Supporting Information

Experimental Section

1. Materials

2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile(IC-2F) was purchased from Shenzhen Ruixun Optoelectronic Materials Technology Co. Ltd. PM6 was purchased from Solarmer Energy Inc. Other chemicals. Other reagents were purchased from Energy Chemical, Shanghai Titan Scientific Co., Ltd or other merchants and were used without further purification. BTP-0-iPr, BTP-1-iPr and BTP-3-iPr were synthesized. ¹H NMR and ¹³C NMR spectra were characterized by a Bruker AV-400 MHZ nuclear magnetic resonance (NMR) spectrometer, as show in **Figure S1** to **Figure S16**.



Scheme S1. Synthetic procedure of BTP-0-iPr, BTP-1-iPr and BTP-3-iPr

Tributyl(thieno[3,2-b] thiophen-2-yl)stannane (1)

Compound thieno[3,2-b]thiophene(5.001 g, 35.66 mmol) was added into a threeneck flask with ultradry tetrahydrofuran(50 mL) under argon atmosphere. The n-BuLi hexane solution(2.5M, 14.3 mL, 35.66 mmol) was added dropwise from the constant pressure dropping funnel at -78°C and the mixture was stirred for 1 h. Tributyltin chloride(12.6 mL, 46.36 mmol) was added dropwise at -78°C and stirred for 0.5 h. Then the mixture stirred at room temperature overnight. The reaction solution was poured into water to quench, extracted with ethyl acetate. The organic phase was dried with anhydrous sodium sulfate(Na₂SO₄). Compound **1** was obtained by rotary evaporating the organic phase, which was used directly in the next step (colorless oily liquid).

5,6-dinitro-4,7-bis(thieno[3,2-b]thiophen-2-yl)benzo[c][1,2,5]thiadiazole (2)

The compound 1(15.336 g, 35.66 mmol) and 4,7-dibromo-5,6-dinitrobenzo[c][1,2,5] thiadiazole(5.475 g, 14.26 mmol) were added into a three-neck flask with ultradry tetrahydrofuran(80 mL) under argon atmosphere. The reaction was raised to 75°C, and stirred overnight after adding bis(triphenylphosphine)palladium dichloride (400 mg, 0.57 mmol). The solution was cooled to room temperature and spun to dryness. Compound **2** was obtained by suction filtration after petroleum ether was added to beat, which was used directly in the next step (red solid, 6.471 g, 90.3 % yield).

12,13-bis(2-butyloctyl)-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2'',3'':4',5'] thieno [2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole (3)

Compound **2**(6.471 g, 12.88 mmol) and triphenylphosphine(33.782 g, 128.81 mmol) were added into a three-neck flask under argon atmosphere. The reaction was raised to 180 °C, and stirred overnight after adding ultradry *N*-methylpyrrolidone(NMP, 80 mL). After cooled to room temperature, potassium hydroxide(7.226 g, 128.81 mmol), potassium iodide(641 mg, 3.86 mmol), 2-butyl-1-bromooctane(32.102 g, 128.81 mmol) and ultradry NMP (50 mL) were added into the reaction. The mixture was stirred at 90°C overnight under argon atmosphere. The reaction solution was poured into water to extract with dichloromethane. The organic layer was washed with water and dried with Na₂SO₄. Compound **3** was obtained by column chromatography in a silica gel column using petroleum ether/dichloromethane(4:1, v/v) as the eluent (red solid, 5.072 g, 50.8 % yield).

¹H NMR (400 MHz, Chloroform-d) δ 7.42 (q, J = 5.1 Hz, 4H), 4.62 (d, J = 7.8 Hz, 4H), 2.07 (q, J = 6.7 Hz, 2H), 0.96 (ddt, J = 12.6, 8.2, 5.1 Hz, 14H), 0.90 – 0.78 (m, 16H), 0.69 – 0.57 (m, 14H).

