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Supporting Information

Simultaneously improving photovoltaic parameters of organic solar cells via isomerization of benzo[b]benzo[4,5]thieno[2,3-d] thiophene-based octacyclic non-fullerene acceptors

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1. Experimental details

Fabrication of inverted solar cells. An inverted-type device with the configuration of ITO/ZnO/active layer/MoO_3/Al was utilized for photovoltaic characterization. Patterned ITO glass was carefully washed with acetone, water, ethanol and isopropanol, then subjected to UV-ozone treatments for 20 min. The thin ZnO layer was spin-coated onto the ITO glass from the ZnO precursor solution, and then annealed at 220°C for 30 min in the air. The D:A blend solution in chlorobenzene

(12.5 mg mL^{-1} in total) was spin-coated by varying spin rates on the ZnO layer to form a photoactive layer. Finally, the MoO_3 layer and Al electrode were sequentially evaporated onto the surface of the active layer in a vacuum chamber with a pressure of 5×10^{-5} Pa. The *J-V* characteristics were measured using a Keithley 2602 Source Meter and an Oriel Sol3A solar simulator equipped with an AM 1.5G solar spectrum filter with an intensity of 100 mW cm^{-2} as the light source. The IPCE spectrum was measured using a Zolix Solar Cell Scan 100 QE/IPCE measurement system.

Materials. Unless stated otherwise, solvents and chemicals were obtained commercially and were used without further purifications. All materials and solvents were purchased from Tianjin Kemiou Chemical Reagent, Alfa Aesar and were used without further purifications. PM6 was purchased from Suna Tech Inc. Compound 1 was obtained according to methods described earlier in the literature.[1] Nuclear magnetic resonance (NMR) spectra of the compounds were collected using a Bruker AVANCE 400 MHz spectrometer with deuterated chloroform ($CDCl_3$) as the solvent and tetramethylsilane (TMS) as the internal reference. Mass spectrometry (MS) data were obtained on a Bruker Aupoflex III MALDI-TOF analyzer with α-cyano-4-hydroxycinnamic acid as a matrix. The photophysical and electrochemical properties were characterized by UV–visible–near infrared spectroscopy (Perkin–Elmer Cary 60 UV–Vis–NIR) and cyclic voltammetry (electrochemistry workstation CHI660A, Chenhua Shanghai), respectively. Atomic force microscopy (AFM) images were measured on a Dimension Icon AFM (MUITIMODEPICOFOREE) in a tapping mode. Grazing incidence wide angle X-ray scattering (GIWAXS) measurements were accomplished at PLS-II 9A U-SAXS beamline of the Pohang Accelerator Laboratory in Korea.

Space-charge-limited current (SCLC): The J–V characteristics of the hole-only and electron-only devices were fitted by the Mott–Gurney equation.

$J = (9/8)\varepsilon_r\varepsilon_0\mu(V^2/L^3)$

where J is the current density, ε_r is the dielectric permittivity of the active layer, ε_0 is the vacuum permittivity, L is the thickness of the active layer, μ is the mobility. $V=V_{app}-V_{bi}$, where V_{app} is the applied voltage, V_{bi} is the offset voltage. The mobility can be calculated from the slope of the $J^{0.5}$ vs. V curves.

Synthesis of compound 2. To a two-necked round bottom flask were added BTBT-Br (1 g, 2.51 mmol), bis(pinacolato)diboron (2.54 g, 10 mmol), CH_3COOK (0.98 g, 10 mmol), $Pd(dppf)_2Cl_2$ (100 mg, 0.164 mmol) and toluene (50 mL). The mixture was deoxygenated with nitrogen for 30 min and stirred for 24 h at 90 ℃ under argon. Water and dichloromethane (300 mL) were added, and the organic layer was separated and washed with water three times. After removal of the solvent, the crude product was chromatographically purified on silica gel column (eluted with ethyl acetate/petrolem ether = 1:20) to afford compound 4 as a white solid (0.74g, 61%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.40 (s, 2H), 7.88 (d, 4H), 1.39 (s, 24H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 142.01, 135.13, 134.99, 130.91, 130.68, 121.10, 84.09， 24.95. MALDI-TOF MS(m/z): calcd for $C_{26}H_{30}B_2O_4S_2$: 492.2620; Found: 492.2006.

Synthesis of compound 3. To a two-necked round bottom flask were added compound 3 (0.49 g, 1 mmol), 2-bromothiophene-3-carboxylate (0.94 g, 4 mmol), aqueous $NaCO_3$ (0.64 g, 6 mmol), $Pd(PPh_3)_4$ catalyst (100 mg), and anhydrous toluene (50 mL). The mixture was deoxygenated with nitrogen for 30 min and stirred for 48 h at 90 ℃ under argon. Water and dichloromethane were added, and the organic layer was dried over $MgSO_4$. After removal of the solvent, the crude product was chromatographically purified on silica gel column (eluted with dichloromethane/petrolem ether = 2:3) to afford compound 6 as a yellow solid (0.22 g, 40%). ^{1}H NMR (400MHz，$CDCl_3$) δ (ppm): 8.07 (s, 2H), 7.92 (d, 2H), 7.62 (d, 2H), 7.58 (d, 2H), 7.31 (d, 2H), 4.24 (m, 4H), 1.21 (m, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 163.30, 150.14, 142.15, 134.26, 132.97, 130.51, 130.25, 128.71, 127.23, 125.25, 124.43, 120.91, 60.64, 14.14. MALDI-TOF MS(m/z): calcd for $C_{28}H_{20}O_4S_4$: 548.7040; Found: 548.1167.

Synthesis of compound BT-aa, BT-ab and BT-bb. To a three-necked round bottom flask were added 1-bromo-4-hexybenzene (723.51 mg, 3 mmol) and dry THF (10 mL). The mixture was degassed with a nitrogen flow for 10 min and stirred for 15 min at -78 ℃ under argon. The n-BuLi solution (2.5 mol L^{-1}, 1.1 mL) was added dropwise to the above solution at -78 ℃, and then stirred for 1.5h. Compound 4 (274 mg, 0.5 mmol) in THF (20 mL) under nitrogen was added dropwise to the above solution at -78 ℃. Then the resulting mixture was stirred under reflux for 12 h at room temperature. 100 mL of ammonium chloride saturated solution was added and the mixture was extracted with dichloromethane (2 × 100 mL). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, a brown liquid was obtained and directly used for next step reaction without further purification. Secondly, a solution of the brown liquid in toluene (50 mL) with a catalyst of Amberlyst15 was stirred at 70 °C for 4 h under nitrogen. After removal of the octane under reduced pressure, the residue was washed with saturated aq. sodium carbonate solution (50 mL × 3) and extracted by diethyl ether (50 mL × 2). Then, after removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 10/1) to give a yellow solid. No ^{1}H NMR and ^{13}C NMR measurements because the three isomers were with no need for separating. MALDI-TOF MS(m/z): calcd for $C_{72}H_{76}S_4$: 1069.6400; found: 1069.3766.

