The crude residue was recrystallized from chloroform/methanol to give **PPAB-Br** as a green solid (100 mg, 45%).

¹H NMR (495 MHz, CD₂Cl₂, 298 K): δ [ppm] = 9.43 (d, *J* = 4.0 Hz, 2H), 7.92 (t, *J* = 6.5 Hz, 2H), 7.76 (d, *J* = 5.5 Hz, 1H), 7.32–7.23 (m, 4H), 7.13 (m, 2H), 4.05 (m, 4H), 2.09 (m, 2H), 1.58–1.25 (m, 48H), 0.83 (m, 12H).

T1: **DPP-Br** (46.9 mg, 0.05 mmol), **CPDT-2SnMe**₃ (18.3 mg, 0.025 mmol) and Pd(PPh₃)₄ (2.88 mg, 0.05 eq) were dissolved in dry toluene (3 mL). After degassing three times by freeze–pump–thaw cycles, the mixture was stirred for 16 h at 120 °C. Then the mixture was added to methanol (10 mL) and filtered. After the crude residue was dissolved in dichloromethane, the mixture was filtered to remove the deactivated palladium reagent. The filtrate was concentrated in vacuo. The crude residue was purified by silica gel column chromatography (hexane/dichloromethane = 1:2 and then 1:1) and preparative TLC (hexane/dichloromethane = 1:1) to give **T1** as a dark solid (20 mg, 38%). HR-MS (FAB) (m/z): 2119.4676 (calcd. for C₁₃₃H₂₁₀N₄O₄S₆ = 2119.4666 [M⁺]); ¹H NMR (495 MHz, CD₂Cl₂, 298 K): δ [ppm] = 8.99–8.94 (m, 2H), 8.83 (d, *J* = 3.5 Hz, 2H), 7.66 (d, *J* = 5.0 Hz, 2H), 7.34 (d, *J* = 4.0 Hz, 2H), 7.28 (t, *J* = 5.0 Hz, 2H), 7.25 (s, 2H), 4.03 (t, *J* = 7.0 Hz, 8H), 2.01–1.89 (m, 8H), 1.33–1.22 (m, 128H), 1.04–0.97 (m, 16H), 0.88–0.84 (m, 24H), 0.76–0.72 (m, 8H), 0.69–0.65 (m, 6H); UV/vis/NIR (CHCl₃): λ_{max} [nm] (ε [M⁻¹cm⁻¹]) = 302 (16000), 347 (10000), 400 (6600), 463 (7700), 650 (60000).

T2: The same synthetic procedure to the synthesis of **T1** was performed. **DPP-Br** (46.9 mg, 0.05 mmol), **CPDT-2SnMe₃** (36.5 mg, 0.05 mmol), **PPAB-Br** (55.3 mg, 0.05 mmol) and $PdCl_2(PPh_3)_2$ (3.5 mg, 0.005 mmol) were used as the starting materials. The crude product was purified by silica gel column chromatography (hexane/dichloromethane = 3:1, 2:1 and then 1:1) and preparative TLC (hexane/dichloromethane = 1:1) to give pure **T2** as a dark solid (55 mg, 48%).

HR-MS (FAB) (m/z): 2287.4139 (calcd. for C₁₃₅H₂₀₀B₂F₄N₈O₄S₆ = 2287.4131 [M⁺]); ¹H NMR (495 MHz, CD₂Cl₂, 298 K): δ [ppm] = 10.16 (m, 1H), 9.37 (s, 1H), 8.98 (m, 1H), 8.83 (s, 1H), 7.99–7.93 (m, 2H), 7.76–7.66 (m, 2H), 7.40–7.26 (m, 8H), 7.16–7.11 (m, 2H), 4.09 (m, 8H), 2.15–1.89 (m, 8H), 1.63 (m, 8H), 1.45–1.25 (m, 104H), 1.05–0.99 (m, 16H), 0.86 (m, 24H), 0.76 (m, 8H), 0.69 (6H); UV/vis/NIR (CHCl₃): λ_{max} [nm] (ε [M⁻¹cm⁻¹]) = 305 (36000), 414 (33000), 480 (22000), 626 (92000), 782

(108000).

