Supporting information

Enhancing photovoltaic performance by modulating fractal dimensions of non-fullerene acceptors

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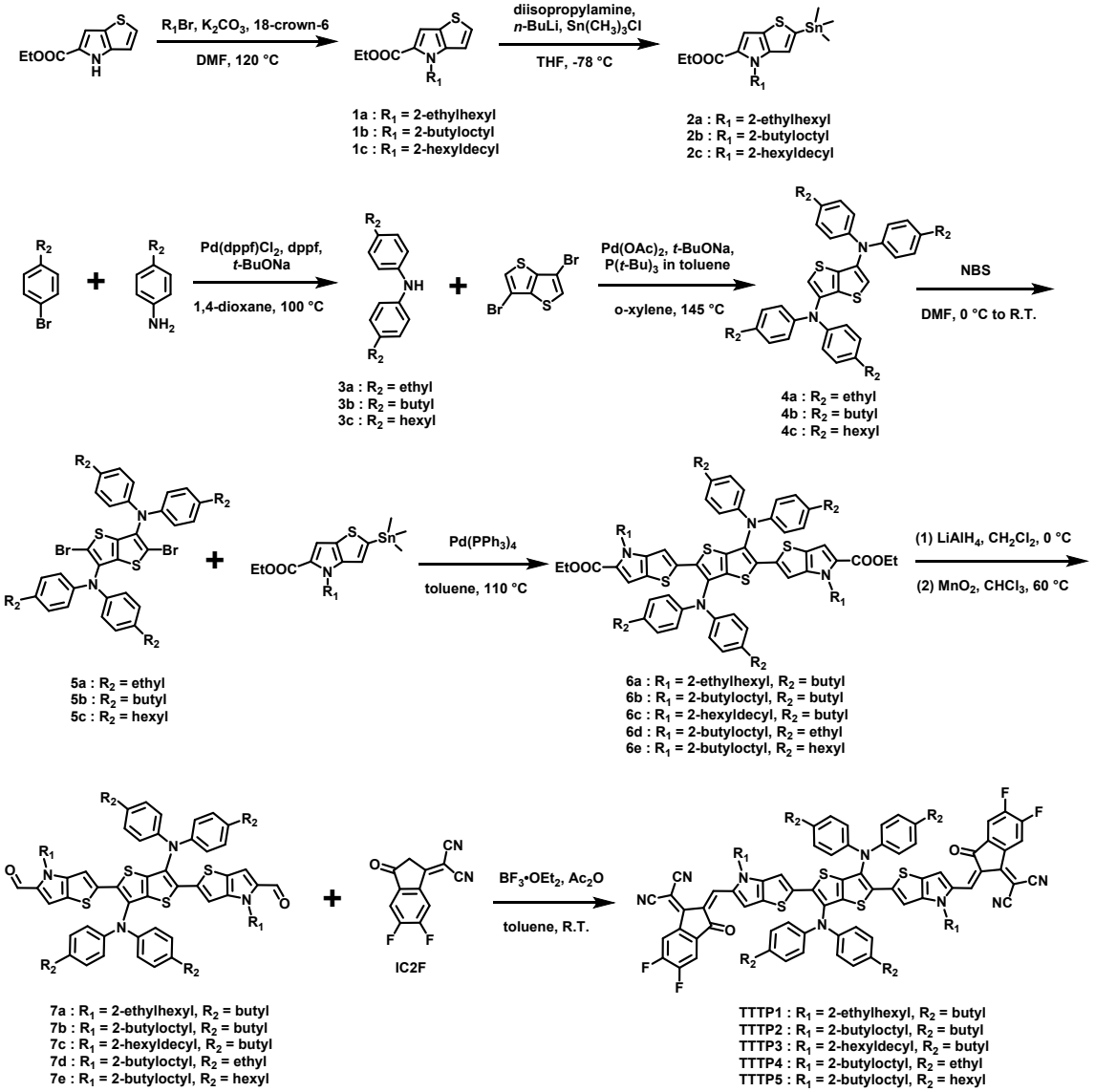
Materials and synthesis

Unless stated otherwise, all the solvents and chemical reagents used were obtained commercially and were used without further purification. Toluene and tetrahydrofuran (THF) were distilled from sodium benzophenone under argon prior to use. 4H-thieno[3,2-*b*]pyrrole-5-carboxylate was purchased from Bide Pharmatech Ltd. 3-(1,1-dicyanomethylene)-5,6-difluoro-1-indanone (IC2F) was synthesized according to our previous work.[S1] PBDB-T and PDINN were purchased from Solarmer Inc.



Scheme 1. Synthetic routes of the TTTP-series acceptors.

Synthesis of compound ***1a***

To a dry three-necked round bottom flask was added 4H-thieno[3,2-*b*]pyrrole-5-carboxylate (0.78 g, 4.0 mmol), K_2CO_3 (1.16 g, 8.4 mmol), 18-crown-6 (53 mg, 0.20 mmol) and distilled *N*,*N*-dimethylformamide (10 mL). The mixture was deoxygenated with argon for 20 min and stirred at 100 °C for 2 hours. 1-bromo-2-ethylhexane (1.62 g, 8.40 mmol) was added dropwise and stirred overnight at 120 °C. After cooling to room temperature, the mixture was quenched with deionized water (50 mL), extracted with ethyl acetate (50 mL × 3) and dried with anhydrous Na_2SO_4. After filtering, the solvent was then removed under reduced pressure, pure compound was obtained by column chromatography on silica gel using petroleum ether: ethyl acetate (100:1, v/v) as the eluent yielding colorless oil (1.20 g, 98%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30 (d, J = 5.4 Hz, 1H), 7.23 (s, 1H), 6.92 (d, J = 5.4 Hz, 1H), 4.41 (dd, J = 7.5, 3.5 Hz, 2H), 4.35 (q, J = 7.1 Hz, 2H), 1.98–1.91 (m, 1H), 1.40 (t, J = 7.1 Hz, 3H), 1.34–1.24 (m, 8H), 0.91–0.87 (m, 6H). MS (ESI): 307.2.

Synthesis of compound ***1b***

To a dry three-necked round bottom flask was added 4H-thieno[3,2-*b*]pyrrole-5-carboxylate (0.78 g, 4.0 mmol), K_2CO_3 (1.16 g, 8.4 mmol), 18-crown-6 (53 mg, 0.20 mmol) and distilled *N*,*N*-dimethylformamide (10 mL). The mixture was deoxygenated with argon for 20 min and stirred at 100 °C for 2 hours. 1-bromo-2-butyloctane (2.10 g, 8.40 mmol) was added dropwise and stirred overnight at 120 °C. After cooling to room temperature, the mixture was quenched with deionized water (50 mL), extracted with ethyl acetate (50 mL × 3) and dried with anhydrous Na_2SO_4. After filtering, the solvent was then removed under reduced pressure, pure compound was obtained by column chromatography on silica gel using petroleum ether: ethyl acetate (100:1, v/v) as the eluent yielding colorless oil (1.41 g, 97%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34 (d, J = 5.4 Hz, 1H), 7.26 (s, 1H), 6.95 (d, J = 5.4 Hz, 1H), 4.44 (d, J = 7.6 Hz, 2H), 4.38 (q, J = 7.1 Hz, 2H), 2.06–1.99 (m, 1H), 1.43 (t, J = 7.1 Hz, 3H), 1.34–1.23 (m, 16H), 0.94–0.89 (m, 6H). MS (ESI): 363.2.

*Synthesis of compound **1c***

To a dry three-necked round bottom flask was added 4H-thieno[3,2-*b*]pyrrole-5-carboxylate (0.78 g, 4.0 mmol), K_2CO_3 (1.16 g, 8.4 mmol), 18-crown-6 (53 mg, 0.20 mmol) and distilled *N*,*N*-dimethylformamide (10 mL). The mixture was deoxygenated with argon for 20 min and stirred at 100 °C for 2 hours. 1-bromo-2-hexyldecane (2.56 g, 8.40 mmol) was added dropwise and stirred overnight at 120 °C. After cooling to room temperature, the mixture was quenched with deionized water (50 mL), extracted with ethyl acetate (50 mL × 3) and dried with anhydrous Na_2SO_4. After filtering, the solvent was then removed under reduced pressure, pure compound was obtained by column chromatography on silica gel using petroleum ether: ethyl acetate (100:1, v/v) as the eluent yielding colorless oil (1.60 g, 96%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 (d, J = 5.4 Hz, 1H), 7.23 (s, 1H), 6.92 (d, J = 5.4 Hz, 1H), 4.41 (d, J = 7.6 Hz, 2H), 4.34 (q, J = 7.1 Hz, 2H), 2.02–1.96 (m, 1H), 1.40 (t, J = 7.1 Hz, 3H), 1.29–1.19 (m, 24H), 0.92–0.88 (m, 6H). MS (ESI): 419.2.

*Synthesis of compound **2a***

To a solution of diisopropyl amine (405 mg, 4.0 mmol) in 10 mL dry THF at −78 °C was added *n*-BuLi (2.5 M in hexane, 1.6 mL, 4.0 mmol) dropwise under argon to yield lithium diisopropylamide (LDA). A solution of **1a** (1.00 g, 3.26 mmol) in 10 mL dry THF was then added dropwise over 20 min and the resulting solution was stirred at −78 °C for 1 h. To the mixture was added dropwise trimethyltin chloride (1.0 M in hexane, 4.0 mL, 4.0 mmol) and stirred for 4 hours at −78 °C. The reaction mixture was quenched with H_2O. The compound was extracted with hexane (50 mL × 3) and after dying with anhydrous Na_2SO_4 and filtered, the solvent was then removed under reduced pressure. The crude product **2a** was dissolved in 10 mL dry toluene and used without further purification in the next step. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.23 (s, 1H), 6.92 (s, 1H), 4.41 (dd, J = 7.5, 3.5 Hz, 2H), 4.35 (q, J = 7.1 Hz, 2H), 1.98–1.91 (m, 1H), 1.40 (t, J = 7.1 Hz, 3H), 1.34–1.24 (m, 8H), 0.91–0.87 (m, 6H), 0.37 (m, 9H).

