Electronic Supplement Information for

A triptycene-cored perylenediimide derivative and its application in organic solar cells as a non-fullerene acceptor

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Materials

All of solvents were purified according to standard methods. All reagents were commercially obtained from Alfa Aesar Chemical Co. and J&K Chemical Co. and used without further purification unless otherwise specified. All manipulations involving air-sensitive reagents were performed in an atmosphere of dry argon. 2,6(7),14-Tribromo-triptycene (**TRIP-3Br**) was synthesized according to the reference procedure.[1]

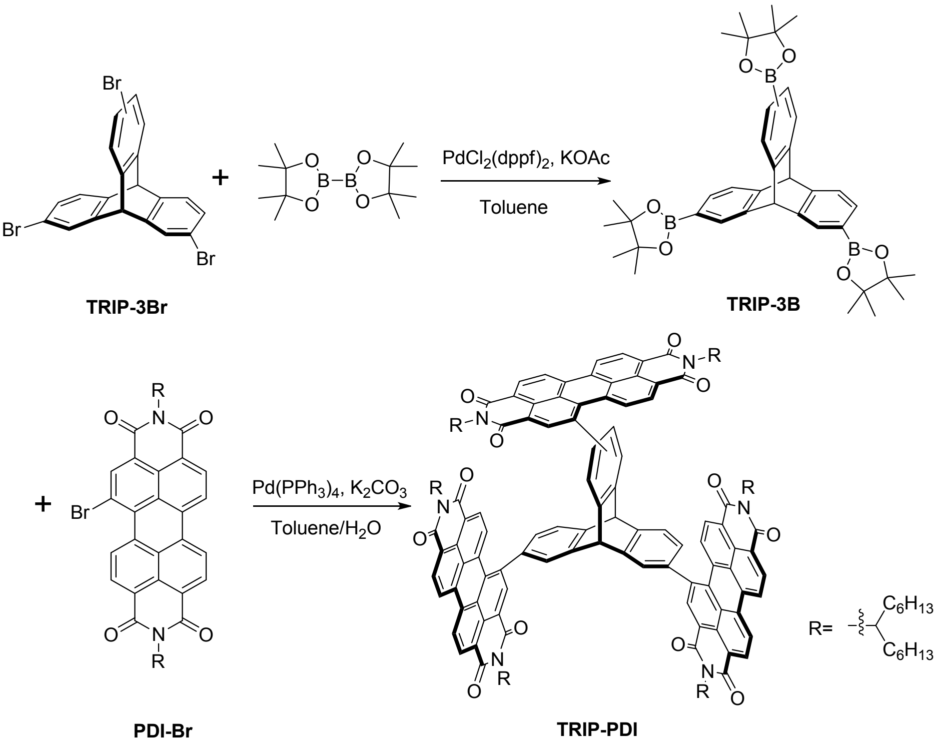
Measurements and characterization

NMR spectra were recorded on a BRUKER AVANCE 400 MHz instrument. The residual solvent protons (^{1}H) or the solvent carbons (^{13}C) were used as internal standards. ^{1}H NMR data are presented as follows: the chemical shift in ppm (δ) downfield from tetramethylsilane (multiplicity, coupling constant (Hz), integration). The following abbreviations are used in the NMR data reported: s, singlet; d, doublet; t, triplet; q, quartet; and m, multiplet. UV-vis absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Mass spectra were taken on a Bruker Daltonics Inc. spectrometer. Cyclic voltammetry measurements were carried out on a Shanghai Chenhua CHI660C electrochemical workstation. The thermal properties were tested on a Netzsch TG209 F3 thermogravimetric analyzer and a TA Q2000 DSC analyzer. The active layer film thickness data were obtained *via* the surface profilometer (Bruker Dektak XT). The photoactive area of 4.15 mm^2 was achieved using a shadow mask. The J–V test were conducted using a Class AAA solar simulator (SAN-EI) affording a value of 100 mW cm^{-2}. The EQE data were obtained using an IPCE measurement system (QE-R3011, Enli Technology Co. Ltd., Taiwan).