Synthesis of BT-aa-CHO, BT-ab-CHO and BT-bb-CHO. A Vilsmeier reagent was prepared firstly. 4 mL anhydrous DMF was added to a dry 100 mL two-necked round bottom flask, and the solution was cooled to 0 °C and 0.4 mL phosphorous oxychloride ($POCl_3$) was added by syringe under argon protection. The mixture was kept at 0 °C for 2 h, and then the mixture of BT-aa, BT-ab and BT-bb (255 mg, 0.2 mmol) in dry dichloroethane (DCE) (20 mL) was added. Then, the mixture solution was allowed to reflux overnight. After cooling to room temperature, 100 mL water was added to quench the reaction. The mixture was extracted with dichloromethane, and the organic layer was collected, washed with water and dried with anhydrous MgSO4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 1/1) to give a yellow solid. No ^{1}H NMR and ^{13}C NMR measurements because the three isomers were with no need for separating.

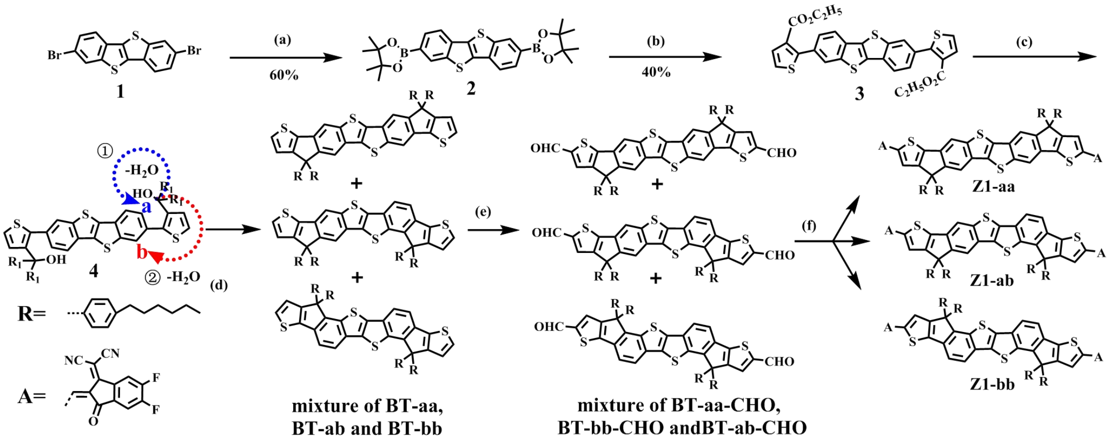
MALDI-TOF MS(m/z): calcd for $C_{74}H_{76}O_2S_4$: 1125.6600; found: 1125.3240.

Synthesis of Z1-aa, Z1-bb and Z1-ab. To a 100 mL two-necked round bottom flask were added INCN-2F (276 mg, 1.2 mmol), the mixture of BT-aa-CHO, BT-ab-CHO and BT-bb-CHO (225 mg, 0.2 mmol) and anhydrous chloroform (30 mL). Then a mixed solvent of chloroform (10 mL) and pyridine (1 mL) were added drop by drop. The reaction flask was placed in an oil bath at 75 ℃ and was stirred overnight. We first used silica-gel column chromatography with a mixed solvent as the eluent (petroleum ether/dichloromethane, v/v = 3/2) to separate Z1-aa as a black gold solid (80 mg, yield 26%), followed by the mixture of Z1-ab and Z1-bb. Z1-ab was then further purified by recrystallization from ethyl acetate to yield Z1-bb as a black gold solid (40 mg, yield 13%). Finally, we obtained Z1-ab as a purple solid (50 mg, yield 16%) by silica-gel column chromatography using a mixed solvent as the eluent (petroleum ether/ethyl acetate, v/v = 1/1). Z1-aa: ^{1}H NMR (400 MHz， $CDCl_3$) δ (ppm): 8.75 (s, 2H), 8.38 (s, 2H), 7.82 (d, 4H), 7.58 (s, 4H), 6.80~7.45 (m, 16H), 2.56~2.76 (m, 8H), 1.27~1.26 (m, 32H), 0.81~0.87 (m, 12H). No ^{13}C NMR measurements because it was hard to dissolve. MALDI-TOF MS(m/z): calcd for $C_{98}H_{80}F_4O_2S_4$: 1549.9776; Found: 1549.2169.

Z1-ab: ^{1}H NMR (400 MHz，$CDCl_3$) δ (ppm): 8.95 (d, 2H), 8.57 (m, 2H), 8.06 (d, 1H), 7.95 (d, 1H), 7.88~7.92 (m, 2H), 7.71 (m, 1H), 7.60 (m, 1H), 7.50 (d, 4H), 7.45 (s, 1H), 7.06~7.12 (m, 12H), 2.46~2.56 (m, 8H), 1.27~1.26 (m, 26H), 0.81~0.87 (m, 12H), 0.71 (m, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 186.01, 185.58, 160.78, 159.18, 159.05, 158.45, 155.82, 155.69, 154.21, 153.21, 153.10, 150.87, 143.19, 142.50, 142.32, 141.55, 140.82, 140.19, 139.84, 139.34, 139.15, 138.88, 138.61, 137.18, 136.52, 136.46, 136.34, 135.78, 134.72, 133.84, 133.34, 129.54, 128.98, 128.70, 128.65, 127.59, 125.16, 123.65, 122.74, 121.23, 121.04, 119.41, 115.12, 114.29, 114.21, 112.52, 69.56, 64.02, 63.22, 35.52, 35.47, 31.94, 31.69, 31.63, 31.32, 31.17, 29.71, 29.05, 28.87, 22.70, 22.58, 22.49, 14.09, 14.02. MALDI-TOF MS(m/z): calcd for $C_{98}H_{80}F_4O_2S_4$: 1549.9766; Found: 1550.4771.