*Synthesis of compound **2b***

To a solution of diisopropyl amine (405 mg, 4.0 mmol) in 10 mL dry THF at −78 °C was added *n*-BuLi (2.5 M in hexane, 1.6 mL, 4.0 mmol) dropwise under argon to yield lithium diisopropylamide (LDA). A solution of **1b** (1.20 g, 3.30 mmol) in 10 mL dry THF was then added dropwise over 20 min and the resulting solution was stirred at −78 °C for 1 h. To the mixture was added dropwise trimethyltin chloride (1.0 M in hexane, 4.0 mL, 4.0 mmol) and stirred for 4 hours at −78 °C. The reaction mixture was quenched with H_2O. The compound was extracted with hexane (50 mL × 3) and after dying with anhydrous Na_2SO_4 and filtered, the solvent was then removed under reduced pressure. The crude product **2b** was used dissolved in 10 mL dry toluene and without further purification in the next step. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.23 (s, 1H), 6.92 (s, 1H), 4.41 (dd, J = 7.5, 3.5 Hz, 2H), 4.35 (q, J = 7.1 Hz, 2H), 2.06–1.99 (m, 1H), 1.43 (t, J = 7.1 Hz, 3H), 1.34–1.23 (m, 16H), 0.94–0.89 (m, 6H), 0.37 (m, 9H).

*Synthesis of compound **2c***

To a solution of diisopropyl amine (405 mg, 4.0 mmol) in 10 mL dry THF at −78 °C was added *n*-BuLi (2.5 M in hexane, 1.6 mL, 4.0 mmol) dropwise under argon to yield lithium diisopropylamide (LDA). A solution of **1c** (1.40 g, 3.33 mmol) in 10 mL dry THF was then added dropwise over 20 min and the resulting solution was stirred at −78 °C for 1 h. To the mixture was added dropwise trimethyltin chloride (1.0 M in hexane, 4.0 mL, 4.0 mmol) and stirred for 4 hours at −78 °C. The reaction mixture was quenched with H_2O. The compound was extracted with hexane (50 mL × 3) and after dying with anhydrous Na_2SO_4 and filtered, the solvent was then removed under reduced pressure. The crude product **2c** was dissolved in 10 mL dry toluene and used without further purification in the next step. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.23 (s, 1H), 6.92 (s, 1H), 4.41 (dd, J = 7.5, 3.5 Hz, 2H), 4.35 (q, J = 7.1 Hz, 2H), 2.03–1.97 (m, 1H), 1.42 (t, J = 7.1 Hz, 3H), 1.29–1.21 (m, 24H), 0.94–0.89 (m, 6H), 0.38 (m, 9H).

*Synthesis of compound **3a***

To a dry three-necked round bottom flask was added 1-bromo-4-ethylbenzene (1.00 g, 5.40 mmol), 4-ethylaniline (0.79 g, 6.48 mmol), *t*-BuONa (1.04 g, 10.8 mmol), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) ($PdCl_2$(dppf)) (198 mg, 0.27 mmol), 1,1'-bis(diphenylphosphino)ferrocene (dppf) (0.60 g, 1.08 mmol), and 1,4-dioxane (15 mL). The mixture was deoxygenated with argon for 30 min and stirred at 100 °C for 24 hours. After cooling, the reaction mixture was quenched with water and extracted with CH_2Cl_2 (50 mL × 3). The organic layer was dried over anhydrous Na_2SO_4 and filtered. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate (20:1, v/v) as the eluent yielding colorless oil (1.0 g, 85%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.07 (d, J = 6Hz, 4H), 7.00 (d, J = 6Hz, 4H), 2.57–2.54 (m, 4H), 0.95–0.92 (m, 6H).

*Synthesis of compound **3b***

To a dry three-necked round bottom flask was added 1-bromo-4-butylbenzene (1.00 g, 4.70 mmol), 4-butylaniline (0.85 g, 5.63 mmol), *t*-BuONa (0.91 g, 9.4 mmol), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) ($PdCl_2$(dppf)) (176 mg, 0.24 mmol), 1,1'-bis(diphenylphosphino)ferrocene (dppf) (0.53 g, 0.96 mmol), and 1,4-dioxane (15 mL). The mixture was deoxygenated with argon for 30 min and stirred at 100 °C for 24 hours. After cooling, the reaction mixture was quenched with water and extracted with CH_2Cl_2 (50 mL × 3). The organic layer was dried over anhydrous Na_2SO_4 and filtered. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate (20:1, v/v) as the eluent yielding colorless oil (1.1 g, 83%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.07 (d, J = 6Hz, 4H), 7.00 (d, J = 6Hz, 4H), 2.57–2.54 (m, 4H), 1.61–1.56 (m, 4H), 1.38–1.35 (m, 4H), 0.95–0.92 (m, 6H).

*Synthesis of compound **3c***

To a dry three-necked round bottom flask was added 1-bromo-4-hexylbenzene (1.00 g, 4.15 mmol), 4-hexylaniline (0.88 g, 4.98 mmol), *t*-BuONa (0.80 g, 8.3 mmol), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) ($PdCl_2$(dppf)) (154 mg, 0.21 mmol), 1,1'-bis(diphenylphosphino)ferrocene (dppf) (0.46 g, 0.84 mmol), and 1,4-dioxane (15 mL). The mixture was deoxygenated with argon for 30 min and stirred at 100 °C for 24 hours. After cooling, the reaction mixture was quenched with water and extracted with CH_2Cl_2 (50 mL × 3). The organic layer was dried over anhydrous Na_2SO_4 and filtered. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate (20:1, v/v) as the eluent yielding colorless oil (1.1 g, 79%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.09 (d, J = 6Hz, 4H), 7.02 (d, J = 6Hz, 4H), 2.59–2.56 (m, 4H), 1.63–1.58 (m, 8H), 1.39–1.36 (m,8H), 0.95–0.92 (m, 6H).

*Synthesis of compound **4a***

To a dry three-necked round bottom flask was added 3,6-dibromothieno[3,2-*b*]thiophene (0.55 g, 1.85 mmol), compound **3a** (1.00 g, 4.44 mmol), $Pd(OAc)_2$ (21 mg, 0.093 mmol), tri-*tert*-butylphosphine (P(*t*-Bu)$_3$) (10% in toluene, 0.75 g, 1.36 mmol), *t*-BuONa (0.71 g, 7.40 mmol), and *o*-xylene (20 mL). The mixture was deoxygenated with argon for 30 min and stirred at 145 °C for 36 hours. After cooling, the reaction mixture was filtered by a short silica gel column and the filtrate was evaporated to dryness under reduced pressure. Then, the residue was purified by column chromatography on silica gel using petroleum ether: dichloromethane (5:1, v/v) as the eluent yielding colorless oil (0.78 g, 72%).^{1}H NMR (600 MHz, $CDCl_3$): δ 7.08–7.03 (m, 18H), 2.59–2.57 (m, 8H), 0.95–0.93 (m, 12H). MS (MALDI-TOF): *m*/*z* 587.86 $[MH]^+$.

*Synthesis of compound **4b***

To a dry three-necked round bottom flask was added 3,6-dibromothieno[3,2-*b*]thiophene (0.55 g, 1.85 mmol), compound **3b** (1.25 g, 4.44 mmol), $Pd(OAc)_2$ (21

mg, 0.093 mmol), tri-*tert*-butylphosphine (P(*t*-Bu)$_3$) (10% in toluene, 0.75 g, 1.36 mmol), *t*-BuONa (0.71 g, 7.40 mmol), and *o*-xylene (20 mL). The mixture was deoxygenated with argon for 30 min and stirred at 145 °C for 36 hours. After cooling, the reaction mixture was filtered by a short silica gel column and the filtrate was evaporated to dryness under reduced pressure. Then, the residue was purified by column chromatography on silica gel using petroleum ether: dichloromethane (5:1, v/v) as the eluent yielding colorless oil (0.73 g, 71%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.08–7.04 (m, 18H), 2.59–2.57 (m, 8H), 1.61–1.59 (m, 8H),1.39–1.35 (m, 8H), 0.95–0.92 (m, 12H). MS (MALDI-TOF): *m*/*z* 700.07 $[MH]^+$.

*Synthesis of compound **4c***

To a dry three-necked round bottom flask was added 3,6-dibromothieno[3,2-*b*]thiophene (0.55 g, 1.85 mmol), compound **3c** (1.50 g, 4.44 mmol), $Pd(OAc)_2$ (21 mg, 0.093 mmol), tri-*tert*-butylphosphine (P(*t*-Bu)$_3$) (10% in toluene, 0.75 g, 1.36 mmol), *t*-BuONa (0.71 g, 7.40 mmol), and *o*-xylene (20 mL). The mixture was deoxygenated with argon for 30 min and stirred at 145 °C for 36 hours. After cooling, the reaction mixture was filtered by a short silica gel column and the filtrate was evaporated to dryness under reduced pressure. Then, the residue was purified by column chromatography on silica gel using petroleum ether: dichloromethane (5:1, v/v) as the eluent yielding colorless oil (0.67 g, 67%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.09–7.05 (m, 18H), 2.60–2.58 (m, 8H), 1.62–1.60 (m, 8H), 1.39–1.33 (m, 24H), 0.95–0.92 (m, 12H). MS (MALDI-TOF): *m*/*z* 812.50 $[MH]^+$.

