

Supporting Information

Regulating Molecular Orientations of Dipyran-based Nonfullerene Acceptors through Side-Chain Engineering at the π -Bridge

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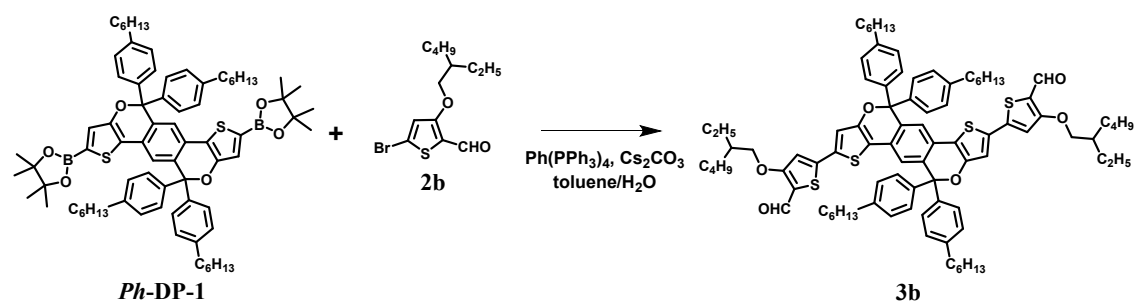
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1. Materials and General Procedures

All commercial chemicals were used without further purification. UV-visible absorption spectra were recorded on a UV-1601pc spectrophotometer. Electrochemical measurements were performed on a CHI 600E Electrochemical Analyzer. Column chromatography was carried out on silica gel (300-400 mesh). Analytical thin-layer chromatography was performed on glass plates of Silica Gel GF-254 with detection by UV. ^1H and ^{13}C NMR spectra were obtained using CDCl_3 as solvent and recorded on a 400 MHz spectrometer. GIWAXS measurements were conducted on a Xenocs-SAXS/WAXS system with X-ray wavelength of 1.5418 Å. The film samples were irradiated at a fixed angle of 0.2° and all film samples were prepared from with *o*-DCB.

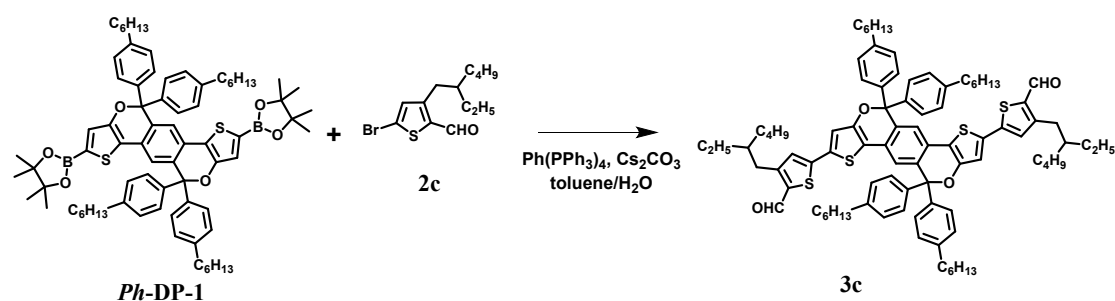
Synthesis of 3b



Ph-DP-1 (247 mg, 0.21 mmol, 1.0 eq), compound **2b** (199 mg, 0.62 mmol, 3.0 eq), Ph(PPh₃)₄ (23 mg), and Cs₂CO₃ (405 mg, 1.24 mmol, 6.0 eq) were added to a 100 mL round-bottom flask. The mixture was deoxygenated with nitrogen for 30 min, then toluene (20 mL) and H₂O (4 mL) was added. The mixture was heated to reflux