Z1-bb: ^{1}H NMR (400 MHz，CDCl$_3$) δ (ppm): 8.87 (s, 2H), 8.54 (s, 2H), 7.90 (d, 2H), 7.85 (s, 2H), 7.76 (s, 2H), 7.70 (m, 2H), 7.09~7.12 (m, 16H), 2.53 (m, 8H), 1.27 (m, 32H), 0.85 (m, 12H). ^{13}C NMR (400 MHz, CDCl$_3$): δ 186.03, 160.67, 159.16, 158.35, 158.33, 153.23, 151.01, 142.65, 140.69, 139.64, 139.10, 138.82, 137.18, 136.43, 134.29, 133.29, 128.65, 128.57, 122.75, 121.00, 119.31, 114.27, 114.19, 112.78, 112.56, 112.30, 69.52, 63.60, 35.57, 31.68, 31.25, 29.73, 29.10, 22.58, 14.08. MALDI-TOF MS(m/z): calcd for $C_{98}H_{80}F_4O_2S_4$: 1549.9766; Found: 1549.4566.

2. Synthesis routes and characterizations of the compounds



Scheme 1 Synthetic route to Z1-aa, Z1-bb, and Z1-ab

Reaction conditions: (a) Pd(PPh$_3$)$_2$Cl$_2$, bis(pinacolato)diboron, toluene, CH$_3$COOK, 90 ℃; (b) Pd(PPh$_3$)$_4$, toluene, K$_2$CO$_3$, ethyl 2-bromothiophene-3-carboxylate, 90 ℃;

(c) n-BuLi, 1-bromo-4-hexylbenzene, THF, -78 ℃; (d) Amberlyst15, toluene, 90 ℃; (e) DMF, $POCl_3$, DCE, 0 ℃ ~ reflux; (f) pyridine, $CHCl_3$, 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile, 65 ℃.