2,10-dibromo-12,13-bis(2-butyloctyl)-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]

thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b] indole (4)

Under 0°C, *N*-bromosuccinimide (NBS, 2.910 g, 16.35 mmol) was added to a solution of compound 3(5.072 g, 6.54 mmol) in THF (50 mL) in batches, which reacted at room temperature overnight in the dark. The reaction solution was poured into water to extract with dichloromethane. The organic layer was washed with water and dried with Na₂SO₄. Compound **4** was obtained by column chromatography in a silica gel column using petroleum ether/dichloromethane (4:1, v/v) as the eluent (orange solid, 5.205 g, 85.3 % yield)

¹H NMR (400 MHz, Chloroform-*d*) δ 7.43 (s, 2H), 4.54 (d, J = 7.8 Hz, 4H), 2.00 (p, J = 5.6, 5.2 Hz, 2H), 1.03 – 0.93 (m, 14H), 0.92 – 0.79 (m, 16H), 0.70 – 0.61 (m, 14H). 3,9-dibromo-12,13-bis(2-butyloctyl)-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno [2'',3'':4', 5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-dicarbaldehyde (5)

Under argon atmosphere, Lithium diisopropylamide, LDA(2M, 13.95 mL, 27.9 mmol) was added dropwise into a solution of compound 4(5.205 g, 5.58 mmol) in dry THF (60mL) at -78 °C. The mixture was stirred at low temperature for 1 h, then stirred at room temperature overnight. Anhydrous *N*,*N*-dimethylformamide (DMF, 15 mL) was directly added at 0 °C and the reaction was stirred at room temperature for 1 hour. The reaction solution was poured into water to extract with dichloromethane. The organic layer was washed with water and dried with Na₂SO₄. Compound **5** was obtained by column chromatography in a silica gel column using petroleum ether/dichloromethane (2:1, v/v) as the eluent (orange solid, 3.716 g, 69.3 % yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 10.09 (s, 2H), 4.62 (q, *J* = 7.0 Hz, 4H), 2.04 – 1.97 (m, 2H), 1.10 – 0.95 (m, 14H), 0.95 – 0.80 (m, 16H), 0.69 – 0.61 (m, 14H). **12,13-bis(2-butyloctyl)-3,9-bis(4-isopropylphenyl)-12,13-dihydro-[1,2,5]** thiadiazolo[3,4-e] thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno [2',3':4,5]thieno[3,2-b]indole-2,10-dicarbaldehyde (6)

Compound **5**(288 mg, 0.3 mmol), 4-isopropylphenylboronic acid (295 mg, 1.8 mmol) and potassium carbonate (332 mg, 2.4 mmol) were added into a three-neck flask under argon atmosphere. After adding tetrakis(triphenylphosphine)palladium, $Pd(PPh_3)_4$, (34.7 mg, 0.03 mmol) and deoxygenated toluene: ethanol: water(18 mL: 3 mL: 3 mL) solvent, the mixture heated to 100 °C and reacted overnight. The reaction solution was poured into water to extract with dichloromethane. The organic layer was washed with

water and dried with Na₂SO₄. Compound **6** was obtained by column chromatography in a silica gel column using petroleum ether/dichloromethane (3:1, v/v) as the eluent (orange solid, 292 mg, 91.2 % yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 9.99 (s, 2H), 7.72 – 7.68 (m, 4H), 7.49 – 7.44 (m, 4H), 4.74 – 4.62 (m, 4H), 3.12 – 3.00 (m, 2H), 2.10 (d, *J* = 6.1 Hz, 2H), 1.36 (d, *J* = 6.9 Hz, 12H), 1.17 – 0.97 (m, 14H), 0.97 – 0.79 (m, 16H), 0.71 – 0.60 (m, 14H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 184.09, 150.91, 147.50, 145.69, 143.09, 137.20, 136.92, 136.90, 132.95, 132.93, 129.70, 129.49, 129.16, 128.02, 127.99, 127.47, 112.55, 55.43, 39.01, 34.10, 31.53, 30.46, 30.31, 30.12, 29.35, 29.32, 28.04, 27.86, 25.29, 25.08, 23.88, 22.79, 22.74, 22.46, 22.44, 13.94, 13.92, 13.75, 13.71. **BTP-1-iPr**