Synthesis

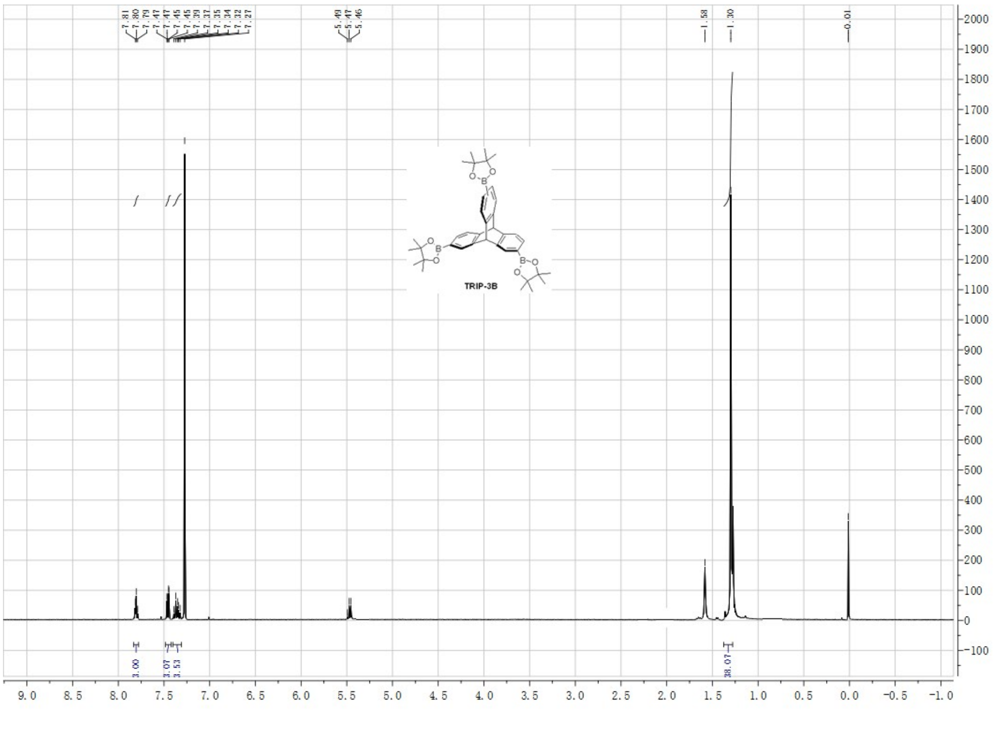
2,6(7),14-Tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-triptycene (TRIP-3B). A mixture of 2,6(7),14-tribromo- triptycene (**TRIP-3Br**)[2] (420 mg, 0.86 mmol), bis(pinacolato)diboron (740 mg, 2.91mmol), $PdCl_2(dppf)_2$ (32 mg, 0.043 mmol), KOAc（420 mg,4.28 mmol）and dry toluene (20 mL) was refluxed for 15 h under a nitrogen atmosphere. After removal of the solvent, the residue was dissolved in ethyl acetate (100 mL). Then the organic phase washed with brine (50 mL), and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was purified by silica gel column chromatography (eluting with dichloromethane) to afford the product **TRIP-3B** (341 mg, 63%) as a white solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.29 (s, 36H), 5.45 (d, 2H), 7.34–7.37 (m, 3H), 7.45 (dd, 3H), 7.80 (d, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 24.7, 24.8, 25.0, 54.1, 54.4, 83.6, 83.6, 123.1, 123.2, 129.5, 129.6, 129.6, 132.2, 132.3, 132.5, 143.8, 144.1, 144.5, 147.7, 148.1, 148.4. HR-MS (MALDI): m/z $[M]^+$ cacld for $C_{38}H_{47}B_3O_6$, 632.3652; found, 632.3613.