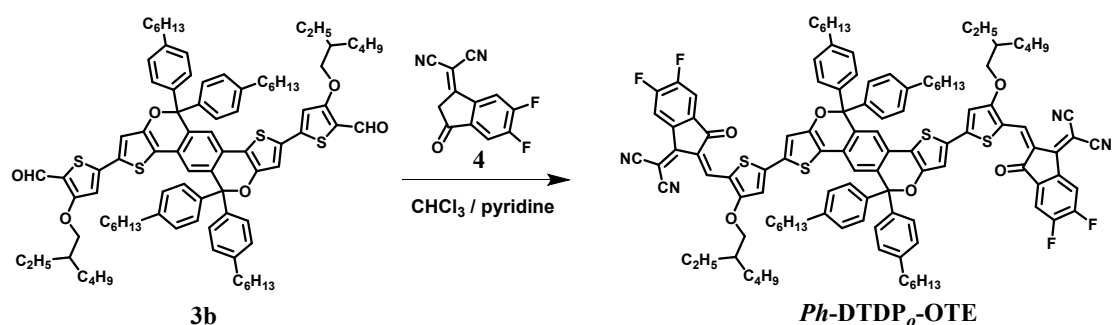
for 24 h. After removal of the solvent, the mixture was extracted with dichloromethane. The crude product was purified by silica gel using hexane/dichloromethane(1:1) as an eluent to give a red solid (194 mg, 66%). ¹H NMR (CDCl₃, 600 MHz): δ 9.92 (s, 2H), 7.14 (m, 16H), 6.99 (s, 2H), 6.77 (s, 2H), 6.53 (s, 2H), 4.01 (d, *J* = 5.4 Hz, 4H), 2.61 (m, 8H), 1.76-1.70 (m, 2H), 1.67-1.38 (m, 16H), 1.37-1.16 (m, 32H), 0.96-0.80 (m, 24H).

Synthesis of 3c



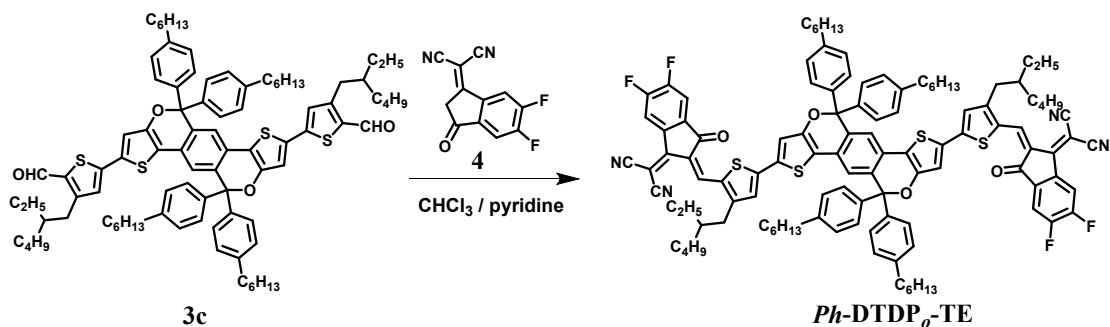
Ph-DP-1 (233 mg, 0.20 mmol, 1.0 eq), compound **2c** (178 mg, 0.59 mmol, 3.0 eq), Ph(PPh₃)₄ (23 mg), and Cs₂CO₃ (382 mg, 1.17 mmol, 6.0 eq) were added to a 100 mL round-bottom flask. The mixture was deoxygenated with nitrogen for 30 min, then toluene (25 mL) and H₂O (5 mL) was added. The mixture was heated to reflux for 24 h. After removal of the solvent, the mixture was extracted with dichloromethane. The crude product was purified by silica gel using hexane/dichloromethane (1:1) as an eluent to give a red solid (192 mg, 71%). ¹H NMR (CDCl₃, 600 MHz): δ 9.93 (s, 2H), 7.14 (m, 16H), 6.98 (s, 2H), 6.91 (s, 2H), 6.52 (s, 2H), 2.78 (d, *J* = 7.2 Hz, 4H), 2.61 (m, 8H), 1.67-1.53 (m, 10H), 1.34-1.20 (m, 40H), 0.91-0.82 (m, 24H).