Compound **6**(85.4 mg, 0.08 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1Hinden-1-ylidene)malononitrile(73.7 mg, 0.32 mmol) were dissolved in chloroform(12 mL) under argon atmosphere. Pyridine (1.5 mL) was added. After stirring at 65 °C for 4.5 h, the mixture was cooled to room temperature and pour the reaction solution into methanol (200 mL). The solid obtained by filtration was extracted with methanol (16 h), dichloromethane: n-hexane=1:20 (6 h), and then dichloromethane was used to collect the crude product. **BTP-1-iPr** was obtained by column chromatography in a silica gel column using petroleum ether/dichloromethane (10:13, v/v) as the eluent (dark blue solid, 98.5 mg, 82.6 % yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.83 (s, 2H), 8.52 (dd, J = 10.0, 6.4 Hz, 2H), 7.71 (t, J = 7.5 Hz, 2H), 7.59 (d, J = 6.2 Hz, 4H), 7.50 (d, J = 8.2 Hz, 4H), 4.80 (d, J = 6.8 Hz, 4H), 3.08 (p, J = 6.9 Hz, 2H), 2.17 (s, 2H), 1.38 (d, J = 6.9 Hz, 12H), 1.24 – 1.03 (m, 14H), 1.03 – 0.86 (m, 16H), 0.76 – 0.60 (m, 14H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 185.82, 158.65, 155.67, 153.06, 152.02, 151.83, 147.53, 144.94, 138.67, 137.66, 136.78, 136.70, 134.94, 134.54, 134.10, 133.47, 131.67, 130.21, 129.86, 127.93, 121.16, 114.92, 114.70, 114.66, 113.61, 113.48, 112.57, 112.39, 69.62, 55.78, 39.32, 34.26, 31.62, 30.64, 30.56, 30.51, 30.41, 29.46, 29.42, 28.19, 27.98, 25.48, 25.24, 23.90, 22.88, 22.83, 22.49, 22.46, 14.01, 13.81, 13.76.

ESI-MS calcd. m/z 1490.4787 for $[C_{86}H_{78}F_4N_8O_2S_5]^+$, found 1491.5074.

12,13-bis(2-butyloctyl)-3,9-bis(2,4,6-triisopropylphenyl)-12,13-dihydro-[1,2,5] thiadiazolo [3,4-e]thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno [2',3':4,5]thieno[3,2-b]indole-2,10-dicarbaldehyde (7)

Compound 5(288 mg, 0.3 mmol), 2,4,6-triisopropylphenylboronic acid(447 mg, 1.8

mmol) and sodium tert-butoxide(202 mg, 2.1 mmol) were added into a three-neck flask under argon atmosphere. After adding Tetrakis(triphenylphosphine)palladium, $Pd(PPh_3)_4$ (174 mg, 0.15 mmol) and the mixed solvent of ethylene glycol dimethyl ether/tert-butanol (25 mL:10 mL), the mixture heated to 90 °C and reacted for 48 h. The reaction solution was poured into water to extract with dichloromethane. The organic layer was washed with water and dried with Na₂SO₄. Compound **7** was obtained by column chromatography in a silica gel column using petroleum ether/dichloromethane (3:1, v/v) as the eluent (orange solid, 298 mg, 80.3 % yield)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.58 (s, 2H), 7.16 (s, 4H), 4.75 – 4.64 (m, 4H), 3.01 (h, *J* = 6.9 Hz, 2H), 2.68 – 2.58 (m, 4H), 2.18 (dd, *J* = 12.4, 6.0 Hz, 2H), 1.35 (d, *J* = 6.9 Hz, 12H), 1.14 (ddd, *J* = 8.4, 6.9, 3.0 Hz, 28H), 1.04 – 0.95 (m, 16H), 0.93 – 0.81 (m, 12H), 0.73 (td, *J* = 7.1, 3.2 Hz, 6H), 0.63 (q, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 183.64, 150.56, 147.99, 147.46, 145.78, 144.98, 138.29, 136.95, 132.63, 132.61, 128.83, 127.88, 127.86, 124.83, 121.46, 112.77, 55.39, 38.80, 34.45, 31.51, 31.28, 30.55, 30.50, 30.19, 30.12, 29.70, 29.67, 29.28, 27.60, 27.51, 26.92, 25.59, 25.52, 24.68, 24.58, 24.04, 22.68, 22.43, 13.96, 13.66.