T3: The same synthetic procedure to the synthesis of **T1** was performed. **CPDT-2SnMe₃** (36.5 mg, 0.05 mmol), **PPAB-Br** (55.3 mg, 0.05 mmol) and $PdCl_2(PPh_3)_2$ (3.5 mg, 0.005 mmol) were used as the starting materials. The reaction mixture was purified by silica gel column chromatography (hexane/dichloromethane = 1:1, 1:2 and then 0:1) to give crude product. Then the crude product was purified by preparative TLC (hexane/dichloromethane = 1:2) to give **T3** (30 mg, 49%) as a dark solid.

HR-MS (FAB) (m/z): 2455.3602 (calcd. for C₁₃₇H₁₉₀B₄F₈N₁₂O₄S₆: 2455.3603 [M⁺]); ¹H NMR (495 MHz, CD₂Cl₂, 298 K): δ [ppm] = 10.22 (m, 2H), 9.41 (s, 2H), 8.00–7.94 (m, 4H), 7.74 (d, *J* =4.5 Hz, 2H), 7.41–7.29 (m, 10H), 7.16–7.09 (m, 4H), 4.11–4.06 (m, 8H), 2.16–2.03 (m, 8H), 1.65 (m, 16H), 1.46–1.28 (m, 80H), 1.08–0.70 (m, 54H); UV/vis/NIR (CHCl₃): λ_{max} [nm] (ε [M⁻¹cm⁻¹]) = 312 (44000), 394 (47000), 416 (49000), 481 (37000), 524 (31000), 637 (45000), 709 (86000), 826 (117000).



Fig. S1 ¹H NMR spectrum of T1 in CD₂Cl₂. * indicate residual solvent signals.



Fig. S2 ¹H-¹H COSY spectrum of T1.



Fig. S3 ¹H NMR spectrum of T2 in CD₂Cl₂. * indicate residual solvent signals.



Fig. S4 ¹H-¹H COSY spectrum of T2.



Fig. S5 ¹H NMR spectrum of T3 in CD₂Cl₂. * indicate residual solvent signals.



Fig. S6 ¹H-¹H COSY spectrum of T3.

vi. Absorption and fluorescence spectra



Fig. S7 UV/vis/NIR absorption spectra of DPP and PPAB^{S5} in CHCl₃.



Fig. S8 UV/vis/NIR absorption (solid line) and fluorescence (dash line) spectra of (a) T1, (b) T2 and (c) T3 in CHCl3.

vii. Optimized structures based on the DFT calculations, theoretical absorptions and molecular orbitals



Fig. S9 Optimized model structures of **T1**, **T2** and **T3**, and theoretical absorption of each model structure at the B3LYP/6-31G(d) level (gray, orange and aqua blue bars) overlaid on the observed absorption spectra of **T1**, **T2** and **T3** in CHCl₃ (black, red and blue lines).



Fig. S10 Frontier molecular orbital diagram of T1, T2 and T3 (B3LYP/6-31G(d)).

Table S1 Summary of TDDFT calculations of T1, T2 and T3

Compound	λ /nm	fª	Major contributions ^b
T1	588	2.73	H−1→L+1 (18%), HOMO→LUMO (76%)
	414	0.28	H−2→LUMO (44%), H−1→L+1 (29%), HOMO→L+2 (19%)
Т2	658	2.00	HOMO→LUMO (79%)
	539	0.71	H–1→LUMO (30%), H–1→L+1 (19%), HOMO→L+1 (38%)
	458	0.49	H–2→LUMO (38%), H–1→LUMO (11%), H–1→L+1 (21%)
	418	0.11	H–2→L+1 (18%), H–1→LUMO (19%), HOMO→L+1 (29%), HOMO→L+2 (15%)
	387	0.20	H–10→LUMO (18%), H–3→LUMO (29%), HOMO→L+3 (12%)
	358	0.19	H–10→LUMO (19%), H–3→LUMO (37%), HOMO→L+2 (12%)
Т3	697	2.11	H−1→L+1 (21%), HOMO→LUMO (72%)
	609	0.81	H−1→LUMO (45%), HOMO→L+1 (48%)
	495	0.55	H−2→LUMO (45%), H−1→L+1 (27%), HOMO→L+2 (13%)
	458	0.12	H−2→L+1 (27%), H−1→LUMO (25%), HOMO→L+1 (37%)
	380	0.36	H−1→L+1 (13%), HOMO→L+2 (10%)
	375	0.38	H−13→LUMO (11%), H−5→LUMO (14%), H−4→L+1 (14%), H−2→L+1 (11%)

^a Oscillator strength. ^b H and L represent the HOMO and LUMO, respectively.