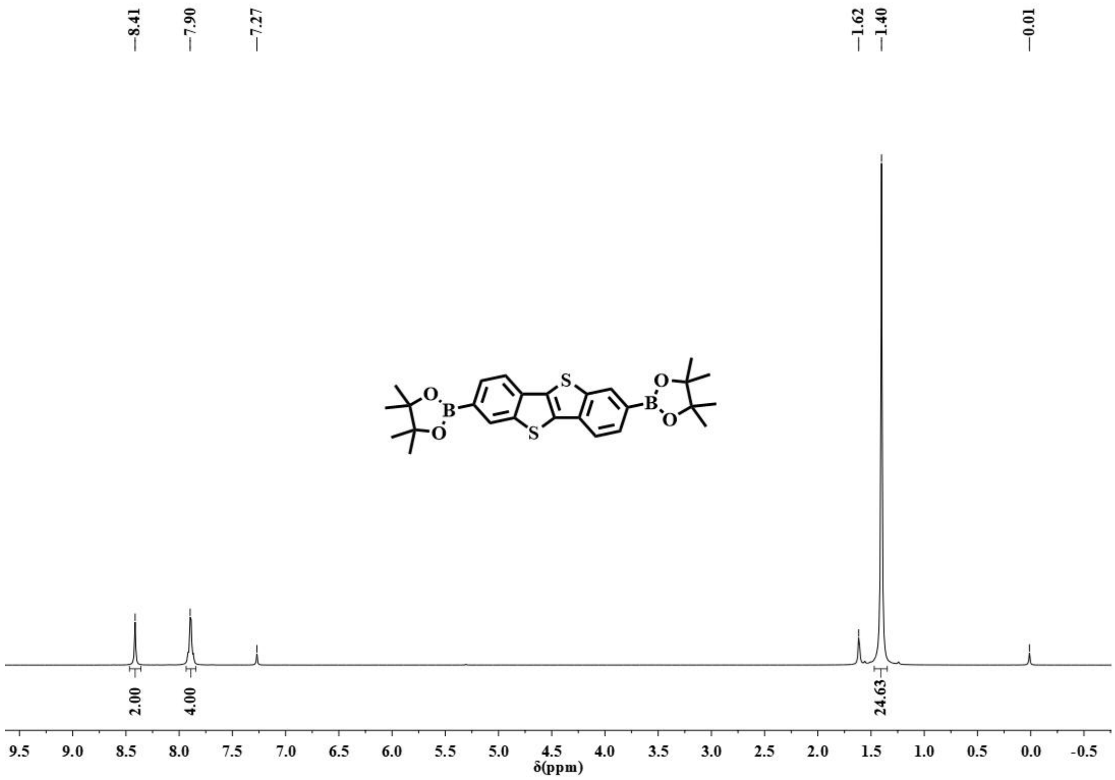


Figure S1. ^{1}H NMR spectrum of compound **2**

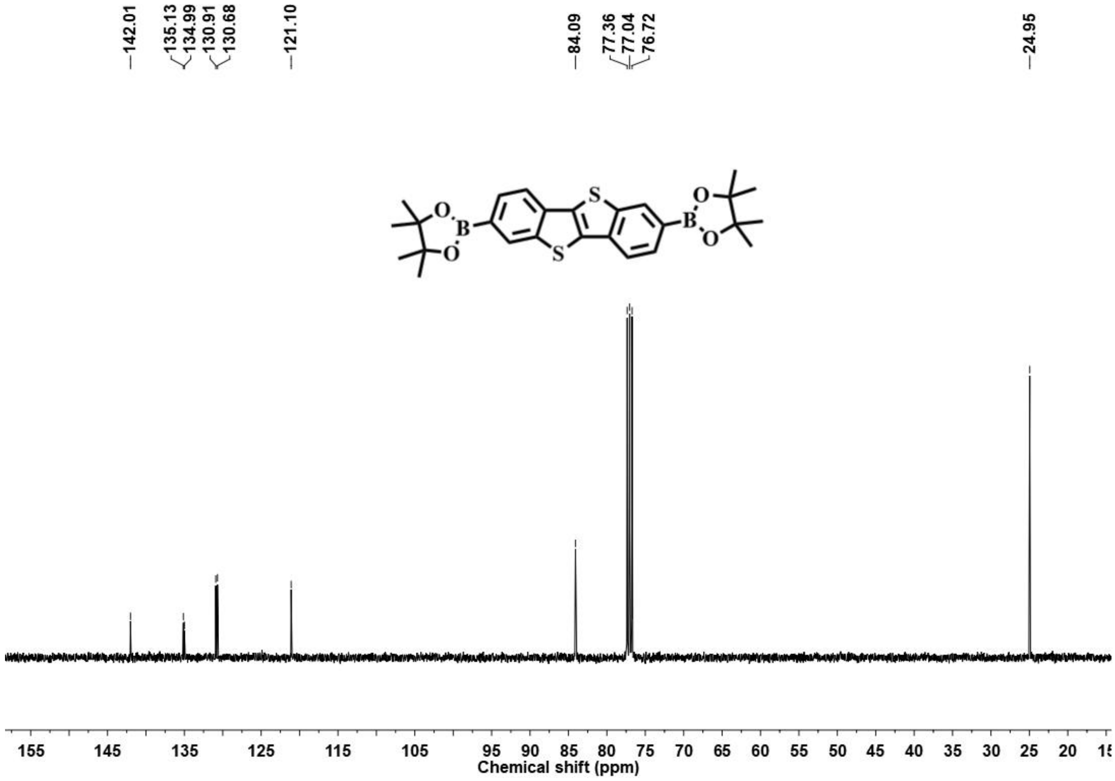


Figure S2. ^{13}C NMR spectrum of compound **2**

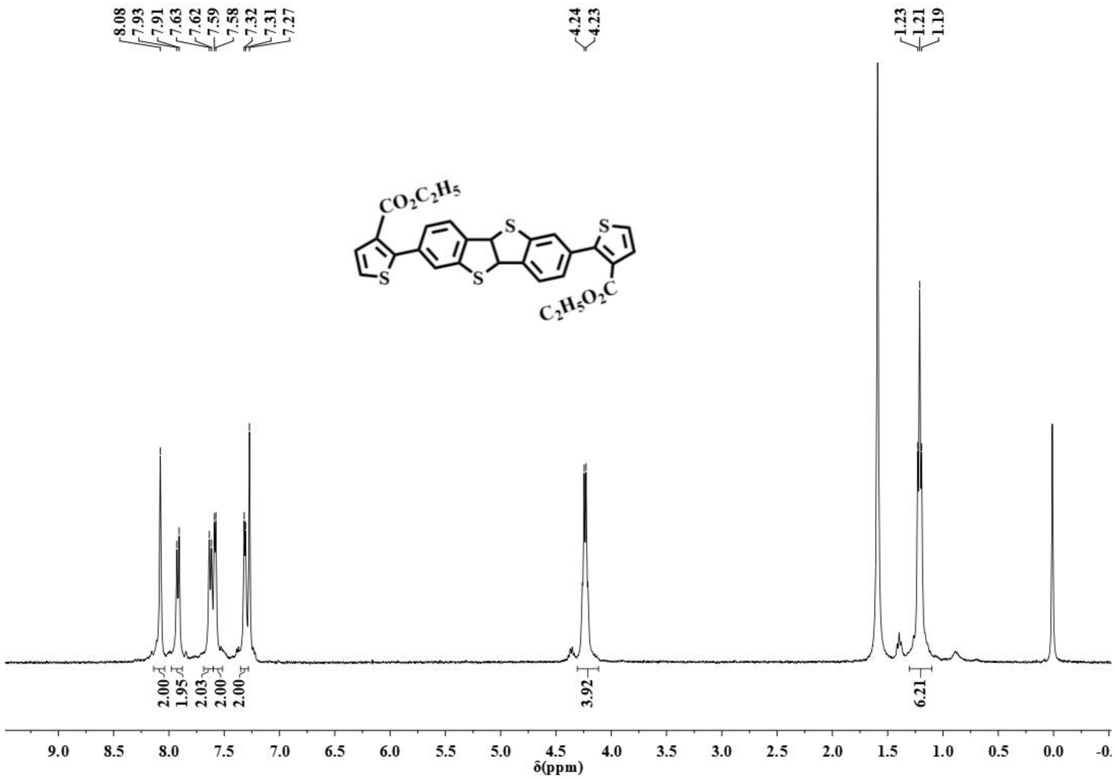


Figure S3. ^{1}H NMR spectrum of compound **3**