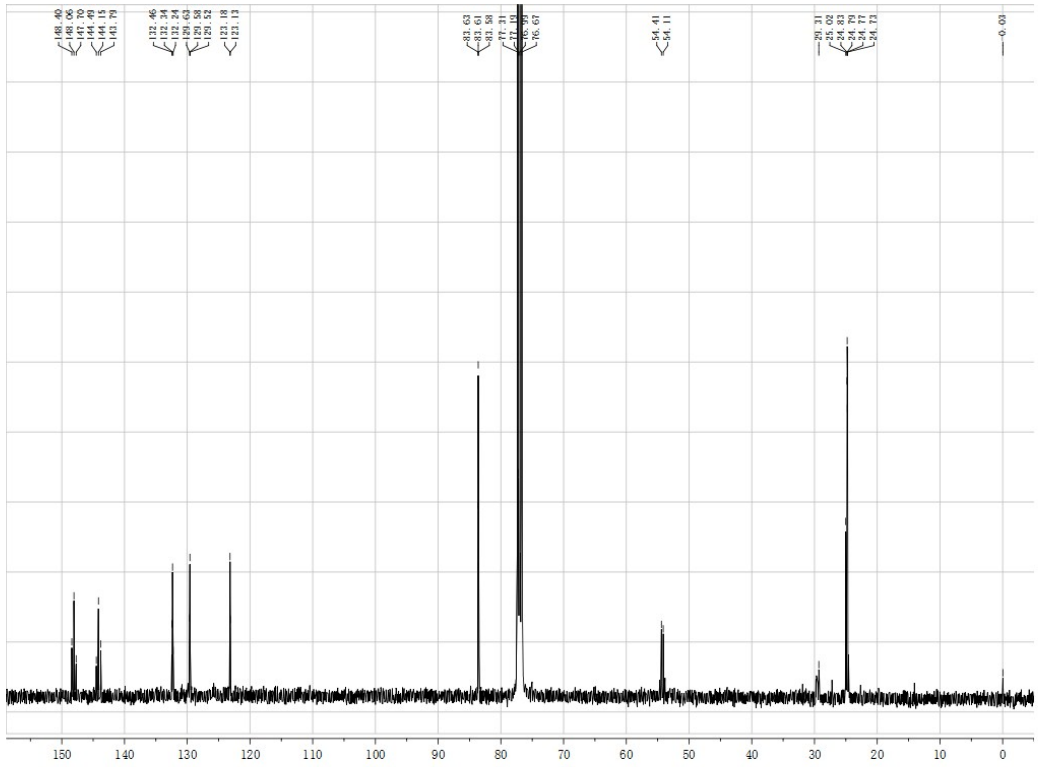
TRIP-PDI$_3$. A mixture of **TRIP-3B** (95 mg, 0.15 mmol), PDI-Br (499 mg, 0.60 mmol), Pd $(PPh_3)_4$ (30 mg), ($K_2CO_3$138 mg, 1.0 mmol) was dissolved in the mixed toluene (25 mL) and H_2O (3mL), and then refluxed for 20 h under a nitrogen atmosphere. After removal of the solvent, the residue was dissolved in dichloromethane (200 mL), and the organic phase washed with brine (50 mL) and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was purified by silica gel column chromatography (eluting with dichloromethane/petroleum ether 15/50, v/v) to afford the product **TRIP-PDI$_3$** (169 mg, 45%) as a red solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 0.81–0.86 (m, 36H), 1.25–1.41 (m, 86H), 1.59 (s, 13 H), 1.70–1.87 (m, 10H), 2.20–2.27 (m, 12H), 5.23 (t, 6H), 5.60–5.73 (m, 2H), 7.05–8.09 (m, 18H), 8.53-8.70 (m, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.02, 163.96, 147.54, 145.48, 141.69, 140.05, 137.08, 135.05, 134.70, 132.83, 131.63, 130.55, 130.14, 129.39, 128.76, 128.42, 127.75, 126.44, 125.88, 125.08, 123.76, 123.27, 122.84, 54.96, 54.78, 53.85, 32.61, 31.97, 29.93, 29.42, 27.44, 27.09, 22.79, 14.24. HR-MS (MALDI): m/z $[M+1]^+$ cacld for $C_{170}H_{194}N_6O_{12}$, 2512.4788; found, 2534.4747 $[M+Na]^+$.