*Synthesis of compound **5a***

To a dry three-necked round bottom flask was added a solution of compound **4a** (0.70 g, 1.19 mmol) in DMF (10 mL) at 0 °C. NBS (0.45 g, 2.50 mmol) in DMF (5 mL) was added dropwise to the solution under darkness. The reaction mixture was stirred at room temperature for 16 hours before being poured into water. After being extracted with CH_2Cl_2 (50 mL × 3), the organic layer was dried over anhydrous

Na_2SO_4 and filtered. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using petroleum ether: CH_2Cl_2 (10:1, v/v) as the eluent yielding colorless oil (0.82 g, 93%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.08 (d, J = 8Hz, 8H), 6.95 (d, J = 8Hz, 8H), 2.59–2.56 (m, 8H), 0.94–0.92 (m, 12H). MS (MALDI-TOF): m/z 745.65 $[MH]^+$.

*Synthesis of compound **5b***

To a dry three-necked round bottom flask was added a solution of compound **4b** (0.70 g, 1.00 mmol) in DMF (10 mL) at 0 °C. NBS (0.40 g, 2.20 mmol) in DMF (5 mL) was added dropwise to the solution under darkness. The reaction mixture was stirred at room temperature for 16 hours before being poured into water. After being extracted with CH_2Cl_2 (50 mL × 3), the organic layer was dried over anhydrous Na_2SO_4 and filtered. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using petroleum ether: CH_2Cl_2 (10:1, v/v) as the eluent yielding colorless oil (0.77 g, 90%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.08 (d, J = 8Hz, 8H), 6.95 (d, J = 8Hz, 8H), 2.59–2.57 (m, 8H), 1.61–1.59 (m, 8H),1.39–1.35 (m, 8H), 0.95–0.93 (m, 12H). MS (MALDI-TOF): m/z 857.19 $[MH]^+$.

*Synthesis of compound **5c***

To a dry three-necked round bottom flask was added a solution of compound **4c** (0.60 g, 0.74 mmol) in DMF (10 mL) at 0 °C. NBS (0.30 g, 1.63 mmol) in DMF (5 mL) was added dropwise to the solution under darkness. The reaction mixture was stirred at room temperature for 16 hours before being poured into water. After being extracted with CH_2Cl_2 (50 mL × 3), the organic layer was dried over anhydrous Na_2SO_4 and filtered. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using petroleum ether: CH_2Cl_2 (10:1, v/v) as the eluent yielding colorless oil (0.65 g, 91%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.08 (d, J = 8Hz, 8H), 6.95 (d, J = 8Hz, 8H), 2.60–2.58 (m, 8H), 1.61–1.58

(m, 8H),1.39–1.33 (m, 24H), 0.95–0.93 (m, 12H). MS (MALDI-TOF): *m*/*z* 970.08 $[MH]^+$.

*Synthesis of compound **6a***

To a dry three-necked round bottom flask was added compound **2a** (0.33 M in toluene, 3.6 mL, 1.2 mmol), compound **5b** (430 mg, 0.5 mmol), and dry toluene (10 mL). After being deoxygenated with argon for 20 min, $Pd(PPh_3)_4$ (29 mg, 0.025 mmol) was added and then deoxygenated with argon for another 20 min. The reaction mixture was stirred at reflux for 24 hours. After cooling, the mixture was extracted with CH_2Cl_2 (50 mL × 3) and the organic layer was dried over anhydrous Na_2SO_4 and filtered. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using petroleum ether: CH_2Cl_2 (5:1, v/v) as the eluent yielding yellow oil (430 mg, 82%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.10 (m, 16H), 7.03 (s, 2H), 7.01 (s, 2H), 4.41 (d, J = 7.6 Hz, 4H), 4.34 (q, J = 7.1 Hz, 4H), 2.59–2.57 (m, 8H), 2.06–1.99 (m, 2H), 1.43 (t, J = 7.1 Hz, 6H), 1.34–1.23 (m, 32H), 0.95–0.89 (m, 24H). MS (MALDI-TOF): *m*/*z* 1310.95 $[MH]^+$.

*Synthesis of compound **6b***

To a dry three-necked round bottom flask was added compound **2b** (0.33 M in toluene, 3.6 mL, 1.20 mmol), compound **5b** (430 mg, 0.50 mmol), and dry toluene (10 mL). After being deoxygenated with argon for 20 min, $Pd(PPh_3)_4$ (29 mg, 0.025 mmol) was added and then deoxygenated with argon for another 20 min. The reaction mixture was stirred at reflux for 24 hours. After cooling, the mixture was extracted with CH_2Cl_2 (50 mL × 3) and the organic layer was dried over anhydrous Na_2SO_4 and filtered. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using petroleum ether: CH_2Cl_2 (5:1, v/v) as the eluent yielding yellow oil (602 mg, 85%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.09 (m, 16H), 7.03 (s, 2H), 7.01 (s, 2H), 4.42 (d, J = 7.6 Hz, 4H), 4.34 (q, J = 7.1 Hz, 4H), 2.58–2.56 (m, 8H), 2.06–1.98 (m, 2H), 1.42 (t, J = 7.1 Hz, 6H), 1.34–1.21 (m, 48H),

0.94–0.88 (m, 24H). MS (MALDI-TOF): *m*/*z* 1421.79 $[MH]^+$.

Synthesis of compound ***6c***

To a dry three-necked round bottom flask was added compound **2c** (0.33 M in toluene, 3.0 mL, 1.00 mmol), compound **5b** (340 mg, 0.40 mmol), and dry toluene (10 mL). After being deoxygenated with argon for 20 min, $Pd(PPh_3)_4$ (23 mg, 0.020 mmol) was added and then deoxygenated with argon for another 20 min. The reaction mixture was stirred at reflux for 24 hours. After cooling, the mixture was extracted with CH_2Cl_2 (50 mL × 3) and the organic layer was dried over anhydrous Na_2SO_4 and filtered. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using petroleum ether: CH_2Cl_2 (5:1, v/v) as the eluent yielding yellow oil (485 mg, 79%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.10 (m, 16H), 7.03 (s, 2H), 7.01 (s, 2H), 4.41 (d, J = 7.6 Hz, 4H), 4.34 (q, J = 7.1 Hz, 4H), 2.57–2.55 (m, 8H), 2.04–1.97 (m, 2H), 1.43 (t, J = 7.1 Hz, 6H), 1.33–1.22 (m, 64H), 0.96–0.88 (m, 24H). MS (MALDI-TOF): *m*/*z* 1533.93 $[MH]^+$.

Synthesis of compound ***6d***

To a dry three-necked round bottom flask was added compound **2b** (0.33 M in toluene, 3.6 mL, 1.20 mmol), compound **5a** (372 mg, 0.50 mmol), and dry toluene (10 mL). After being deoxygenated with argon for 20 min, $Pd(PPh_3)_4$ (29 mg, 0.025 mmol) was added and then deoxygenated with argon for another 20 min. The reaction mixture was stirred at reflux for 24 hours. After cooling, the mixture was extracted with CH_2Cl_2 (50 mL × 3) and the organic layer was dried over anhydrous Na_2SO_4 and filtered. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using petroleum ether: CH_2Cl_2 (5:1, v/v) as the eluent yielding yellow oil (583 mg, 89%).^{1}H NMR (600 MHz, $CDCl_3$): δ 7.10 (m, 16H), 7.03 (s, 2H), 7.01 (s, 2H), 4.41 (d, J = 7.6 Hz, 4H), 4.34 (q, J = 7.1 Hz, 4H), 2.59–2.57 (m, 8H), 2.06–1.99 (m, 2H), 1.43 (t, J = 7.1 Hz, 6H), 1.34–1.23 (m, 44H), 0.93–0.87 (m, 12H). MS (MALDI-TOF): *m*/*z* 1310.94 $[MH]^+$.

*Synthesis of compound **6e***

To a dry three-necked round bottom flask was added compound **2b** (0.33 M in toluene, 3.6 mL, 1.20 mmol), compound **5c** (485 mg, 0.50 mmol), and dry toluene (10 mL). After being deoxygenated with argon for 20 min, $Pd(PPh_3)_4$ (29 mg, 0.025 mmol) was added and then deoxygenated with argon for another 20 min. The reaction mixture was stirred at reflux for 24 hours. After cooling, the mixture was extracted with CH_2Cl_2 (50 mL × 3) and the organic layer was dried over anhydrous Na_2SO_4 and filtered. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using petroleum ether: CH_2Cl_2 (5:1, v/v) as the eluent yielding yellow oil (615 mg, 88%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.11 (m, 16H), 7.04 (s, 2H), 7.02 (s, 2H), 4.43 (d, J = 7.6 Hz, 4H), 4.35 (q, J = 7.1 Hz, 4H), 2.59–2.57 (m, 8H), 2.04–1.98 (m, 2H), 1.42 (t, J = 7.1 Hz, 6H), 1.61–1.57 (m, 8H), 1.37–1.33 (m, 8H), 1.21–1.11 (m, 48H), 0.92–0.88 (m, 24H). MS (MALDI-TOF): m/z 1533.92 $[MH]^+$.

*Synthesis of compound **7a***

To a dry three-necked round bottom flask were added compound **6a** (330 mg, 0.25 mmol) and dry THF (10 mL). The mixture was deoxygenated with argon for 20 min. A solution of $LiAlH_4$ (1.0 M in THF, 1.42 mL, 1.42 mmol) was added dropwise at 0 °C. The mixture was stirred for 2 hours at 0 °C. A saturated NaOH aqueous solution (10 mL) was added and the mixture was extracted with EtOAc (2 × 30 mL). The organic phase was dried over anhydrous Na_2SO_4 and filtered. After removing the solvent, the residue was dissolved in $CHCl_3$ again, and MnO_2 (770 mg, 8.88 mmol) was added in a dry three-necked round bottom flask under argon. The mixture was deoxygenated with argon for 20 min and was refluxed overnight. After cooling to room temperature, the reaction mixture was filtered through a pad of celite and the filtrate was dried over anhydrous Na_2SO_4 and filtered. After removing the solvent, the residue was purified by column chromatography on silica gel using petroleum ether:

EtOAc (20:1, v/v) as eluent yielding orange solid (182 mg, 60%).^{1}H NMR (600 MHz, $CDCl_3$): δ 9.97 (s, 2H), 7.11 (m, 16H), 7.02 (s, 2H), 7.01 (s, 2H), 4.34 (q, J = 7.1 Hz, 4H), 2.59–2.57 (m, 8H), 1.75–1.71 (m, 2H), 1.60–1.56 (m, 8H), 1.37–1.33 (m, 8H), 1.24–1.15 (m, 16H), 0.93–0.90 (m, 12H), 0.82–0.78 (m, 12H). MS (MALDI-TOF): m/z 1222.61 $[MH]^+$.