BTP-3-iPr

Compound 7(98.9 mg, 0.08 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1Hinden-1-ylidene)malononitrile(73.7 mg, 0.32 mmol) were dissolved in chloroform(12 mL) under argon atmosphere. Pyridine(1.5 mL) was added. After stirring at 65 °C for 5.5 h, the mixture was cooled to room temperature and pour the reaction solution into methanol(200 mL). The solid obtained by filtration was extracted with methanol (16 h), n-hexane (6 h), and then dichloromethane was used to collect the crude product. **BTP-3-iPr** was obtained by column chromatography in a silica gel column using petroleum ether/dichloromethane (4:3, v/v) as the eluent (dark blue solid, 98.5 mg, 82.6 % yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.68 (s, 2H), 8.58 – 8.49 (m, 2H), 7.72 (t, *J* = 7.5 Hz, 2H), 7.19 (s, 4H), 4.83 (d, *J* = 8.0 Hz, 4H), 3.00 (m, *J* = 7.1 Hz, 2H), 2.47 (m, *J* = 7.2 Hz, 4H), 2.30 – 2.21 (m, 2H), 1.35 (d, *J* = 6.9 Hz, 12H), 1.03 (dt, *J* = 78.3, 7.7 Hz, 54H), 0.69 (dt, *J* = 25.2, 7.1 Hz, 14H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 186.67, 157.03, 155.65, 153.21, 153.08, 152.61, 151.43, 147.49, 147.11, 146.73, 137.90, 137.34, 136.87, 135.29, 135.05, 134.60, 134.55, 133.70, 133.66, 131.20, 125.11, 122.33, 120.41, 115.12, 114.90, 114.68, 113.86, 112.72, 112.45, 112.26, 69.66, 55.78, 39.07, 34.65, 31.59, 31.55, 30.73, 30.64, 30.30, 30.18, 29.36, 27.67, 27.55, 25.76, 25.66, 24.86, 24.71, 24.68, 24.01, 22.78, 22.45, 14.01,

13.74, 13.71.

ESI-MS calcd. m/z 1659.6699 for $[C_{98}H_{102}F_4N_8O_2S_5]^+$, found 1660.6974.

12,13-bis(2-butyloctyl)-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2'',3'':4',5'] thieno [2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10dicarbaldehyde (8)

Compound **3**(233 mg, 0.3 mmol) in ultradry DMF(20 mL) was added into a threeneck flask under argon atmosphere. After adding phosphorus oxychloride(0.82 mL, 9 mmol) dropwise at 0°C, the mixture heated to 90 °C and reacted overnight. The reaction solution was poured into water to extract with dichloromethane. The organic layer was washed with water and dried with Na₂SO₄. Compound **8** was obtained by column chromatography in a silica gel column using petroleum ether/dichloromethane (2:1, v/v) as the eluent (orange solid, 213 mg, 85.6 % yield)