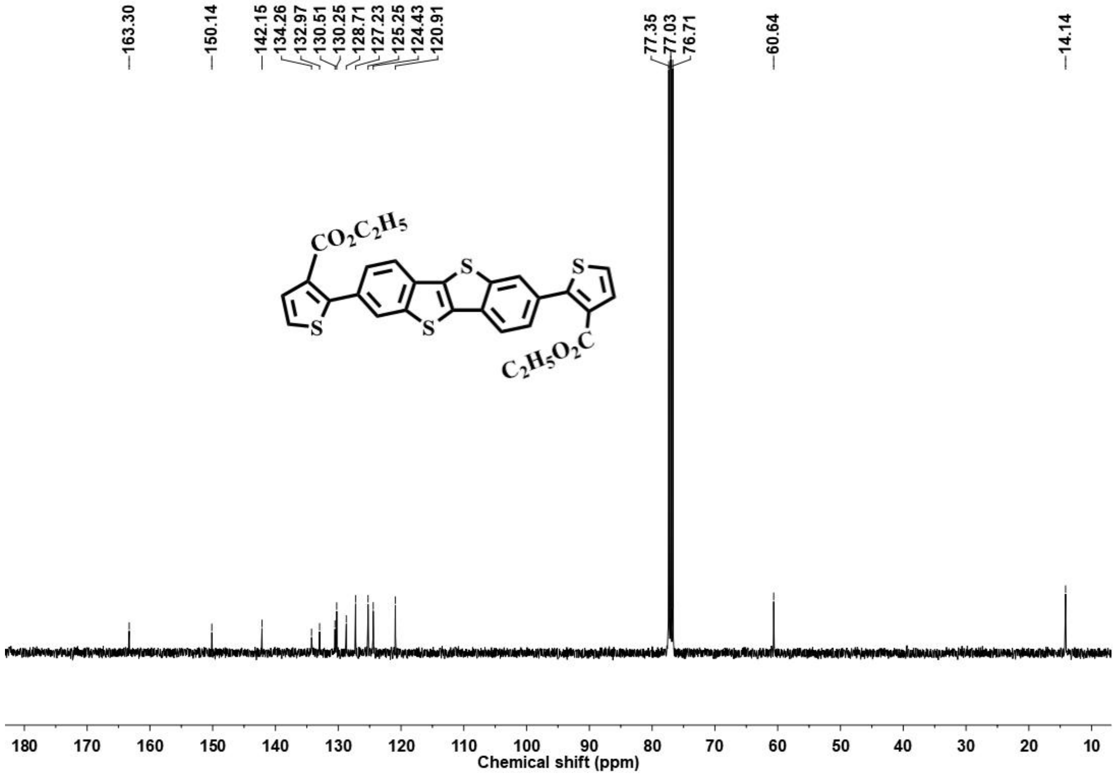


Figure S4. ^{13}C NMR spectrum of compound **3**

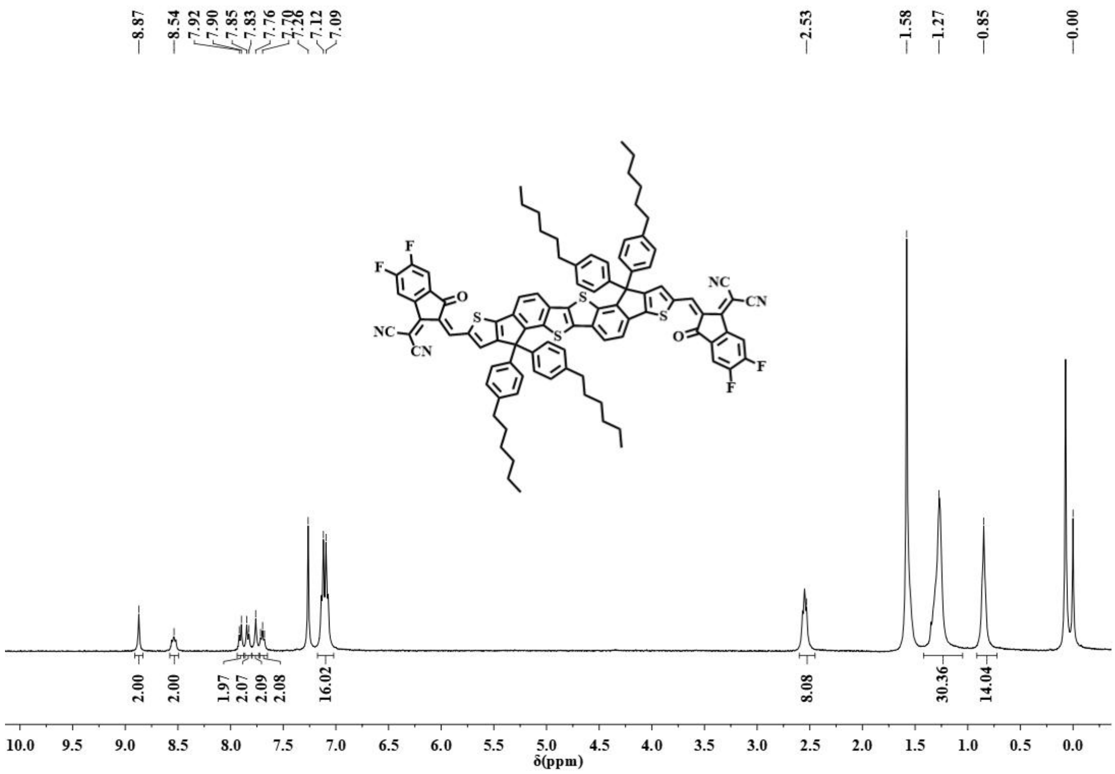


Figure S5. ^{1}H NMR spectrum of **Z1-bb**

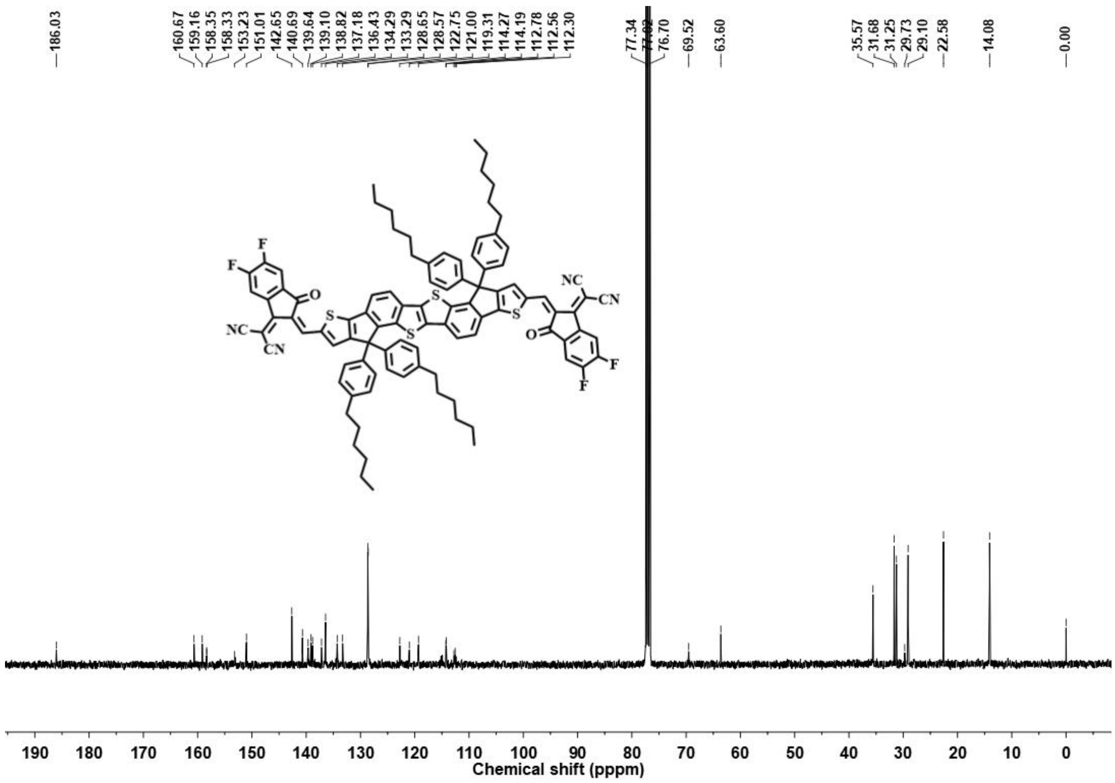