*Synthesis of compound **7b***

To a dry three-necked round bottom flask were added compound **6b** (350 mg, 0.25 mmol) and dry THF (10 mL). The mixture was deoxygenated with argon for 20 min. A solution of $LiAlH_4$ (1.0 M in THF, 1.42 mL, 1.42 mmol) was added dropwise at 0 °C. The mixture was stirred for 2 hours at 0 °C. A saturated NaOH aqueous solution (10 mL) was added and the mixture was extracted with EtOAc (2 × 30 mL). The organic phase was dried over anhydrous Na_2SO_4 and filtered. After removing the solvent, the residue was dissolved in $CHCl_3$ again, and MnO_2 (770 mg, 8.88 mmol) was added in a dry three-necked round bottom flask under argon. The mixture was deoxygenated with argon for 20 min and was refluxed overnight. After cooling to room temperature, the reaction mixture was filtered through a pad of celite and the filtrate was dried over anhydrous Na_2SO_4 and filtered. After removing the solvent, the residue was purified by column chromatography on silica gel using petroleum ether: EtOAc (20:1, v/v) as eluent yielding orange solid (195 mg, 58%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.99 (s, 2H), 7.10 (m, 16H), 7.03 (s, 2H), 7.01 (s, 2H), 4.34 (q, J = 7.1 Hz, 4H), 2.59–2.57 (m, 8H), 1.81–1.76 (m, 2H), 1.60–1.56 (m, 8H), 1.37–1.33 (m, 8H), 1.22–1.12 (m, 32H), 0.93–0.91 (m, 12H), 0.83–0.79 (m, 12H). MS (MALDI-TOF): m/z 1333.75 $[MH]^+$.

*Synthesis of compound **7c***

To a dry three-necked round bottom flask were added compound **6c** (390 mg, 0.25 mmol) and dry THF (10 mL). The mixture was deoxygenated with argon for 20 min. A solution of $LiAlH_4$ (1.0 M in THF, 1.42 mL, 1.42 mmol) was added dropwise

at 0 °C. The mixture was stirred for 2 hours at 0 °C. A saturated NaOH aqueous solution (10 mL) was added and the mixture was extracted with EtOAc (2 × 30 mL). The organic phase was dried over anhydrous Na_2SO_4 and filtered. After removing the solvent, the residue was dissolved in $CHCl_3$ again, and MnO_2 (770 mg, 8.88 mmol) was added in a dry three-necked round bottom flask under argon. The mixture was deoxygenated with argon for 20 min and was refluxed overnight. After cooling to room temperature, the reaction mixture was filtered through a pad of celite and the filtrate was dried over anhydrous Na_2SO_4 and filtered. After removing the solvent, the residue was purified by column chromatography on silica gel using petroleum ether: EtOAc (20:1, v/v) as eluent yielding orange solid (199 mg, 55%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.97 (s, 2H), 7.11 (m, 16H), 7.02 (s, 2H), 7.01 (s, 2H), 4.34 (q, J = 7.1 Hz, 4H), 2.59–2.57 (m, 8H), 1.81–1.76 (m, 2H), 1.63–1.54 (m, 12H), 1.31–1.15 (m, 52H), 0.87–0.84 (m, 12H), 0.82–0.79 (m, 12H). MS (MALDI-TOF): m/z 1445.86 $[MH]^+$.

*Synthesis of compound **7d***

To a dry three-necked round bottom flask were added compound **6d** (330 mg, 0.25 mmol) and dry THF (10 mL). The mixture was deoxygenated with argon for 20 min. A solution of $LiAlH_4$ (1.0 M in THF, 1.42 mL, 1.42 mmol) was added dropwise at 0 °C. The mixture was stirred for 2 hours at 0 °C. A saturated NaOH aqueous solution (10 mL) was added and the mixture was extracted with EtOAc (2 × 30 mL). The organic phase was dried over anhydrous Na_2SO_4 and filtered. After removing the solvent, the residue was dissolved in $CHCl_3$ again, and MnO_2 (770 mg, 8.88 mmol) was added in a dry three-necked round bottom flask under argon. The mixture was deoxygenated with argon for 20 min and was refluxed overnight. After cooling to room temperature, the reaction mixture was filtered through a pad of celite and the filtrate was dried over anhydrous Na_2SO_4 and filtered. After removing the solvent, the residue was purified by column chromatography on silica gel using petroleum ether: EtOAc (20:1, v/v) as eluent yielding orange solid (190 mg, 62%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.98 (s, 2H), 7.10 (m, 16H), 7.03 (s, 2H), 7.01 (s, 2H), 4.34 (q, J = 7.1 Hz,

4H), 2.59–2.57 (m, 8H), 1.75–1.71 (m, 2H), 1.60–1.56 (m, 8H), 1.37–1.15 (m, 24H), 0.93–0.90 (m, 12H), 0.82–0.78 (m, 12H). MS (MALDI-TOF): m/z 1222.85 $[MH]^+$.

*Synthesis of compound **7e***

To a dry three-necked round bottom flask were added compound **6e** (380 mg, 0.25 mmol) and dry THF (10 mL). The mixture was deoxygenated with argon for 20 min. A solution of $LiAlH_4$ (1.0 M in THF, 1.42 mL, 1.42 mmol) was added dropwise at 0 °C. The mixture was stirred for 2 hours at 0 °C. A saturated NaOH aqueous solution (10 mL) was added and the mixture was extracted with EtOAc (2 × 30 mL). The organic phase was dried over anhydrous Na_2SO_4 and filtered. After removing the solvent, the residue was dissolved in $CHCl_3$ again, and MnO_2 (770 mg, 8.88 mmol) was added in a dry three-necked round bottom flask under argon. The mixture was deoxygenated with argon for 20 min and was refluxed overnight. After cooling to room temperature, the reaction mixture was filtered through a pad of celite and the filtrate was dried over anhydrous Na_2SO_4 and filtered. After removing the solvent, the residue was purified by column chromatography on silica gel using petroleum ether: EtOAc (20:1, v/v) as eluent yielding orange solid (210 mg, 58%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.99 (s, 2H), 7.10 (m, 16H), 7.03 (s, 2H), 7.01 (s, 2H), 4.34 (q, J = 7.1 Hz, 4H), 2.59–2.57 (m, 8H), 2.06–1.99 (m, 2H), 1.80–1.75 (m, 2H), 1.61–1.57 (m, 8H), 1.37–1.33 (m, 8H), 1.21–1.11 (m, 48H), 0.94–0.91 (m, 12H), 0.86–0.81 (m, 12H). MS (MALDI-TOF): m/z 1445.86 $[MH]^+$.

*Synthesis of compound **TTTP1***

To a dry three-necked round bottom flask were added compound **7a** (60 mg, 0.049 mmol), IC2F (28 mg, 0.12 mmol), toluene (10 mL), acetic anhydride (0.5 mL) and $BF_3{\cdot}Et_2O$ (0.3 mL). The reaction mixture was stirred at room temperature for 30 min and poured into methanol (50 mL). After filtered, the residue was purified by column chromatography on silica gel using petroleum ether: CH_2Cl_2 (2:1, v/v) as eluent yielding black solid (65 mg, 80%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.79 (s, 2H),

8.46 (s, 2H), 8.36 (s, 2H), 7.58 (s, 2H), 7.12 (d, J = 8.3 Hz, 8H), 7.07 (d, J = 8.5 Hz, 8H), 6.75 (s, 2H), 4.03–3.97 (m, 4H), 2.50–2.56 (m, 8H), 1.75–1.71 (m, 2H), 1.60–1.56 (m, 8H), 1.37–1.33 (m, 8H), 1.24–1.15 (m, 16H), 0.93–0.90 (m, 12H), 0.82–0.78 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 184.86, 160.45, 152.31, 146.35, 142.89, 138.45, 136.56, 135.91, 135.32, 132.64, 129.45, 128.67, 128.19, 121.89, 119.48, 119.10, 115.81, 115.16, 114.51, 114.36, 112.23, 112.11, 106.41, 65.96, 50.22, 41.01, 35.01, 33.57, 30.18, 28.37, 23.74, 22.95, 22.35, 14.00, 10.61. MS (MALDI-TOF): m/z 1646.65 $[MH]^+$.

*Synthesis of compound **TTTP2***

To a dry three-necked round bottom flask were added compound **7b** (64 mg, 0.048 mmol), IC2F (28 mg, 0.12 mmol), toluene (10 mL), acetic anhydride (0.5 mL) and $BF_3{\cdot}Et_2O$ (0.3 mL). The reaction mixture was stirred at room temperature for 30 min and poured into methanol (50 mL). After filtered, the residue was purified by column chromatography on silica gel using petroleum ether: CH_2Cl_2 (2:1, v/v) as eluent yielding black solid (72 mg, 85%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.79 (s, 2H), 8.46 (s, 2H), 8.36 (s, 2H), 7.58 (s, 2H), 7.11 (d, J = 8.3 Hz, 8H), 7.06 (d, J = 8.5 Hz, 8H), 6.74 (s, 2H), 4.00–3.96 (m, 4H), 2.59–2.56 (m, 8H), 1.81–1.76 (m, 2H), 1.60–1.56 (m, 8H), 1.37–1.33 (m, 8H), 1.22–1.12 (m, 32H), 0.93–0.91 (m, 12H), 0.83–0.79 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 184.84, 160.45, 152.27, 146.31, 142.90, 138.44, 136.57, 135.92, 135.30, 132.71, 129.45, 128.69, 128.21, 121.88, 119.47, 119.08, 115.80, 115.15, 114.50, 114.36, 112.23, 112.11, 106.44, 65.94, 50.43, 39.72, 35.02, 33.57, 31.70, 31.16, 30.86, 29.56, 28.43, 26.21, 22.94, 22.61, 22.36, 14.08, 14.00. MS (MALDI-TOF): m/z 1758.78 $[MH]^+$.