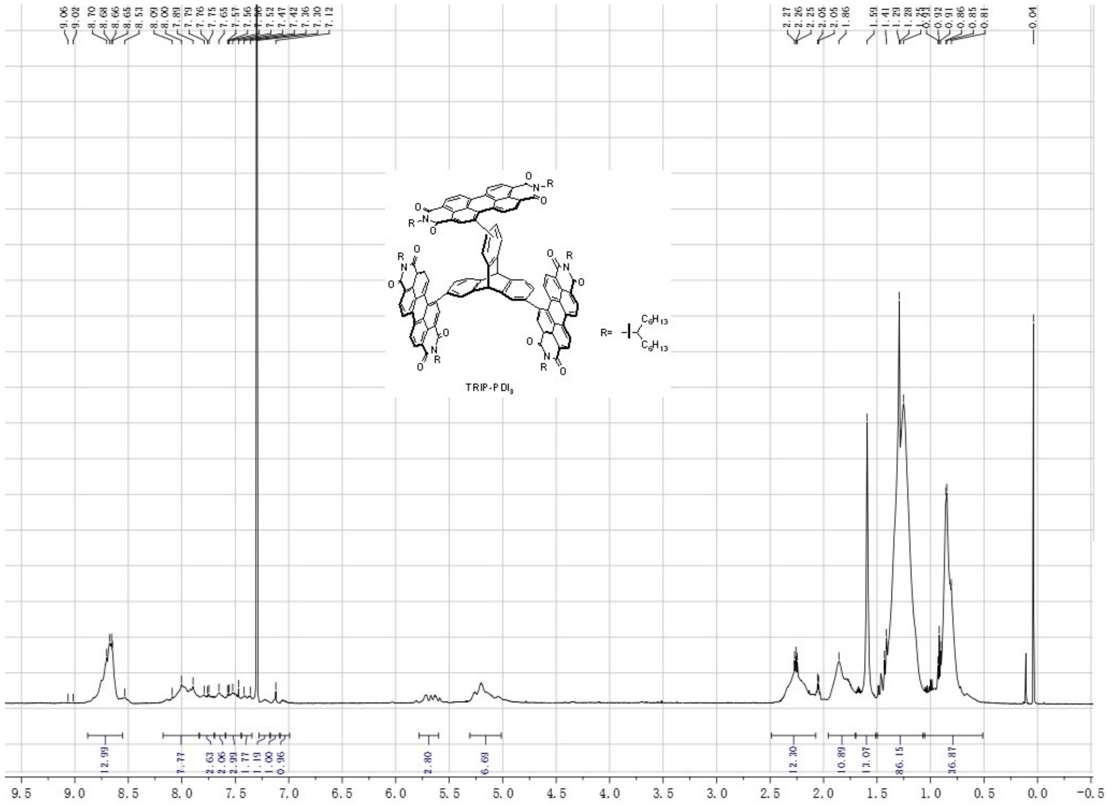
Scheme S1 Synthetic route to **TRIP-PDI$_3$**

NMR spectra of **TRIP-3B** and **TRIP-PDI$_3$**





148.40
148.06
147.70
144.49
144.15
143.79
132.46
132.34
132.24
129.63
129.58
129.52
123.18
123.13
83.63
83.61
83.58
77.31
77.19
76.99
76.67
54.41
54.11
29.31
25.02
24.83
24.79
24.77
24.73
0.03
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