Synthesis of *Ph*-DTDP_o-OTE



3b (110 mg, 77.7 μ mol, 1.0 eq), **4** (89 mg, 0.39 mmol, 5.0 eq) were added to a 100 mL round-bottom flask. The mixture was deoxygenated with argon for 30 min. Pyridine (0.1 mL) and chloroform (20 mL) was added under argon and then was stirred for 12 h, and then it was poured into methanol (200 mL) and filtered. The filtrate was purified by column chromatography on silica gel using hexane/chloroform (1:1, v/v) as eluent yielding dark solids (109 mg, 76%). ¹H NMR (CDCl₃, 400 MHz): δ 9.08 (s, 2H), 8.45 (m, 2 H), 7.60 (m, 2H), 7.17(m, 18H), 6.77(s, 2H), 6.61(s, 2H), 4.05 (s, 4H), 2.63 (m, 8H), 1.85 (m, 2H), 1.72-1.43 (m, 16H), 1.42-1.20 (m, 32H), 1.02-0.77 (m, 24H). ¹³C NMR (100 MHz, CDCl₃): δ 186.49, 169.59, 158.42, 155.27 (m), 153.44, 152.70 (m), 143.25, 139.73, 136.61 (m), 134.48, 134.47, 134.21 (m), 132.94, 132.64, 128.46, 128.10, 126.89, 122.04, 122.00, 119.28, 117.57, 117.51, 115.02, 114.80, 114.59, 114.43, 112.20, 112.01, 109.27, 88.89, 77.22, 75.61, 67.61, 39.40, 35.68, 31.70, 31.17, 30.03, 29.09, 29.04, 23.45, 23.00, 22.60, 14.12, 14.08, 11.02.

Synthesis of *Ph*-DTDP_o-TE



3c (121 mg, 87.4 μmol , 1.0 eq), **4** (101 mg, 0.44 mmol, 5.0 eq) were added to a 100 mL round-bottom flask. The mixture was deoxygenated with argon for 30 min. Pyridine (0.1 mL) and chloroform (20 mL) was added under argon and then was stirred for 12 h, and then it was poured into methanol (200 mL) and filtered. The filtrate was purified by column chromatography on silica gel using hexane/chloroform (1:1, v/v) as eluent yielding dark solids (129 mg, 82%). ^1H NMR (CDCl_3 , 400 MHz): δ 8.90 (s, 2H), 8.52 (m, 2H), 7.66 (m, 2H), 7.17(m, 18H), 7.08(s, 2H), , 6.61 (s, 2H), 2.84 (d, $J = 7.0$ Hz, 4H), 2.64 (m, 8H), 1.72-1.59 (m, 10H), 1.42-1.17 (m, 40H), 0.94 - 0.80 (m, 24H). ^{13}C NMR (100 MHz, CDCl_3): δ 185.97, 162.00, 159.02, 155.73, 155.58, 153.49, 153.06 (m), 151.58, 143.21, 139.75, 136.49 (m), 134.54 (m), , 132.93, 132.91, 132.07, 128.51, 128.08, 127.03, 126.95, 121.99, 121.57, 120.06, 119.05, 114.86 (m), 114.49, 112.57, 112.38 ,99.99, 89.01, 77.23, 68.97, 41.83, 35.65, 34.54, 32.09, 31.70, 31.15, 29.06, 28.60, 25.44, 22.99, 22.60, 14.08, 10.68.