*Synthesis of compound **TTTP3***

To a dry three-necked round bottom flask were added compound **7c** (70 mg, 0.048 mmol), IC2F (28 mg, 0.12 mmol), toluene (10 mL), acetic anhydride (0.5 mL) and $BF_3{\cdot}Et_2O$ (0.3 mL). The reaction mixture was stirred at room temperature for 30

min and poured into methanol (50 mL). After filtered, the residue was purified by column chromatography on silica gel using petroleum ether: CH_2Cl_2 (2:1, v/v) as eluent yielding black solid (72 mg, 80%).^{1}H NMR (600 MHz, $CDCl_3$): δ 8.79 (s, 2H), 8.47 (s, 2H), 8.36 (s, 2H), 7.59 (s, 2H), 7.11 (d, J = 8.3 Hz, 8H), 7.06 (d, J = 8.5 Hz, 8H), 6.75 (s, 2H), 4.00–3.96 (m, 4H), 2.60–2.55 (m, 8H), 1.81–1.76 (m, 2H), 1.63–1.54 (m, 12H), 1.31–1.15 (m, 52H), 0.87–0.84 (m, 12H), 0.82–0.79 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 184.83, 160.46, 152.27, 146.28, 142.98, 138.49, 136.59, 135.92, 135.28, 132.75, 129.42, 128.67, 128.21, 121.86, 119.47, 119.09, 115.80, 115.15, 114.50, 114.36, 112.24, 112.12, 106.45, 65.94, 50.43, 39.71, 35.36, 31.72, 31.42, 31.16, 30.86, 29.56, 29.03, 28.43, 26.22, 22.94, 22.63, 14.09, 13.99. MS (MALDI-TOF): m/z 1870.90 $[MH]^+$.

Synthesis of compound ***TTTP4***

To a dry three-necked round bottom flask were added compound **7d** (60 mg, 0.049 mmol), IC2F (28 mg, 0.12 mmol), toluene (10 mL), acetic anhydride (0.5 mL) and $BF_3{\cdot}Et_2O$ (0.3 mL). The reaction mixture was stirred at room temperature for 30 min and poured into methanol (50 mL). After filtered, the residue was purified by column chromatography on silica gel using petroleum ether: CH_2Cl_2 (2:1, v/v) as eluent yielding black solid (65 mg, 80%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.79 (s, 2H), 8.46 (s, 2H), 8.36 (s, 2H), 7.58 (s, 2H), 7.12 (d, J = 8.3 Hz, 8H), 7.07 (d, J = 8.5 Hz, 8H), 6.75 (s, 2H), 4.03–3.97 (m, 4H), 2.50–2.56 (m, 8H), 1.75–1.71 (m, 2H), 1.60–1.56 (m, 8H), 1.37–1.15 (m, 24H), 0.93–0.90 (m, 12H), 0.82–0.78 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 184.83, 160.46, 152.25, 146.31, 142.90, 138.43, 136.57, 135.92, 135.31, 132.72,129.45, 128.70, 128.22, 121.88, 119.47, 119.08, 115.80, 115.15, 114.50, 114.36, 112.23, 112.10, 106.43, 65.94, 50.43, 39.71, 35.03, 31.70, 31.15, 30.86, 29.55, 28.43, 26.21, 22.62, 22.38, 14.08, 14.00. MS (MALDI-TOF): m/z 1646.65 $[MH]^+$.

*Synthesis of compou*nd ***TTTP5***

To a dry three-necked round bottom flask were added compound **7e** (70 mg, 0.048 mmol), IC2F (28 mg, 0.12 mmol), toluene (10 mL), acetic anhydride (0.5 mL) and $BF_3 \cdot Et_2O$ (0.3 mL). The reaction mixture was stirred at room temperature for 30 min and poured into methanol (50 mL). After filtered, the residue was purified by column chromatography on silica gel using petroleum ether: CH_2Cl_2 (2:1, v/v) as eluent yielding black solid (75 mg, 83%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.79 (s, 2H), 8.46 (s, 2H), 8.36 (s, 2H), 7.58 (s, 2H), 7.12 (d, J = 8.2 Hz, 8H), 7.06 (d, J = 8.3 Hz, 8H), 6.75 (s, 2H), 3.98 (d, J = 7.8 Hz, 4H), 2.59–2.56 (m, 8H), 1.80–1.75 (m, 2H), 1.61–1.57 (m, 8H), 1.37–1.33 (m, 8H), 1.21–1.11 (m, 48H), 0.94–0.91 (m, 12H), 0.86–0.81 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 184.83, 160.43, 152.31, 146.31, 142.91, 138.45, 136.57, 135.93, 135.29, 132.68, 129.45, 128.65, 128.20, 121.90, 119.47, 119.07, 115.80, 115.14, 114.49, 114.35, 112.23, 112.10, 106.48, 65.95, 50.48, 39.74, 35.03, 33.57, 31.86, 31.71, 31.20, 29.89, 29.56, 29.45, 29.28, 26.28, 26.23, 22.66, 22.62, 22.37, 14.12, 14.08, 14.00. MS (MALDI-TOF): m/z 1870.90 $[MH]^+$.

Characterization

The ^{1}H and ^{13}C NMR spectra were measured on Bruker AVANCE 600 MHz spectrometer. Mass spectra were measured on a Bruker Daltonics BIFLEX III MALDI-TOF Analyzer using MALDI mode and a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer using ESI mode. Solution (chloroform) and thin film (on quartz substrate) UV-vis absorption spectra were recorded on a JΛSCO V-570 spectrophotometer. Electrochemical measurements were carried out under nitrogen on a deoxygenated solution of tetra-*n*-butylammonium hexafluorophosphate (0.1 M) in CH_3CN using a computer-controlled CHI660C electrochemical workstation, a glassy-carbon working electrode coated with samples, a platinum-wire auxiliary electrode, and an Ag/AgCl as a reference electrode. The potential scan rate was 100 mV s^{-1}. Potentials were referenced to ferrocenium/ferrocene ($FeCp^{2+/0}$) couple by using ferrocene as an internal standard. The thickness of active layer was measured on a Bruker DektakXT profilometer. AFM measurements were performed on a Dimension

Icon, Bruker, using standard mode. Electroluminescence quantum efficiency was measured on a REPS Measurement System (Enlitech Co., Ltd.).

Computational methodology

Density functional theory (DFT) calculations were carried out at the B3LYP/6-31G(d) level of theory within the Gaussian 16 package,[S2, S3] where all alkyl side chains of TTTP-series acceptors were replaced by methyl groups to simplify the calculations. Geometry optimizations were performed with full relaxation of all atoms in gas phase, following which vibration frequency calculations were used to check that the optimized structures had no imaginary frequency.

SCLC measurements

Hole-only devices were fabricated for hole mobility measurements with the structure of ITO/PEDOT:PSS/active layer/MoO_3/Ag. The ITO substrates were first scrubbed by detergent and then sonicated with deionized water, acetone and isopropanol subsequently, and dried in an oven. The ITO glass substrates were treated by UV-ozone for 20 min before use. PEDOT:PSS was spin-coated onto the ITO substrates at 4000 rpm for 30 s. After annealing at 150 °C for 15 min in air, the active layers were formed by spin-coating a solution of PBDB-T:TTTP series (18 mg mL^{-1} in chloroform) at 2000 rpm for 40 s on PEDOT:PSS in a glovebox. Then, the MoO_3 layer (ca. 5 nm) and Ag (ca. 90 nm) were successively evaporated onto the surface of the photoactive layer under vacuum (ca. 10^{-5} Pa).

Electron-only devices were fabricated for electron mobility measurements with the structure ITO/ZnO/active layer/PDINN/Ag. The mixture of zinc acetate dehydrate (100 mg), 2-methoxyethanol (973 μL) and ethanolamine (28.29 μL) was stirred overnight to prepare the ZnO precursor solution. After the pretreatment of the ITO substrate, ZnO layer (ca. 30 nm) was spin-coated onto the ITO substrate at 4000 rpm for 30 s from ZnO precursor solution. After annealing at 200 °C for 30 min, the active layers were formed by spin-coating a solution of TTTP series and PBDB-T:TTTP

series (18 mg mL^{-1} in chloroform) at 2000 rpm for 40 s on ZnO in a glovebox. Then, a thin PDINN layer (~ 5 nm) was coated on the active layer, followed by the deposition of Ag electrode (90 nm).

The active area of the device was 4 mm^2 and the thickness of the active layer was 90 nm. The mobility was extracted by fitting the *J-V* curves using space charge limited current (SCLC) method:[S4]

$$J = \frac{9\varepsilon_r\varepsilon_r\mu V^2}{8L^3} \quad \text{---------- eqn S1}$$

here, J refers to the current density, μ is hole or electron mobility, ε_r is relative dielectric constant of the transport medium, which is equal to 3, ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1}), $V = V_{appl} - V_{bi}$, where V_{appl} is the applied voltage to the device, and V_{bi} is the built-in voltage due to the difference in work function of the two electrodes, L is the thickness of the active layer.