9.06
9.02
8.70
8.68
8.66
8.65
8.53
8.09
8.00
7.89
7.79
7.76
7.75
7.65
7.57
7.56
7.52
7.47
7.42
7.36
7.30
7.12
2.27
2.26
2.25
2.06
2.05
1.86
1.59
1.41
1.29
1.28
0.92
0.91
0.86
0.85
0.81
0.04
O
N
R
TRIP-PDI$_3$
R= C_6H_{13} C_6H_{13}
12.99
7.77
2.63
2.06
2.99
1.77
1.19
1.00
0.96
2.80
6.69
12.30
10.89
13.07
86.15
36.87
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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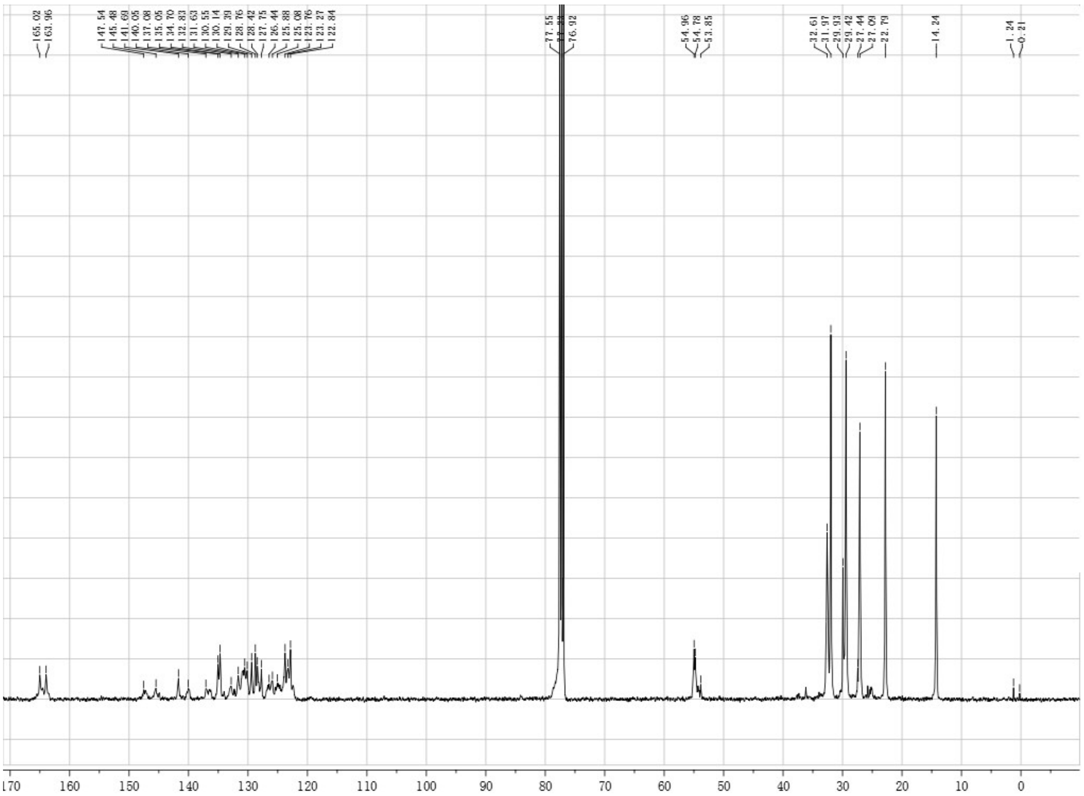
2.0
1.5
1.0
0.5
0.0
-0.5