2. OSCs Fabrication

OSC devices were made with a general configuration of ITO/ZnO/active

layer/MoO₃/Ag. The conductivity of ITO was 15 Ω/sq. The ITO-coated glass substrates were thoroughly cleaned by deionized water, acetone, and isopropanol twice successively at first. After the substrates were dried at 150 °C for 10 minutes, thin layers of sol-gel ZnO (30 nm) were spin-coated on them and then annealed at 200 °C for 20 min in the air. The blend of polymers and small molecule was dissolved in DCB with the polymer concentration of 4 mg mL⁻¹ (with or without additives) and heated at 110 °C at least 1 h to ensure a sufficient dissolution, and then spin-coated onto ZnO modified glass substrates. Followed 8.5nm thick MoO₃ film and 100 nm thick Ag layer were deposited sequentially to complete the inverted device. Six cells were fabricated on one substrate with an effective area of 0.04 cm². Current-voltage characteristics were recorded using an Enli Technology Ltd., Taiwan (SS-F53A) AAA class solar simulator under AM 1.5G with an intensity of 100 mW cm⁻² as the white light source and the intensity was calibrated with a standard single crystal Si photovoltaic cell. The temperature while measuring the *J-V* curves was approximately 25 °C. The *EQE* measurements of PSCs were performed by the solar cell spectral response measurement system QE-R3011 (Enli Technology Ltd., Taiwan), which was calibrated by monocrystalline silicon solar cell in advance.

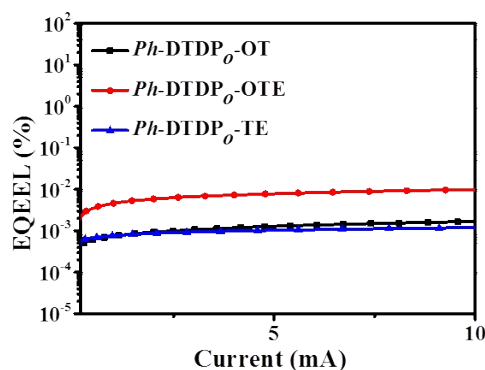


Figure S1. The EQEEL curve of optimized devices of *Ph-DTDP_o-OT*, *Ph-DTDP_o-OTE* and *Ph-DTDP_o-TE*

Table S1. The OSC devices optimization based on ITO/ZnO/active layer/MoO₃/Ag by different weight ratios of PBDB-T to acceptors.

Active layer	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
PBDB-T: <i>Ph-DTDP_o-OT</i>=1:0.8	0.89	13.57	48.96	5.90
PBDB-T: <i>Ph-DTDP_o-OT</i>=1:1	0.89	13.74	49.91	6.13
PBDB-T: <i>Ph-DTDP_o-OT</i>=1:1.2	0.88	11.24	43.26	4.29
PBDB-T: <i>Ph-DTDP_o-OTE</i>=1:0.8	0.90	15.46	55.55	7.73
PBDB-T: <i>Ph-DTDP_o-OTE</i>=1:1	0.91	15.64	59.69	8.45
PBDB-T: <i>Ph-DTDP_o-OTE</i>=1:1.2	0.91	14.39	56.95	7.56
PBDB-T: <i>Ph-DTDP_o-TE</i>=1:0.8	0.85	17.28	64.75	9.50
PBDB-T: <i>Ph-DTDP_o-TE</i>=1:1	0.84	17.94	63.55	9.61
PBDB-T: <i>Ph-DTDP_o-TE</i>=1:1.2	0.84	19.09	56.02	8.97

Table S2. The OSC devices optimization based on ITO/ZnO/active layer/MoO₃/Ag by different additives.

Active layer	additive	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
PBDB-T: <i>Ph-DTDP_o-OT</i>	0.2%1-CN	0.88	14.34	57.72	7.21
PBDB-T: <i>Ph-DTDP_o-OT</i>	0.5%1-CN	0.87	13.74	58.87	7.05
PBDB-T: <i>Ph-DTDP_o-OT</i>	0.7%1-CN	0.87	14.33	54.69	6.77
PBDB-T: <i>Ph-DTDP_o-OT</i>	1%1-CN	0.87	13.32	52.80	6.12
PBDB-T: <i>Ph-DTDP_o-OTE</i>	0.2%1-CN	0.90	16.64	59.24	8.88