Fig. S11 Optimized model structures of **T3** (**T3-a**: a perpendicular conformation and **T3-b** and **T3-c**: coplanar conformations) and theoretical absorption of each model structure at the B3LYP/6-31G(d) level (aqua blue bars) overlaid on the observed absorption spectrum of **T3** in CHCl₃ (blue line).



Fig. S12 Frontier molecular orbital diagram of T3-a, T3-b and T3-c (B3LYP/6-31G(d)).

Table S2 Summary of TDDFT calculations of T3-a, T3-b and T3-c

Compound	λ /nm	fa	Major contributions ^b
T3-a	605	1.78	H−1→L+1 (29%), HOMO→LUMO (65%)
	568	0.33	H−1→LUMO (43%), HOMO→L+1 (50%)
	442	0.87	H−2→LUMO (44%), H−1→L+1 (24%), HOMO→LUMO (12%)
	354	0.16	H−2→LUMO (29%), H−1→L+1 (36%), HOMO→LUMO (14%)
T3-b	590	0.86	HOMO→L+1 (88%)
	566	0.73	H−1→LUMO (91%)
	432	0.79	H−3→L+1 (13%), H−2→L+1 (66%)
	355	0.39	H−15→LUMO (10%), H−6→LUMO (54%)
T3-c	697	2.11	H−1→L+1 (21%), HOMO→LUMO (72%)
	609	0.81	H−1→LUMO (45%), HOMO→L+1 (48%)
	495	0.55	H−2→LUMO (45%), H−1→L+1 (27%), HOMO→L+2 (13%)
	458	0.12	H−2→L+1 (27%), H−1→LUMO (25%), HOMO→L+1 (37%)
	380	0.36	H−1→L+1 (13%), HOMO→L+2 (10%)
	375	0.38	H−13→LUMO (11%), H−5→LUMO (14%), H−4→L+1 (14%), H−2→L+1 (11%)

^a Oscillator strength. ^b H and L represent the HOMO and LUMO, respectively.

viii. Photovoltaic parameters for OPV device based on T1:PC71BM, T2:PC71BM and T3:PC71BM



Fig. S13 An inverted device structure of BHJ-OPVs based on **T1**:PC₇₁BM, **T2**:PC₇₁BM and **T3**:PC₇₁BM and the corresponding energy diagram.

Table S3 Device characteristics of T3:PC₆₁BM BHJ-OPVs with different DIO ratios

Blend ratio	Solvent and additive ^a	Thickness (nm)	J _{sc} (mA cm ^{−2})	V _{oc} (V)	FF	PCE (%)
T3 :PC ₆₁ BM (1:1)	CF	102	3.13	0.71	0.28	0.63
T3 :PC ₆₁ BM (1:1)	CF:DIO (99.5:0.5 vol%)	93	8.84	0.71	0.45	2.85
T3 :PC ₆₁ BM (1:1)	CF:DIO (99:1 vol%)	93	8.56	0.71	0.43	2.62
T3 :PC ₆₁ BM (1:1)	CF:DIO (98.5:1.5 vol%)	109	7.54	0.71	0.41	2.21



Fig. S14 (a) *J-V* curves and (b) EQE of T3:PC₆₁BM BHJ-OPVs with different DIO ratios corresponding to Table S3.

Blend ratio	Solvent and additive ^a	Thickness (nm)	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF	PCE (%)
T3 :PC ₇₁ BM (1:1)	CF:DIO (99:1 vol%)	97	9.36	0.70	0.43	2.80
T3 :PC ₇₁ BM (1:2)	CF:DIO (99:1 vol%)	102	9.61	0.70	0.48	3.06
T3 :PC ₇₁ BM (1:3)	CF:DIO (99:1 vol%)	108	8.39	0.69	0.48	2.78
T3 :PC ₇₁ BM (2:1)	CF:DIO (99:1 vol%)	106	4.82	0.72	0.36	1.24

Table S4 Device characteristics of T3:PC71BM BHJ-OPVs with different D:A ratios

^{*a*} CF: chloroform, DIO: 1,8-diiodooctane.



Fig. S15 (a) J-V curves and (b) EQE of T3:PC71BM BHJ-OPVs with different D:A ratios corresponding to Table S4.