Figure S6. ^{13}C NMR spectrum of **Z1-bb**

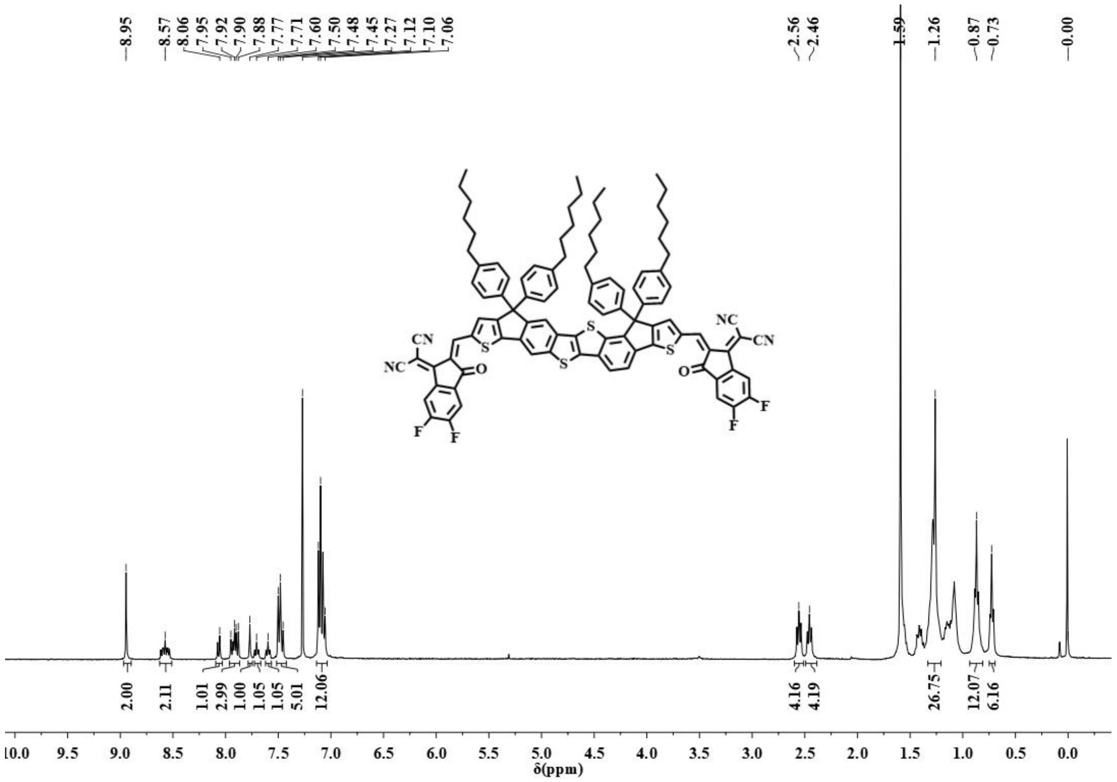


Figure S7. ^{1}H NMR spectrum of **Z1-ab**

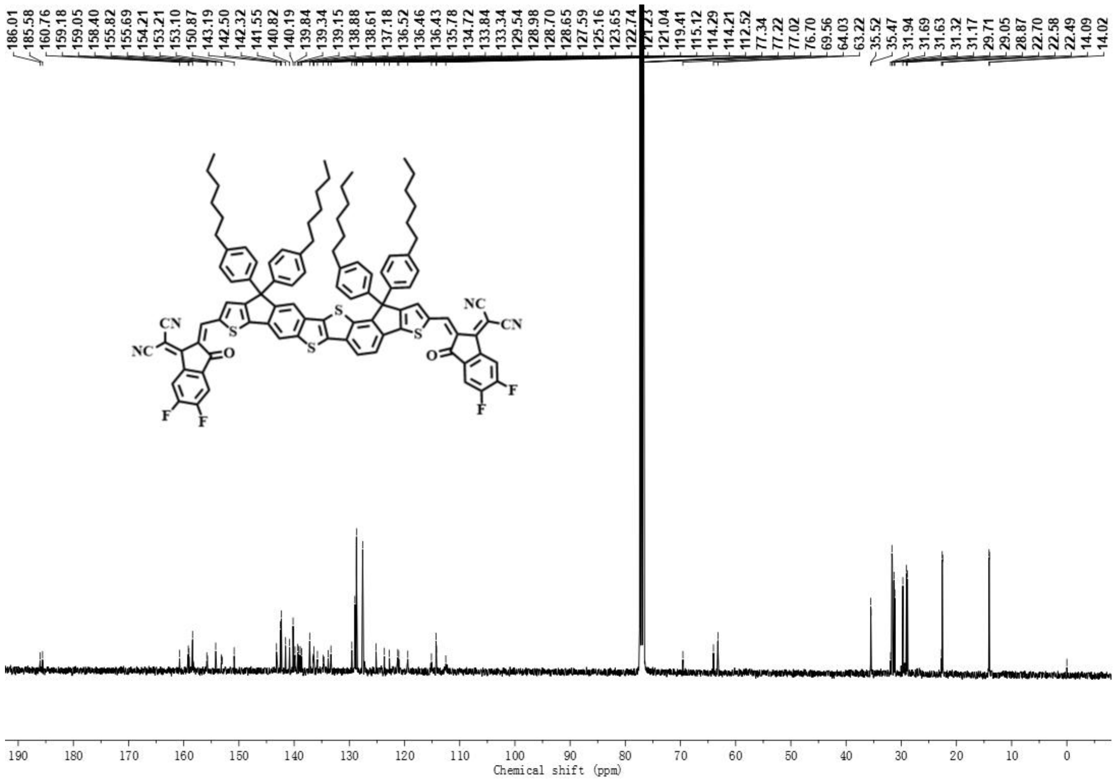


Figure S8. ^{13}C NMR spectrum of **Z1-ab**

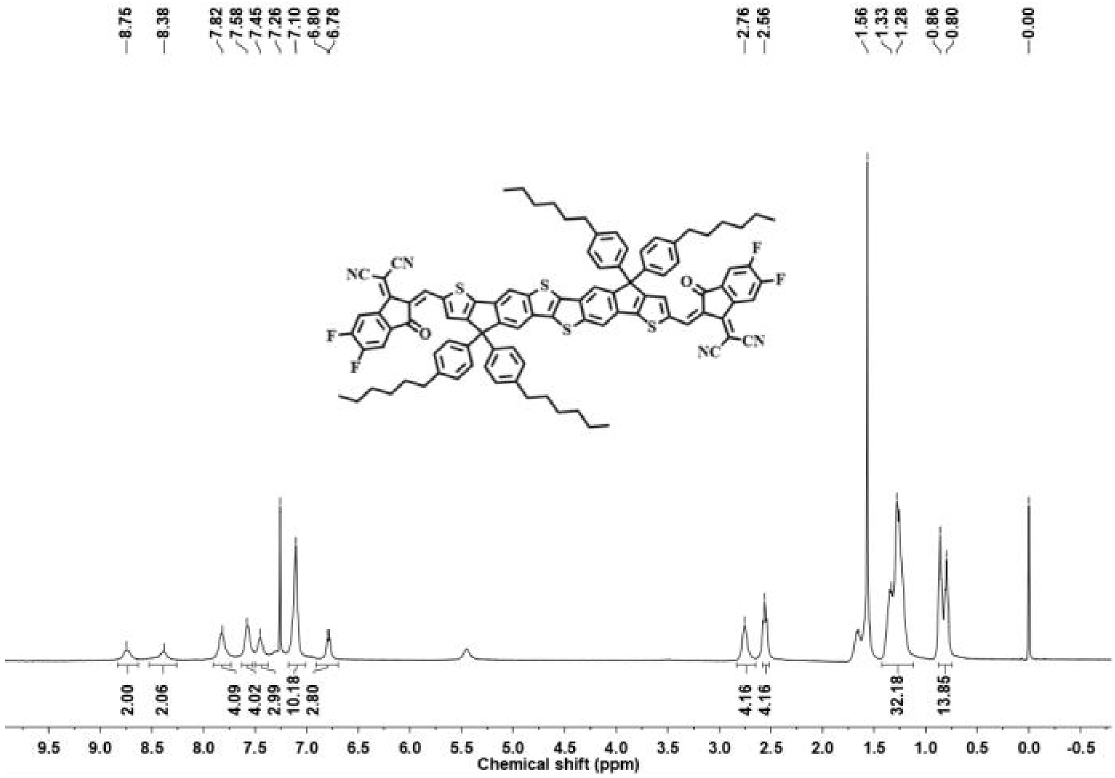