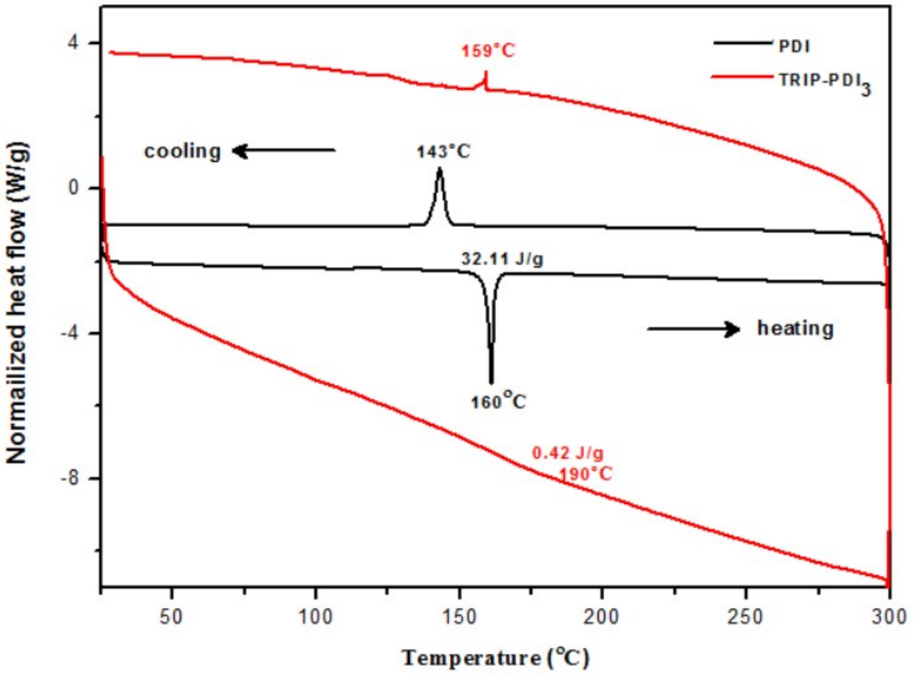


Figure S1 DSC curves of **TRIP-PDI$_3$** under N_2 atmosphere

SCLC measurements

The hole and electron mobility data was extracted from the dark *J*–*V* characteristics of hole-only devices, ITO/PEDOT:PSS/**PBDT-TS1:TRIP-PDI$_3$**/Au, and electron only devices ITO/ZnO/**PBDT-TS1:TRIP-PDI$_3$**/Al devices. The electrical characteristics were measured with a source/measure unit (Keithley 4200) in a N_2-filled glove box. The dark *J–V* curves were fitted by using the Mott-Gurney equation (eq. 1), where *J* is the dark current density, ε_0 is the vacuum permittivity, ε is the static dielectric constant of the medium, μ_0 is the zero-field mobility, γ is the disorder parameter, *V* is the effective voltage and *L* is the film thickness. For the case of hole-only devices the built in voltage (V_{bi}) value of 0V and for electron only devices V_{bi} = 1.5 V was used.[2]

$$J(V) = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_0\exp(0.89\gamma\sqrt{V/L})\frac{V^2}{L^3} \quad \text{..................} \quad (1)$$

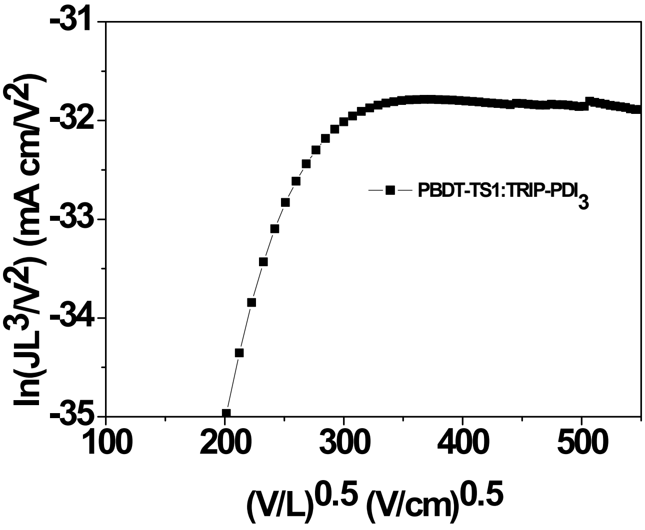


Fig. S2 $J_{0.5}$–*V* curves of the electron-only devices based on **PBDT-TS1:TRIP-PDI$_3$** films.

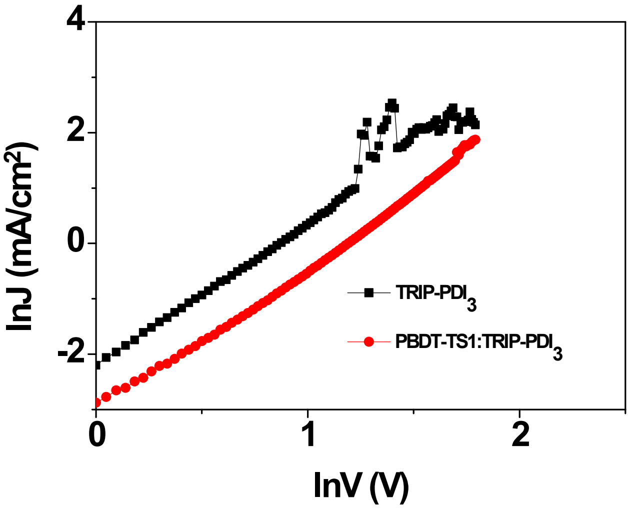


Fig. S3 $J_{0.5}$–V curves of the electron-only devices based on **PBDT-TS1:TRIP-PDI$_3$** films and **TRIP-PDI$_3$**

Table S1. The detailed photovoltaic performances of the solar cells based on **PBDT-TS1** and **TRIP-PDI$_3$**