 Table S5
 Device characteristics of T3:PC71BM BHJ-OPVs with different thicknesses

Blend ratio	Solvent and	Thickness	J _{SC}	Voc	FF	PCE
	additive ^a	(nm)	(mA cm ⁻²)	(V)		(%)
	CF:DIO	70	10.1	0.67	0.53	3.56
	(99.5:0.5 vol%)	90	11.7	0.67	0.50	3.88
T3 :PC ₇₁ BM (1:2)	CF:DIO (99:1 vol%)	79	8.51	0.69	0.51	3.00
		89	10.03	0.69	0.46	3.16
		102	9.61	0.70	0.48	3.06



Fig. S16 (a) J-V curves and (b) EQE of T3:PC₇₁BM BHJ-OPVs with different thicknesses corresponding to Table S5.

 Table S6
 Device characteristics of T3:PC61BM BHJ-OPVs with different additives

Blend ratio	Solvent and additive ^a	Thickness (nm)	J _{sc} (mA cm ^{−2})	V _{oc} (V)	FF	PCE (%)
T3 :PC ₆₁ BM (1:1)	CF:DIO (99:1 vol%)	110	8.56	0.71	0.43	2.62
	CF:CN (99:1 vol%)	102	4.46	0.64	0.34	0.98

^a CF: chloroform, DIO: 1,8-diiodooctane, CN: 1-chloronaphthalene.



Fig. S17 (a) J-V curves and (b) EQE of T3:PC₆₁BM BHJ-OPVs with different additives corresponding to Table S6.

Blend ratio	Solvent and additive ^a	thickness (nm)	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF	PCE (%)
T2:PC ₇₁ BM (1:1)	CF	97	2.79	0.72	0.38	0.76
T2:PC ₇₁ BM (1:1)	CF:DIO (99:1 vol%)	112	1.18	0.74	0.36	0.31
T2 :PC ₇₁ BM (1:2)	CF:DIO (99.5:0.5 vol%)	90	4.20	0.73	0.48	1.49
T2 :PC ₇₁ BM (1:2)	CF:DIO (99.5:0.5 vol%)	73	3.89	0.74	0.52	1.49
T2 :PC ₇₁ BM (1:2)	CF	78	3.09	0.72	0.40	0.89

Table S7 Device characteristics of T2:PC₇₁BM BHJ-OPVs with different D/A ratios, DIO ratios and thicknesses



Fig. S18 (a) *J-V* curves and (b) EQE of **T2**:PC₇₁BM BHJ-OPVs with different D/A ratios, DIO ratios and thicknesses corresponding to **Table S7**.

Solvent and additive ^a	thickness (nm)	J _{sc} (mA cm⁻²)	V _{oc} (V)	FF	PCE (%)
CFª:DIO ^b (99.5:0.5 vol%)	85	0.81	0.43	0.37	0.13
CF:DIO (99.5:0.5 vol%)	110	0.69	0.61	0.37	0.16
CF	101	0.94	0.43	0.36	0.14
CF:DIO (99.5:0.5 vol%)	90	3.89	0.52	0.36	0.18
	Solvent and additive ^a CF ^a :DIO ^b (99.5:0.5 vol%) CF:DIO (99.5:0.5 vol%) CF CF:DIO (99.5:0.5 vol%)	Solvent and additive ^a thickness (nm) $CF^a:DIO^b$ (99.5:0.5 vol%) 85 $CF:DIO$ (99.5:0.5 vol%) 110 CF 101 $CF:DIO$ (99.5:0.5 vol%) 90	Solvent and additive ^a thickness (nm) J_{SC} (mA cm ⁻²) CF ^a :DIO ^b (99.5:0.5 vol%) 85 0.81 CF:DIO (99.5:0.5 vol%) 110 0.69 CF 101 0.94 CF:DIO (99.5:0.5 vol%) 90 3.89	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

 Table S8
 Device characteristics of T1:PC71BM BHJ-OPVs with different D/A ratios, DIO ratios and thicknesses



Fig. S19 (a) *J-V* curves and (b) EQE of **T1**:PC₇₁BM BHJ-OPVs with different D/A ratios, DIO ratios and thicknesses corresponding to **Table S8**.



Fig. S20 TEM images of BHJ active layers composed of (a) **T3**:PC₇₁BM (1:2, w/w) blends. The *D* value represents the average domain size. (b) PSD profile of the blend film obtained from radially averaged 2D-FFT analysis of the TEM image.

ix. Reference

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