Figure S9. ^{1}H NMR spectrum of **Z1-aa**

3. Supporting Figure

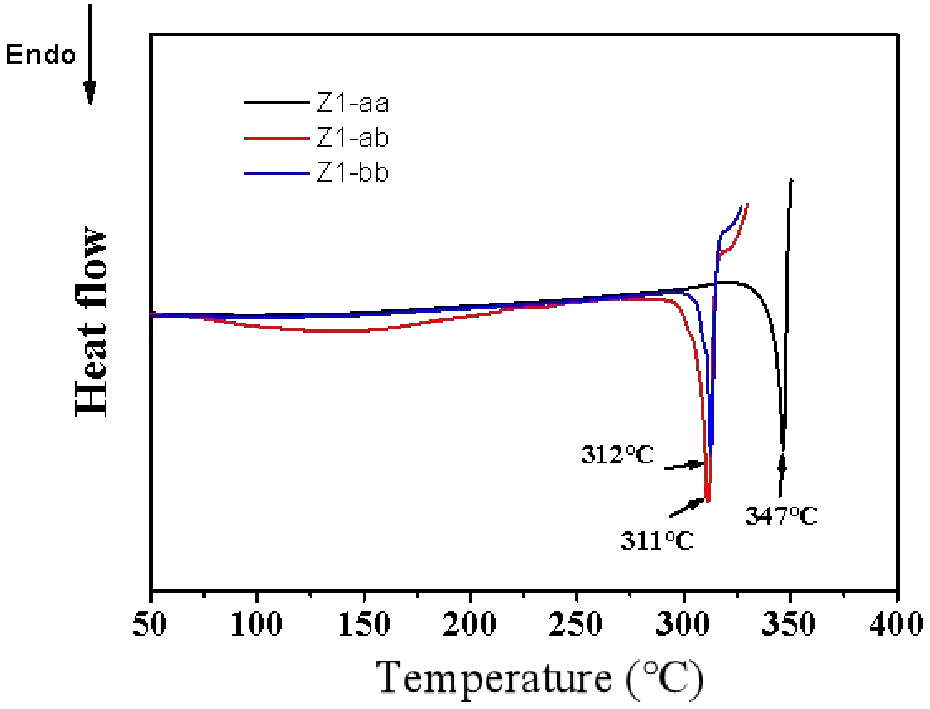


Figure S10. DSC curves of Z1-aa, Z1-ab and Z1-bb.

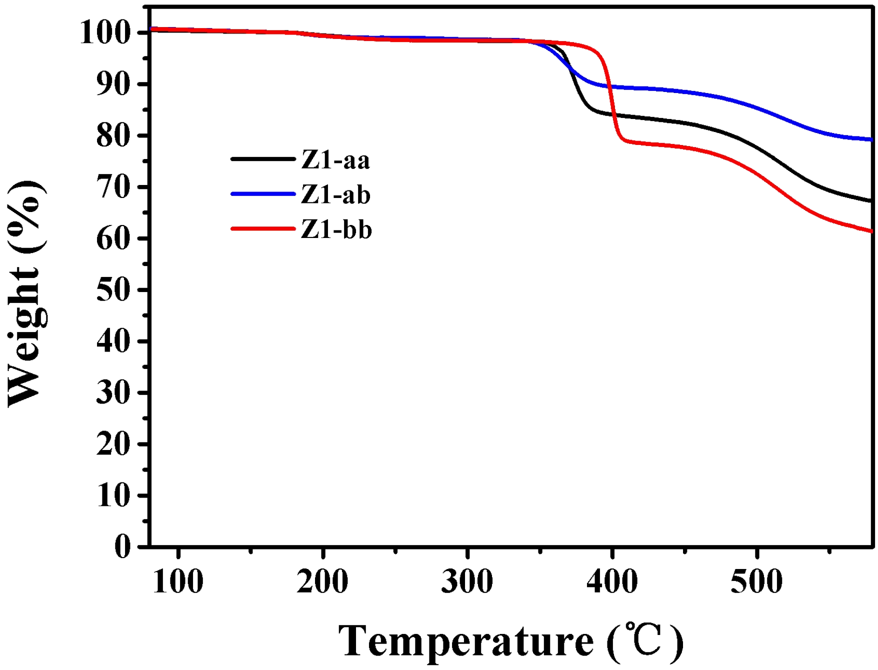


Figure S11. TGA curves of Z1-aa, Z1-ab and Z1-bb.