D/A (w/w)	Spin-coating (rpm)	J_{sc} (mA cm^{-2})[b]	V_{oc} (V)	FF	PCE (%)	Aver. PCE (±Std. dev.) (%)[c]	Thickness (nm)[d]
1.5 : 1[a]	1000	10.27	0.96	0.35	3.45	---	110
	1500	9.19	0.96	0.41	3.61	3.53(±0.112)	73
	2000	8.52	0.96	0.41	3.35	---	56
1 : 1[a]	1000	10.68	0.98	0.37	3.87	---	120
	1500	9.77	0.98	0.43	4.11[e]	3.98(±0.102)	74
	2000	8.62	0.98	0.46	3.89	---	63
1 : 1	1500	10.26	0.96	0.46	4.53	4.41(±0.095)[f]	85
	1500	11.43	0.95	0.40	4.34 [g]	---	85
	1500	10.83	0.96	0.42	4.37 [h]	---	85
	1500	10.43	0.97	0.40	4.05 [i]	3.89(±0.102)	87
	1500	10.22	0.96	0.41	4.02 [j]	3.92(±0.10)	84
	1500	11.17	0.97	0.40	4.33 [k]	4.22(±0.10)	86
1 : 1.5[a]	1000	7.11	0.97	0.31	2.14	---	188
	1500	10.33	0.98	0.38	3.85	3.68(±0.114)	122
	2000	9.89	0.97	0.36	3.45	---	110

[a] As-cast. [b] Calculated by convoluting the spectral response with the AM 1.5G spectrum (100mW cm^{-2}). [c] Average values from 6 pieces of devices. [d] The thickness data were obtained *via* the surface profilometer (Bruker Dektak XT). [e] Without additive. [f] With 0.5% 1,8-diiodooctane (DIO). [g] With 1.0% DIO. [h] With 1.5% DIO. [I] With 0.5% 1-chloronaphthalene CN. [j] With 0.5% *N*-methyl pyrrolidone (NMP). [K] With 0.5% diphenyl ether(DPE).