Fabrication and characterization of organic solar cells

All the devices are based on a conventional sandwich structure, patterned ITO glass/PEDOT:PSS/active layer/PNINN/Ag. The ITO substrates were first scrubbed by detergent and then sonicated with deionized water, acetone and isopropanol subsequently, and dried in an oven. The glass substrates were treated by UV-ozone for 20 min before use. PEDOT:PSS (Heraeus Clevios PVP AI 4083) was spin-cast onto the ITO substrates at 4000 rpm for 30 s, and then annealed at 150 °C for 15 min in air. Then, the active layers were spin-coated on PEDOT:PSS (PBDB-T: acceptors, 7:7 mg mL^{-1} in chloroform). Active layers were annealed on a 90 °C hotplate for 5 min after being coated. A thin PDINN layer (~ 5 nm) was coated on the active layer, followed by the deposition of Ag electrode (90 nm). The active area of the device was 4.00 mm^2, under the barrier of the mask plat. The *J-V* curve was measured using a computer-controlled B2912A Precision Source/Measure Unit (Agilent Technologies). An SS-X50 (Enlitech Co., Ltd.) solar simulator (3A+ grade, 50 × 50 mm^2 photobeam size) coupled with AM 1.5G solar spectrum filters was used as the light source, and

the optical power at the sample was 100 mW cm^{-2}. A 2 × 2 cm^2 monocrystalline silicon reference cell (SRC-1000-TC-QZ) was purchased from VLSI Standards Inc. The EQE spectra were measured using a Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech Co., Ltd.). The light intensity at each wavelength was calibrated using a standard single crystal Si photovoltaic cell.

Transient photovoltage

Transient photovoltage was tested by an oscilloscope (Tektronix MDO3104); the perturbed signals were emitted by a laser (AO-S-532, CNI) with a wavelength of 532 nm; the bias light was emitted through a LED white light source (LSH-150, Taiwan Fiber Optics, Inc.).

Voltage loss measurements

The total voltage loss of organic solar cells is related to three factors according to eqn S2: [S5]

$$qV_{loss} = E_g - qV_{OC} = \left(E_g - qV_{OC,\,sq}\right) + \left(qV_{OC,\,sq} - qV_{OC,\,rad}\right) + q\Delta V_{OC,\,nr} = q\Delta V_1 + q\Delta V_2 + q\Delta V_3$$

---------- eqn S2

where q is the elementary charge, E_g is the bandgap of the blend; $V_{OC,sq}$ is the maximum voltage derived from the Shockley-Queisser theory, assuming that the EQE is a step function; $V_{OC,rad}$ is the radiative limit for the open-circuit voltage, assuming that there is only radiative recombination loss in the device, which can be calculated using eqn S3;

$$V_{OC,\,rad} = \frac{k_B T}{q} ln(\frac{J_{SC}}{J_{0,rad}})$$ ---------- eqn S3

where the radiative saturation current density ($J_{0,rad}$) can be calculated using eqn S4:

$$J_{0,rad} = q\int_{-\infty}^{\infty} EQE(E)\emptyset_{BB}(E)d(E)$$ ----------eqn S4

$\Delta V_{OC,nr}$ is the voltage loss due to non-radiative recombination of charge carriers, which can be determined by measuring electroluminescence external quantum efficiencies (EQE_{EL}) of the devices, according to eqn S5: [S6]

$$q\Delta V_{OC,\,nr} = \frac{k_B T}{q} ln(EQE_{EL}^{-1}) \quad \text{---------- eqn S5}$$

where k_B is the Boltzmann constant, T is absolute temperature in Kelvin.

EQE_{EL} measurements were carried out using a home built setup: electric current was injected into the solar cells by using a digital sourcemeter (Keithley 2400), and the emitted photons were collected by a Si diode. The current generated by the Si diode was recorded by a picoammeters (Keithley 6482).

GIWAXS and GISAXS measurements

GIWAXS and GISAXS measurements for neat and blend films were carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu source, which emits X-rays with a photon energy of 8.05 keV, equivalent to a wavelength of 1.54 Å. A Pilatus3R 300 K detector with a pixel size of 0.172 μm was used for the detection of scattered X-ray signal. The sample-to-detector distance was calibrated as 162.1 mm by standard silver behenate (AgBH). The incidence angle was 0.2 °.

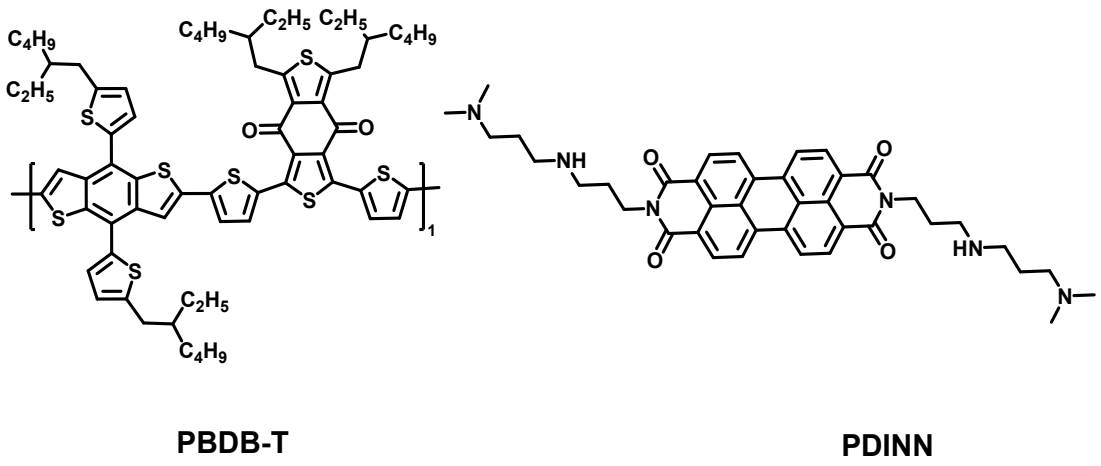


Fig. S1 Chemical structures of PBDB-T and PDINN.

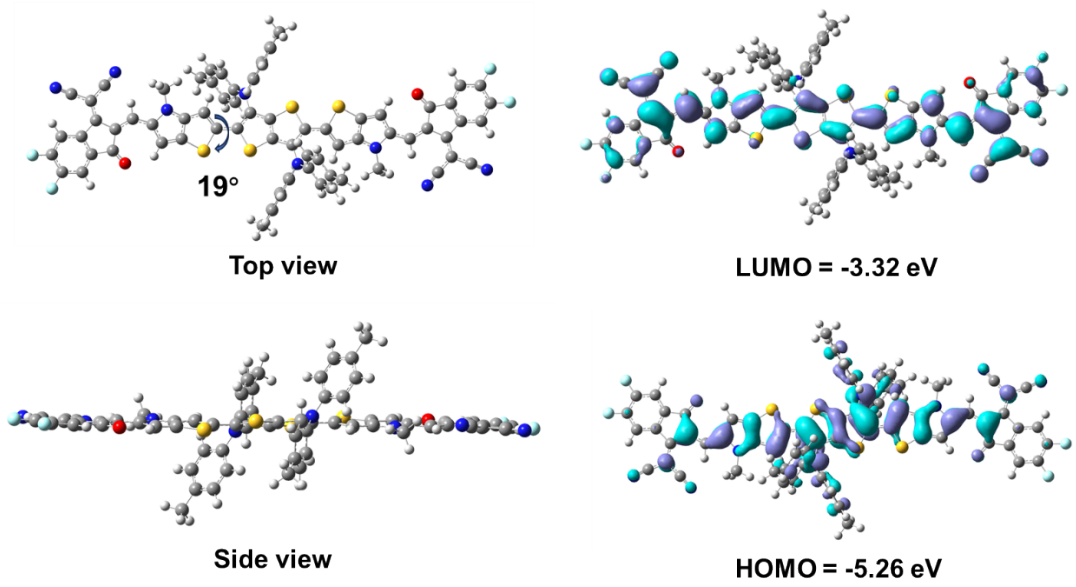


Fig. S2 DFT calculation results for TTTP-series acceptors. All alkyl side chains were replaced by methyl groups to simplify the calculations.

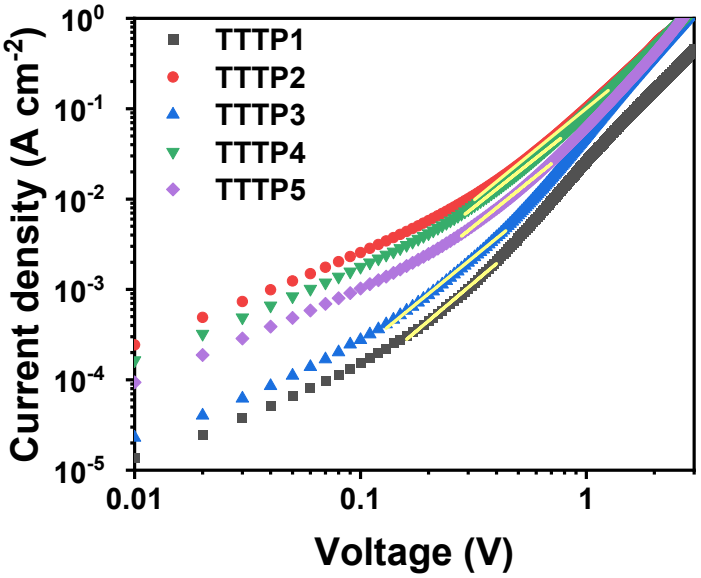


Fig. S3 *J-V* characteristics in dark for electron-only devices based on TTTP-series acceptors.