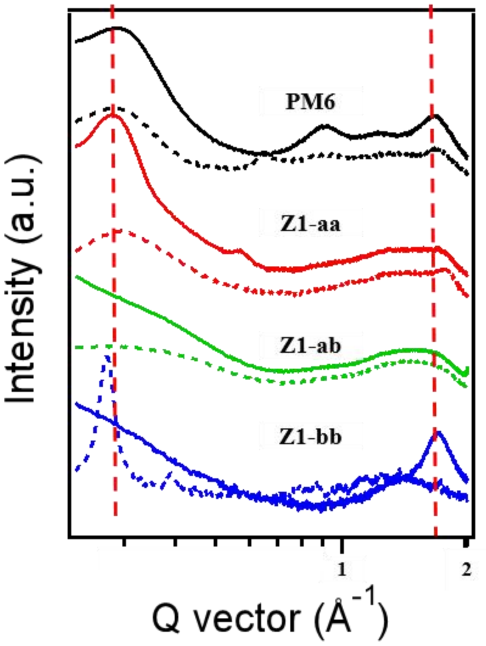


Figure S12. Line-cuts of GIWAXS patterns of Z1-aa, Z1-ab, Z1-bb and PM6 (solid line: out-of-plane; dash line: in-plane).

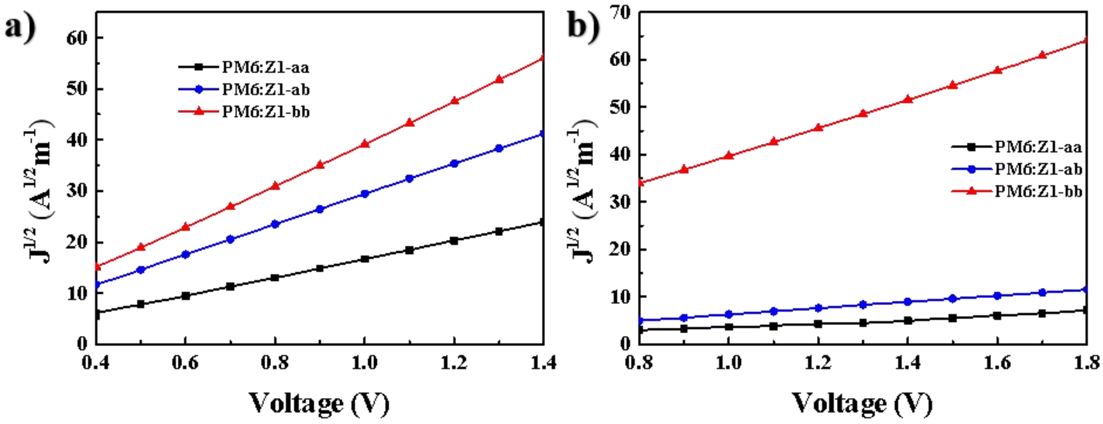


Figure S13. $J^{0.5}$-V curves of (a) hole-only and (b) electron-only devices based on the blend films of PM6:Z1-aa, PM6:Z1-bb, and PM6:Z1-ab.

4. Photovoltaic data tables

Table S1. Summary of photovoltaic device data of OSCs in literatures.

Blend films	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE$_{max}$ [%]	Ref.
PBDB-T:IEICO-4F	0.77	20.10	56	8.66	28
PBDTTT-EFT:IEICO-4F	0.74	21.9	58.5	10.0	15
PTB7-Th:IUIC	0.796	21.74	65	11.2	19
PBDB－T:IDT-EDOT	0.86	21.34	62.0	11.32	24
PTB7-Th:F8IC	0.640	25.12	67.6	10.9	20
PTB7-Th:FOIC	0.74	24.0	67.1	12.0	21
PTB7-Th:IHIC	0.75	18.75	68.1	9.77	14
PCE-10:BT-ClC	0.70	22.5	71.0	11.2	23
PBDB－T:TDTOT2F	0.85	20.87	72	12.79	28
PBDB－T:INPIC-4F	0.85	21.61	71.50	13.13	26
PTB7-Th:FNIC2	0.741	23.93	73.4	13.0	22
J51:ITIC5	0.897	18.48	75.5	12.5	29
PDBT-T1:IDIC	0.834	16.98	0.732	10.37	27
PBT1-EH:ITIC	0.95	16.5	75	11.8	18
PBDB-T:ITC6-IC	0.97	16.41	73	11.61	30

PBDB - T:ITCC	1.01	15.09	71.0	11.4	11
J52-Cl:BTA3	1.24	13.16	66.62	10.62	12
J52:BTA3	1.07	14.62	60.34	9.41	12
PBDB-T:NCIC	1.00	12.69	57.6	7.31	28
PffT2-FTA2-2IDT:IEIC	1.00	12.2	56	6.9	25
PBDB-T:IDT-BOC6	1.01	17.52	54	9.60	16
PBDB-T:DTCClC-C17	0.97	14.25	64.1	9.48	13
PM6:3TP3T-IC	1.05	13.0	65.6	9.0	10
PM6:3TP3T-4F	0.92	20.3	73.9	13.7	10
PBDB-TF:IDIC-C4Ph	0.941	19.06	78.32	14.04	31
PM6:Z1-bb	0.98	18.52	70.05	12.66	This work

Table S2. Summary of photovoltaic parameters under the illumination of AM 1.5G (100 mW cm^{-2})

Blend films	D/A [wt/wt]	Additive [vol]	J_{sc} [mA/cm^{-2}]	V_{oc} [V]	FF [%]	PCE [%]
PM6:Z1-bb	1:0.8	-	0.97	17.15	68.76	11.39
PM6:Z1-bb	1:1	-	0.98	17.37	69.32	11.62
PM6:Z1-bb	1:1.2	-	0.95	16.70	66.96	10.67
PM6:Z1-bb	1:1	0.1%	0.98	16.70	72.63	11.83
PM6:Z1-bb	1:1	0.3%	0.98	17.08	71.84	12.02
PM6:Z1-bb	1:1	0.5%	0.98	18.52	70.05	12.66
PM6:Z1-bb	1:1	0.8%	0.98	17.41	69.45	11.85
PM6:Z1-bb	1:1	1%	0.98	17.36	64.32	10.95

References

1. V. S. Vyas, R. Gutzler, J. Nuss, K. Kern, B. V. Lotsch, CrystEngComm., 2014, **16**, 7389-7392.