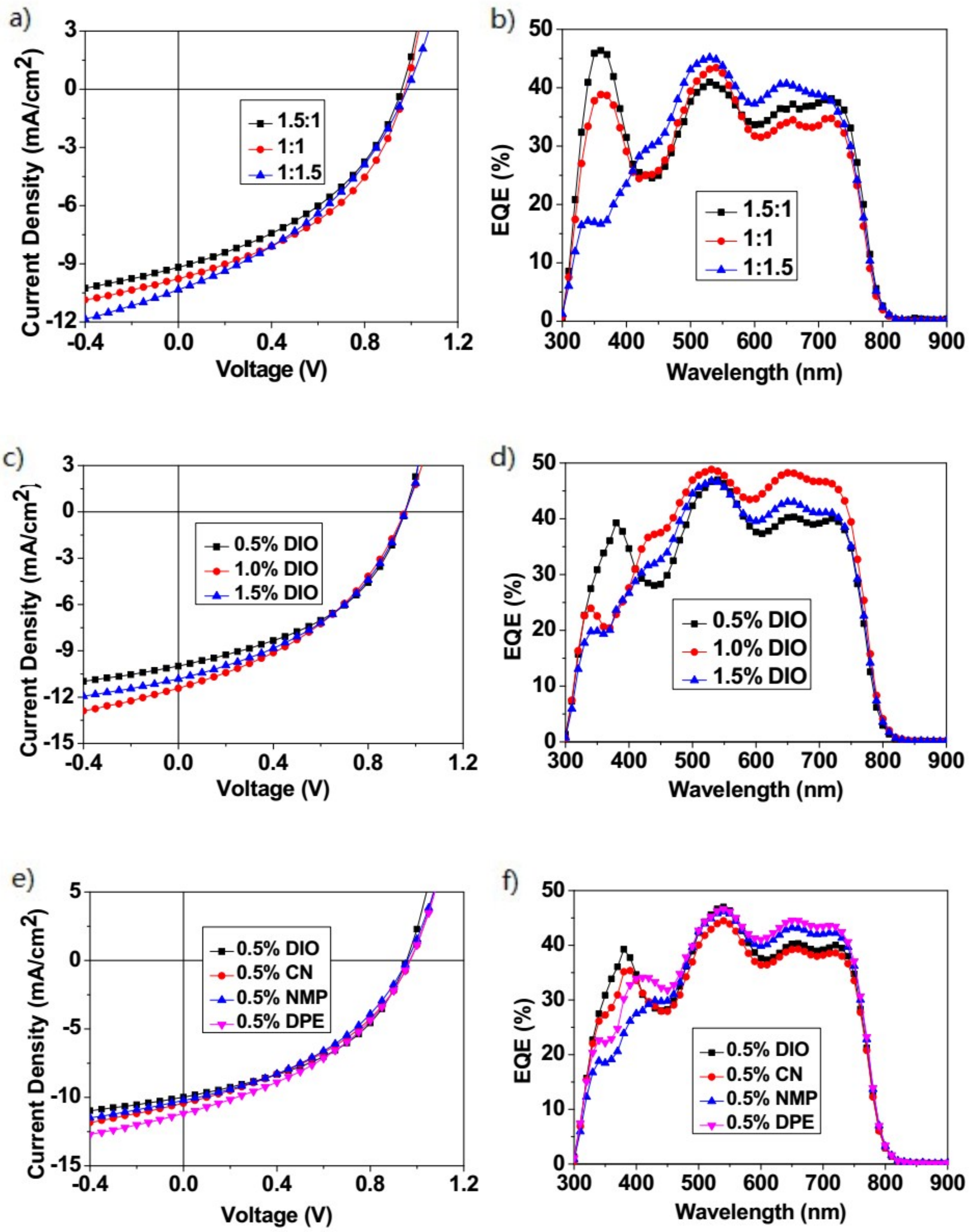


Fig. S4 *J*–*V* curves of OSCs based on **PBDT-TS1** and **TRIP-PDI$_3$** : a) with different D/A ratios, c) with different amount of additive and e) with different additives; EQE spectra of **PBDT-TS1:TRIP-PDI$_3$** based OSCs: d) with different D/A ratios, d) with different amount of additive and f) with different additives.

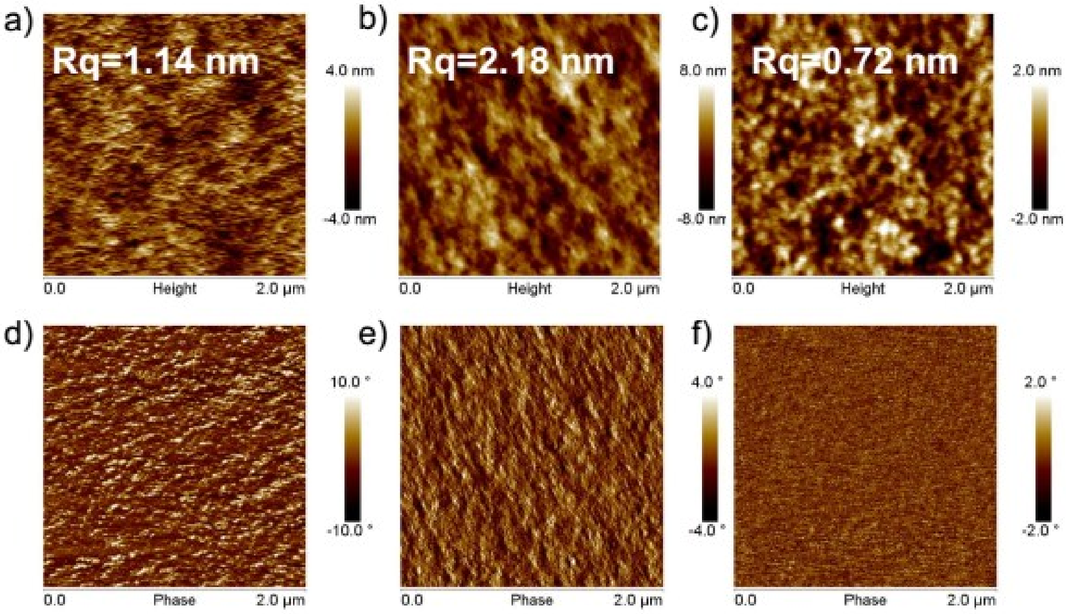


Fig. S5 Morphology images of the D/A blend film: a), b) and c) are the AFM height images, a) with 0.5% CN, b) with 0.5% NMP, c) with 0.5% DPE; d), e) and f) are the AFM phase images, d) with 0.5% CN, e) with 0.5% NMP, f) with 0.5% DPE.

References

1. C. Zhang and C. F. Chen, *J. Org. Chem.*, 2006, **71**, 6626.

2. T. Ye, R. Singh, H. -J. Butt, G. Floudas, and P. E. Keivanidis, *ACS Appl. Mater. Interfaces,* 2013, **5**, 11844.