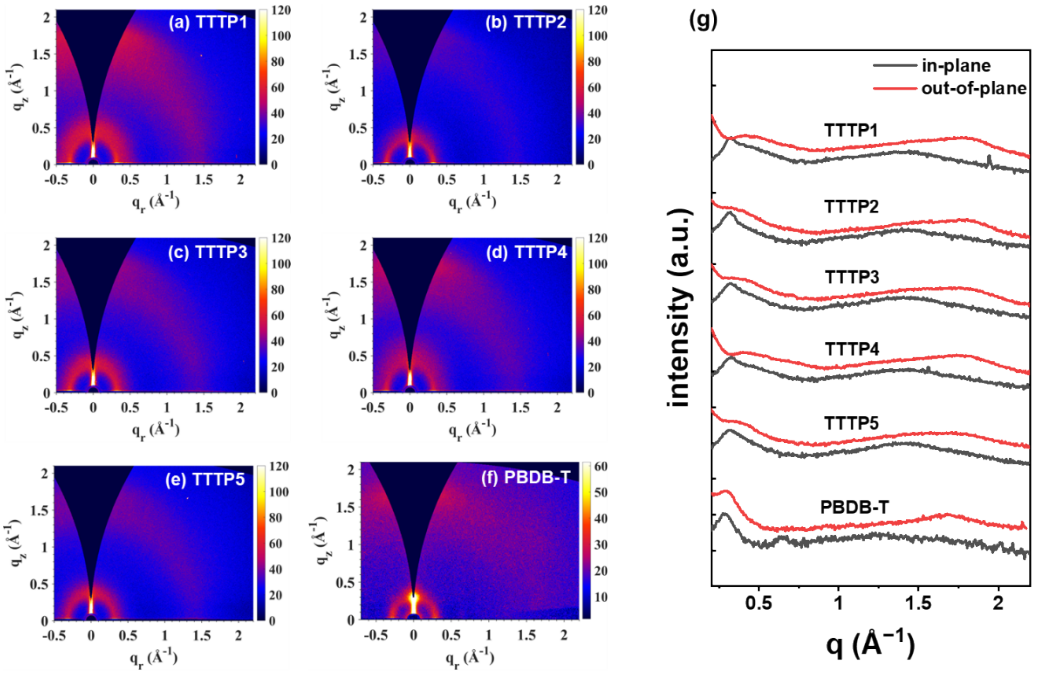


Fig. S4 2D GIWAXS patterns of (a-e) TTTP-series acceptors and (f) PBDB-T. (g) The corresponding intensity profiles along the in-plane (black line) and out of plane (red line) directions.

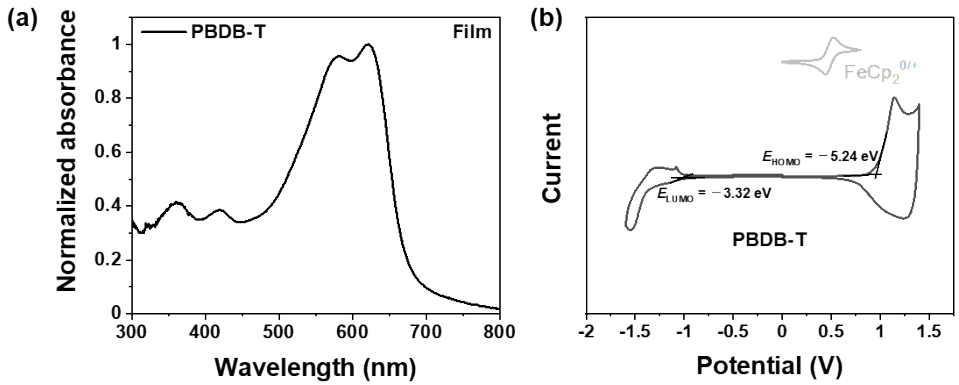


Fig. S5 (a) Normalized absorption spectrum of the PBDB-T film. (b) Cyclic voltammogram and energy levels of PBDB-T.

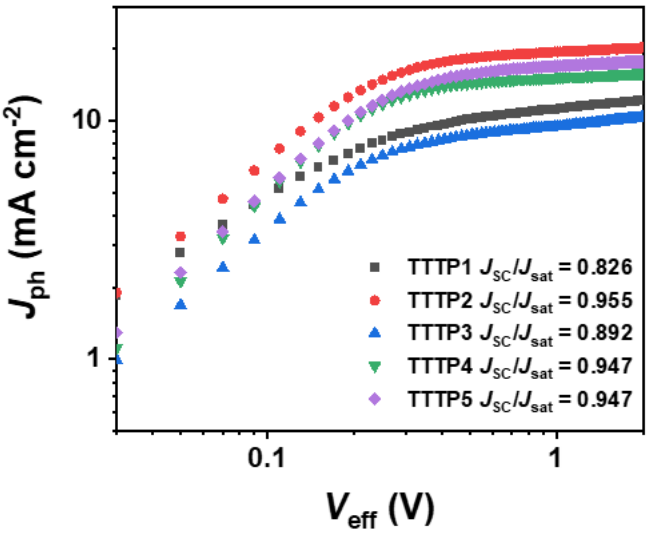


Fig. S6 J_{ph} versus V_{eff} characteristics of the optimal OSCs based on PBDB-T:TTTP series.

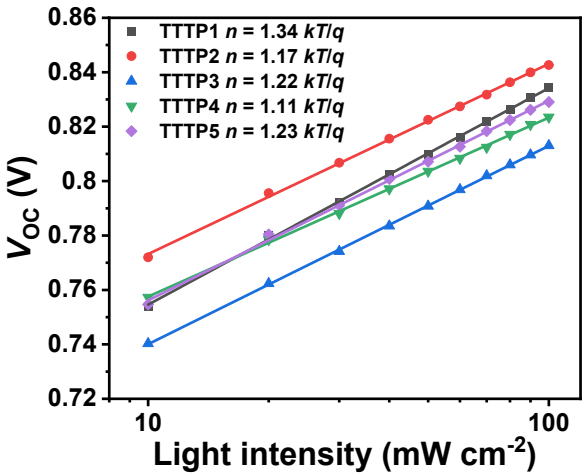


Fig. S7 V_{OC} versus light intensity of the optimal OSCs based on PBDB-T:TTTP series.

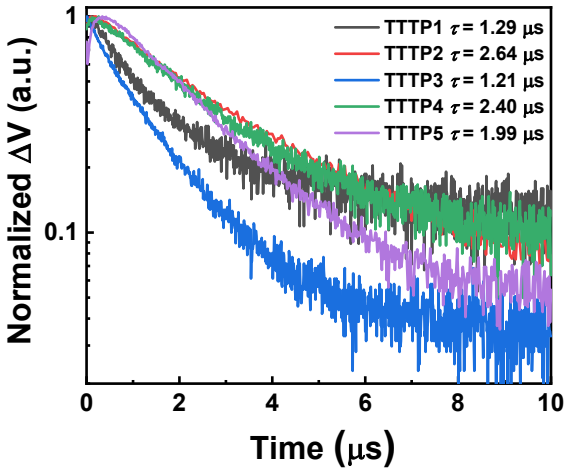


Fig. S8 Transient photoelectric voltage decay of the optimal OSCs based on PBDB-T:TTTP series.

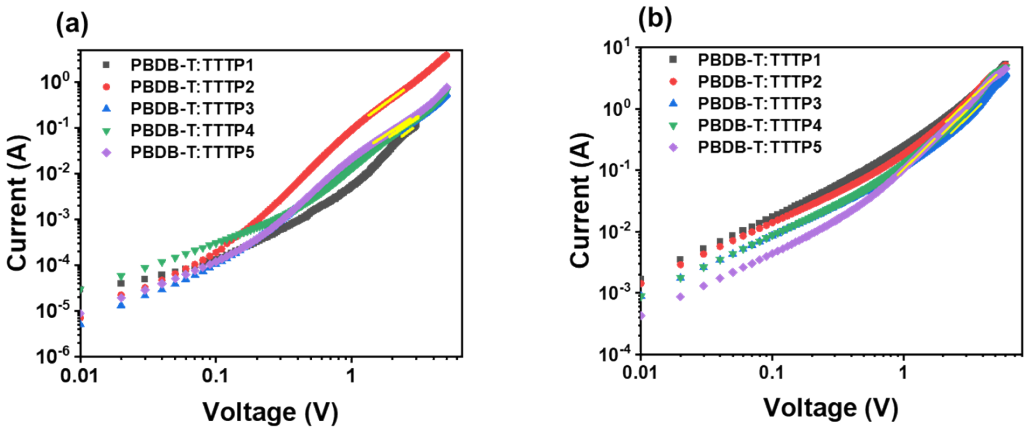


Fig. S9 *J*–*V* characteristics in dark for (a) electron-only and (b) hole-only devices based on PBDB-T:TTTP series.

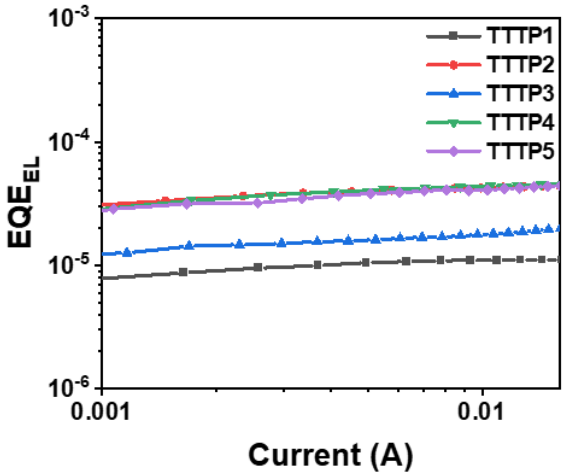


Fig. S10 EQE_{EL} of the optimal OSCs based on PBDB-T:TTTP series.