¹H NMR (400 MHz, Chloroform-*d*) δ 10.03 (s, 2H), 8.10 (s, 2H), 4.71 – 4.59 (m, 4H), 2.02 (p, *J* = 6.7 Hz, 2H), 0.95 (dddd, *J* = 15.9, 11.9, 12.2, 7.2 Hz, 30H), 0.69 – 0.58 (m, 14H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 182.69, 147.48, 143.10, 141.57, 136.54, 133.14, 130.91, 130.69, 128.68, 128.65, 112.58, 55.30, 38.97, 31.47, 30.35, 30.26, 30.23, 30.12, 29.28, 29.26, 27.92, 27.77, 25.27, 25.10, 22.70, 22.67, 22.41, 22.39, 13.89, 13.68, 13.65.

BTP-0-iPr

Compound **8**(66.5 mg, 0.08 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1Hinden-1-ylidene)malononitrile(73.7 mg, 0.32 mmol) were dissolved in chloroform (12 mL) under argon atmosphere. Pyridine(1.5 mL) was added. After stirring at 65 °C for 4 h, the mixture was cooled to room temperature and pour the reaction solution into methanol(200 mL). The solid obtained by filtration was extracted with methanol (16 h), dichloromethane: n-hexane=1:8 (6 h), and then dichloromethane was used to collect the crude product. **BTP-0-iPr** was obtained by column chromatography in a silica gel column using petroleum ether/dichloromethane (1:3, v/v) as the eluent (dark blue solid, 70.1 mg, 69.8 % yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 9.02 (s, 2H), 8.58 (dd, J = 9.9, 6.4 Hz, 2H), 8.25 (s, 2H), 7.72 (t, J = 7.4 Hz, 2H), 4.83 – 4.71 (m, 4H), 2.10 (d, J = 6.5 Hz, 2H), 1.15 – 0.85 (m, 30H), 0.67 (dt, J = 16.6, 7.4 Hz, 14H).

¹³C NMR (151 MHz, Chloroform-*d*) δ 186.23, 158.18, 155.58, 153.81, 153.74, 147.60, 143.66, 138.50, 138.35, 138.23, 138.09, 137.59, 136.90, 134.62, 134.29,

132.20, 121.61, 115.29, 115.15, 114.37, 114.33, 113.78, 112.83, 112.71, 77.37, 77.16, 76.95, 70.09, 55.77, 39.30, 31.69, 30.61, 30.57, 30.50, 30.45, 29.85, 29.52, 29.49, 28.19, 28.01, 25.56, 25.37, 22.95, 22.90, 22.60, 22.57, 14.12, 13.92, 13.88.
ESI-MS calcd. *m*/*z* 1254.3222 for[C₆₈H₅₈F₄N₈O₂S₅]⁺, found 1255.3441.

2. Thermogravimetric Analyzer (TGA)

Under N₂ atmosphere and 10 °C/min, BTP-0-iPr, BTP-1-iPr and BTP-3-iPr were tested TGA/STA8000-FTIR-GCMS-ATD (PerkinElmer), as show in **Figure S17**.

3. Electronic energy level measurement by cyclic voltammetry

Cyclic voltammetry measurements were performed on a CHI660E electrochemical workstation, with a glassy carbon electrode as the working electrode, platinum wire as the counter electrode, Ag/AgCl as the reference electrode, and ferrocene/ferrocene (Fc/Fc+) pair as the internal Reference, 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile. According to the cyclic voltammetry curve of the material (**Figure S18**), the oxidation potential (E_{onset, ox}) and reduction potential (E_{onset,red}) of each material can be known by making a tangent line. HOMO/LUMO is calculated by the formula: $E_{HOMO/LUMO}$ =-e[4.8- $E_{1/2}$,Fc/Fc++Eonset,ox/E_{onset,red}]