PBDB-T: <i>Ph</i> -DTDP _o -OTE	0.5%1-CN	0.90	17.53	62.33	9.81
PBDB-T: <i>Ph</i> -DTDP _o -OTE	0.7%1-CN	0.90	17.41	58.80	9.20
PBDB-T: <i>Ph</i> -DTDP _o -OTE	1%1-CN	0.89	15.91	60.83	8.61
PBDB-T: <i>Ph</i> -DTDP _o -TE	0.2%1-CN	0.84	17.34	62.27	9.04
PBDB-T: <i>Ph</i> -DTDP _o -TE	0.5%1-CN	0.83	17.37	67.96	9.83
PBDB-T: <i>Ph</i> -DTDP _o -TE	0.7%1-CN	0.83	18.56	71.73	10.91
PBDB-T: <i>Ph</i> -DTDP _o -TE	1%1-CN	0.83	17.70	67.83	10.04

Table S3. The OSC devices parameters based on ITO/ZnO/active layer/MoO₃/Ag with 1-CN as additives and different annealing temperatures.

Active layer	T (°C)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
PBDB-T: <i>Ph</i> -DTDP _o -OT	100	0.87	14.15	60.18	7.44
PBDB-T: <i>Ph</i> -DTDP _o -OT	120	0.87	15.00	58.60	7.65
PBDB-T: <i>Ph</i> -DTDP _o -OT	140	0.87	14.86	58.51	7.55
PBDB-T: <i>Ph</i> -DTDP _o -OTE	100	0.89	18.10	63.99	10.30
PBDB-T: <i>Ph</i> -DTDP _o -OTE	120	0.88	18.28	68.57	10.98
PBDB-T: <i>Ph</i> -DTDP _o -OTE	140	0.88	18.34	65.53	10.60
PBDB-T: <i>Ph</i> -DTDP _o -TE	100	0.84	19.68	70.32	11.63
PBDB-T: <i>Ph</i> -DTDP _o -TE	120	0.82	20.83	71.14	12.21
PBDB-T: <i>Ph</i> -DTDP _o -TE	140	0.82	19.72	68.75	11.18

3. Space-Charge Limited Current Measurement

Hole/electron devices with a structure of ITO/PEDOT:PSS/active layer/Au and ITO/ZnO/active layer/Al were fabricated. Dark $J-V$ curves of the hole/electron

devices were measured by the space-charge limited current (SCLC) method. Hole and electron mobilities of devices were calculated according to the Mott-Gurney equation: $J = 9\varepsilon_0\varepsilon_r\mu V^2 / 8d^3$, where J is the space charge limited current, ε_0 is the vacuum permittivity ($\varepsilon_0=8.85\times 10^{-12}$ F/m), ε_r is the permittivity of the active layer ($\varepsilon_r = 3$ F/m), μ is mobility, and d is the thickness of the active layer.

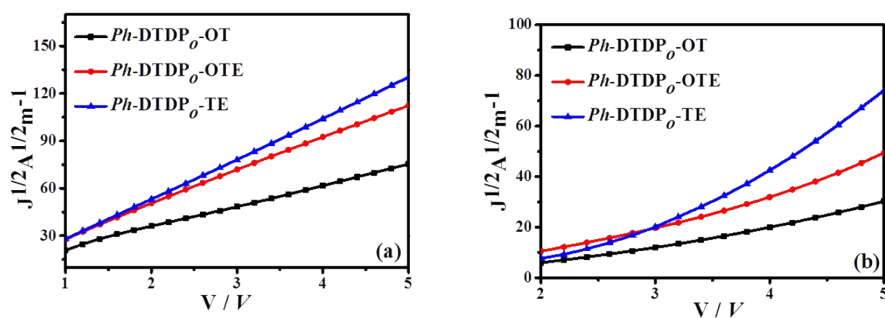


Figure S2. The curves of (a) hole and (b) electron mobility of *Ph-DTDP_o-OT*, *Ph-DTDP_o-O TE* and *Ph-DTDP_o-TE* blend films.