4. Device fabrications and Characterization

Device preparation: The battery adopts a glass sheet/ITO/PEDOT:PSS/Acceptors: PM6/PDINN/Ag device structure. The ITO glass was ultrasonically cleaned twice with deionized water and isopropyl alcohol for about 15 minutes each time. After blowing dry with high-purity nitrogen, the ITO glass was placed in a UV-ozone cleaning machine and continued cleaning for 25 minutes. Subsequently, a thin layer of PEDOT:PSS film was coated on the cleaned ITO glass sheet by spin coating at a rotation speed of 5000 rpm for 30 s, and then heat the ITO at 150°C for 15 minutes in atmospheric atmosphere. Next, the active layer (16 mg/mL, donor-acceptor mass ratio 1:1.2, 0.5 vol% chloronaphthalene) was spin-coat on the PEDOT: PSS layer in a glove box (nitrogen atmosphere), and rotate at 3000 rpm for 30 s. The blend film was then thermally annealed at 100 °C for 10 min. After cooling to room temperature, the layer of PDINN film (1 mg/mL, rotated at 3000 rpm for 30 s) was spin-coated on the active layer. Finally, under a vacuum of 1.5×10^{-4} Pa, a layer of Ag electrode was evaporated on the top of the battery with a thickness of about 100 nm. The area is 4.84 mm².

5. Exciton dissociation and recombination

The photocurrent density (J_{ph}) under different effective voltage (V_{eff}) for the OSCs were measured. Among them, J_{ph} = bright state current density (J_{light}) - dark state current density (J_{dark}) . When $J_{ph} = 0$, the voltage is V_0 , $V_{eff} = V_0$ - external bias voltage (V_{bias}) . Exciton dissociation efficiency: $P_{diss} = J_{sc}/J_{sat}$, charge collection efficiency: $P_{coll} = J_{max}/J_{sat}$. when $V_{eff}=0$, the current is saturation photocurrent (J_{sat}) , and the J_{max} at the maximum power point.

Active layer	P _{diss} (%)	P_{coll} (%)
PM6: BTP-0-iPr	98.10	87.16
PM6: BTP-1-iPr	98.30	89.77
PM6: BTP-3-iPr	96.83	82.77

Table S1 Mobility data based on BTP-0-iPr/BTP-1-iPr/BTP-3-iPr:PM6 OSCs devices

6. Hole mobility and electron mobility measurements

The test device structure of μ_h is ITO/PEDOT:PSS/active layer/MoO₃/Ag, and the test device structure of μ_e is ITO/ZnO/active layer/PFN-Br/Ag. The mobility of holes and electrons can be calculated based on the space charge limited current model (SCLC). MOTT-Gurney formula: $J = 9\epsilon_0\epsilon_r\mu V^2/8L^3$, where J is the current measured under dark conditions for pure hole and pure electron devices, μ is the mobility, ϵ_0 is the vacuum dielectric constant value of 8.85 C·V⁻¹·s⁻¹, and ϵ_r is the relative dielectric constant (for organic substances and polymers, ϵ_r is assumed to be 3.0), L is the thickness of the active layer and V is the external voltage of the device.

-			
Active layer	$\mu_{\rm h}({\rm cm}^2{ m V}^{-1}{ m S}^{-1})$	$\mu_{\rm e} ({\rm cm}^2 {\rm V}^{-1} {\rm S}^{-1})$	$\mu_{ m h}/\mu_{ m e}$
PM6: BTP-0-iPr	9.251×10 ⁻⁵	1.018×10 ⁻⁴	0.908
PM6: BTP-1-iPr	9.439×10 ⁻⁵	9.321×10 ⁻⁵	1.013
PM6: BTP-3-iPr	2.307×10 ⁻⁵	2.002×10 ⁻⁵	1.152

 Table S2 Mobility data based on BTP-0-iPr/BTP-1-iPr/BTP-3-iPr:PM6 OSCs devices

7. GIWAXS, AFM and TEM measurements

The XRD/GIXRD/GIWAXS/XRR data were obtained at 1W1A Diffuse X-ray Scattering Station, Beijing Synchrotron Radiation Facility (BSRF-1W1A). The morphologies of the PM6/acceptor blend films were investigated by atomic force microscopy (AFM, Agilent Technologies, 5500 AFM/SPM System, USA) in contacting mode with a 5 µm scanner. Transmission electron microscopy (TEM) measurements were performed in a Tecnai G2 F20 S-TWIN (American FEI Corporation). Samples for

the TEM measurements were prepared as following: The active layer films were spincasted on ITO/PEDOT:PSS substrates, and the substrates with active layers were submerged in deionized water to make the active layers floats onto the air-water interface. Then, the floated films were picked upon an unsupported 200 mesh copper grids for the TEM measurements.

Films	Out of plane			
	Location (Å ⁻¹)	d-spacing ^a (Å)	FWHM (Å ⁻¹)	CCL ^b (Å)
PM6: BTP-0-iPr	1.710	3.67	0.470	12.03
PM6: BTP-1-iPr	1.714	3.66	0.418	13.53
PM6: BTP-3-iPr	1.602	3.92	0.481	11.76

 Table S3 GIWAXS data of the PM6: BTP-0-iPr, PM6: BTP-1-iPr, PM6: BTP-3-iPr blend films

^aObtained using the equation of $d = 2\pi/q$, in which q is the corresponding x-coordinate of the diffraction peak. ^bCalculated using the equation: CCL= $2\pi K/w$, in which w is the full-width-at-half-maximum and K is a form factor (0.9 here).







Figure S2. ¹H NMR spectrum of compound 6 in CDCl₃.



Figure S4. ¹H NMR spectrum of BTP-1-iPr in CDCl₃.



Figure S5. ¹³C NMR spectrum of BTP-1-iPr in CDCl₃.









Figure S8. ¹³C NMR spectrum of compound 7 in CDCl₃.







Figure S10. ¹³C NMR spectrum of BTP-3-iPr in CDCl₃.







Figure S14. ¹H NMR spectrum of BTP-0-iPr in CDCl₃.



Figure S15. ¹³C NMR spectrum of BTP-0-iPr in CDCl₃.





Figure S17. TGA curves of BTP-0-iPr, BTP-1-iPr, BTP-3-iPr with a heating rate of 10 °C/min.



Figure S18. The C-V curves of BTP-0-iPr, BTP-1-iPr, BTP-3-iPr and PM6 in solid state.



Figure S19. (a) J_{sc}-P_{light}, (b) V_{oc}-P_{light} for BTP-0-iPr/BTP-1-iPr/BTP-3-iPr:PM6 devices.



Figure S20. (a) (b) (c)AFM height images (2 μ m × 2 μ m). (d) (e) (f) AFM phase images. (g) (h) (i) TEM images (1 μ m × 1 μ m).



Figure S21. BTP-3-iPr single crystal processing diagram

Compound	BTP-3-iPr	
Moiety formula	$C_{98}H_{102}F_4N_8O_2S_5$	
Formula weight	1660.18	
Temperature (K)	193	
Volume (Å ³)	4784.7(15)	
Space group	P-1	
Crystal system	Triclinic	
a (Å)	8.9288(17)	
b (Å)	22.308(4)	
c (Å)	24.351(4)	
α (°)	85.219(6)	
β (°)	82.075(7)	
γ (°)	87.480(7)	
Z	2	
ρ (g cm ⁻³)	1.152	
Mu (mm ⁻¹)	1.031	
F(000)	1756.0	
h, k, l_{\max}	10, 26, 28	
N_{ref}	16913	
T_{min}, T_{max}	0.884, 0.911	
Data completeness	0.989	
Theta(max)	52.979	
R(reflections)	0.1464(6769)	
WR2 (reflections)	0.3547(16726)	
S	1.225	
N _{par}	1095	

Table S4 Single crystal data summary