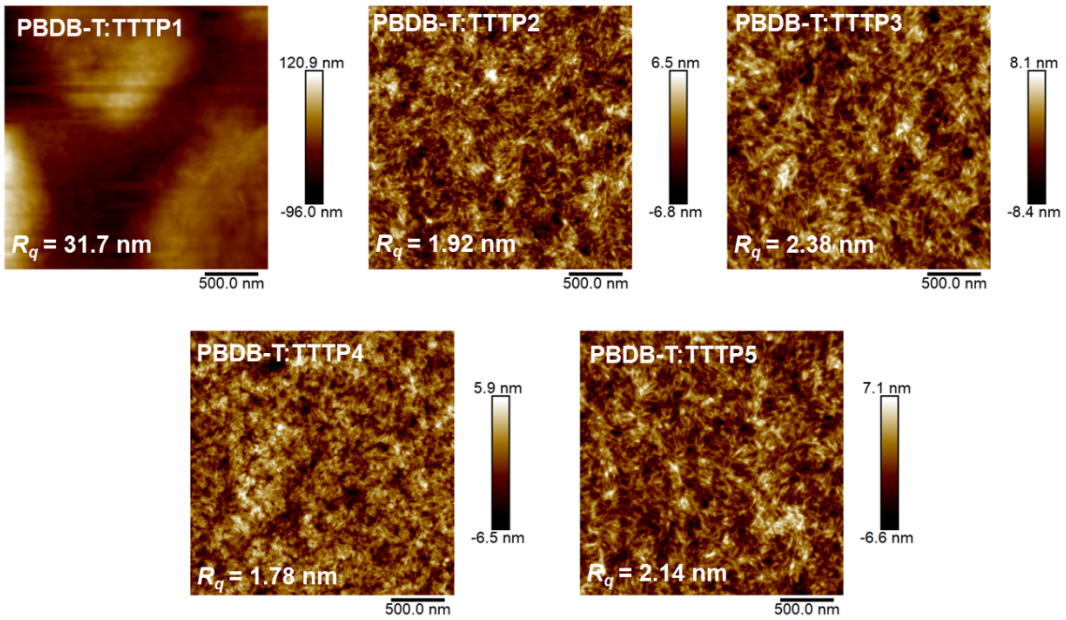


Fig. S11 AFM images and corresponding roughness (R_q) of PBDB-T:TTTP series blends.

Table S1 Summary of the GIWAXS parameters for the in-plane and out-of-plane directions of the TTTP-series neat films.

acceptor	in-plane				out-of-plane			
	q (Å^{-1})	*d* (Å)	FWHM	CL (Å)	*q* (Å^{-1})	*d* (Å)	FWHM	CL (Å)
TTTP1	0.34	18.5	0.099	57.1	1.73	3.63	0.529	10.7
TTTP2	0.32	19.6	0.091	62.1	1.71	3.67	0.461	12.3
TTTP3	0.32	19.6	0.126	44.9	1.68	3.74	0.730	7.7
TTTP4	0.33	19.0	0.102	55.4	1.72	3.65	0.522	10.8
TTTP5	0.32	19.6	0.143	39.5	1.65	3.81	0.709	8.0

Table S2 Optimization of donor:acceptor ratio in the OSCs based on PBDB-T:TTTP series.

acceptor	D:A (*w*:*w*)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)
TTTP1	1:0.8	0.757 ± 0.002 (0.757)	7.6 ± 0.2 (7.7)	0.433 ± 0.004 (0.437)	2.5 ± 0.1 (2.5)
	1:1	0.785 ± 0.004 (0.789)	9.4 ± 0.3 (9.7)	0.449 ± 0.008 (0.457)	3.3 ± 0.1 (3.5)
	1:1.2	0.782 ± 0.002 (0.782)	9.1 ± 0.2 (9.3)	0.444 ± 0.008 (0.439)	3.1 ± 0.1 (3.2)
TTTP2	1:0.8	0.792 ± 0.004 (0.789)	18.1 ± 0.2 (18.4)	0.538 ± 0.004 (0.536)	7.7 ± 0.1 (7.8)
	1:1	0.804 ± 0.003 (0.806)	18.0 ± 0.3 (18.3)	0.582 ± 0.007 (0.589)	8.4 ± 0.1 (8.5)
	1:1.2	0.799 ± 0.002 (0.801)	18.5 ± 0.2 (18.2)	0.559 ± 0.007 (0.566)	8.2 ± 0.1 (8.3)
TTTP3	1:0.8	0.742 ± 0.007 (0.744)	9.2 ± 0.2 (9.2)	0.415 ± 0.007 (0.420)	2.8 ± 0.1 (2.9)
	1:1	0.796 ± 0.006 (0.802)	9.0 ± 0.2 (9.1)	0.540 ± 0.004 (0.544)	3.8 ± 0.2 (4.0)
	1:1.2	0.782 ± 0.011 (0.790)	9.3 ± 0.1 (9.4)	0.466 ± 0.015 (0.481)	3.4 ± 0.2 (3.6)
TTTP4	1:0.8	0.798± 0.009 (0.807)	15.1± 0.3 (14.8)	0.514 ± 0.010 (0.517)	6.0 ± 0.2 (6.2)
	1:1	0.804 ± 0.003 (0.807)	16.4 ± 0.3 (16.7)	0.518 ± 0.013 (0.517)	6.8 ± 0.2 (7.0)
	1:1.2	0.800± 0.004 (0.798)	15.4 ± 0.3 (15.4)	0.533± 0.019 (0.552)	6.5 ± 0.2 (6.7)
TTTP5	1:0.8	0.800 ± 0.002 (0.801)	15.6 ± 0.3 (15.4)	0.568 ± 0.012 (0.580)	7.0 ± 0.2 (7.2)
	1:1	0.812 ± 0.003 (0.813)	16.5 ± 0.3 (16.2)	0.536 ± 0.011 (0.547)	7.1 ± 0.1 (7.2)
	1:1.2	0.802 ± 0.001 (0.803)	15.5 ± 0.3 (15.8)	0.595 ± 0.005 (0.595)	7.4 ± 0.2 (7.6)

Table S3 Optimization of additives in the OSCs based on PBDB-T:TTTP series.

acceptor	additive	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)
TTTP1	none	0.775 ± 0.004 (0.779)	9.4 ± 0.3 (9.7)	0.449 ± 0.008 (0.457)	3.3 ± 0.1 (3.4)
	0.5% DIO	0.774 ± 0.004 (0.774)	9.8 ± 0.4 (10.2)	0.453 ± 0.021 (0.439)	3.4 ± 0.1 (3.5)
	0.5% CN	0.770 ± 0.002 (0.772)	9.0 ± 0.3 (9.3)	0.438 ± 0.008 (0.446)	3.0 ± 0.2 (3.2)
TTTP2	none	0.804 ± 0.003 (0.805)	18.0 ± 0.3 (18.3)	0.582 ± 0.007 (0.589)	8.4 ± 0.1 (8.5)
	0.5% DIO	0.836 ± 0.003 (0.839)	18.6 ± 0.2 (18.6)	0.657 ± 0.014 (0.674)	10.2 ± 0.2 (10.5)
	0.5% CN	0.812 ± 0.003 (0.814)	15.8 ± 0.3 (15.9)	0.632 ± 0.006 (0.638)	8.1 ± 0.2 (8.3)
TTTP3	none	0.798 ± 0.004 (0.802)	9.0 ± 0.2 (9.1)	0.540 ± 0.004 (0.544)	3.8 ± 0.2 (4.0)
	0.5% DIO	0.809 ± 0.002 (0.810)	9.8 ± 0.1 (9.8)	0.582 ± 0.004 (0.586)	4.5 ± 0.1 (4.6)
	0.5% CN	0.800 ± 0.002 (0.798)	9.5 ± 0.2 (9.7)	0.553 ± 0.006 (0.552)	4.2 ± 0.1 (4.3)
TTTP4	none	0.804 ± 0.003 (0.807)	16.4 ± 0.3 (16.7)	0.518 ± 0.013 (0.517)	6.8 ± 0.2 (7.0)
	0.5% DIO	0.814 ± 0.002 (0.816)	15.9 ± 0.3 (15.9)	0.594 ± 0.007 (0.601)	7.7 ± 0.1 (7.8)
	0.5% CN	0.807± 0.003 (0.810)	15.2 ± 0.2 (15.4)	0.564 ± 0.013 (0.577)	7.0 ± 0.2 (7.2)
TTTP5	none	0.802 ± 0.001 (0.803)	15.5 ± 0.3 (15.8)	0.595 ± 0.005 (0.595)	7.4 ± 0.2 (7.6)
	0.5% DIO	0.812 ± 0.001 (0.813)	16.4 ± 0.3 (16.8)	0.582 ± 0.008 (0.590)	7.8 ± 0.3 (8.1)
	0.5% CN	0.803 ± 0.003 (0.806)	15.5 ± 0.2 (15.7)	0.576 ± 0.011 (0.587)	7.2 ± 0.2 (7.4)

Table S4 Optimization of annealing temperature and time in the PBDB-T:TTTP2-based OSCs.

annealing		V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)
80 ℃	1 min	0.831 ± 0.002 (0.832)	18.0 ± 0.1 (18.1)	0.671 ± 0.014 (0.685)	10.0 ± 0.1 (10.3)
	5 min	0.835 ± 0.004 (0.839)	19.5 ± 0.3 (19.6)	0.692 ± 0.006 (0.700)	11.3 ± 0.1 (11.5)
	10 min	0.833 ± 0.001 (0.834)	19.2 ± 0.2 (19.5)	0.695 ± 0.010 (0.703)	11.1 ± 0.2 (11.4)
90 ℃	1 min	0.833 ± 0.002 (0.834)	19.4 ± 0.2 (19.6)	0.677 ± 0.007 (0.684)	10.9 ± 0.2 (11.2)
	5 min	0.839 ± 0.002 (0.840)	21.3 ± 0.3 (21.7)	0.720 ± 0.006 (0.725)	12.9 ± 0.2 (13.2)
	10 min	0.842 ± 0.002 (0.844)	20.2 ± 0.2 (20.5)	0.713 ± 0.005 (0.720)	12.0 ± 0.2 (12.5)
100 ℃	1 min	0.832 ± 0.003 (0.834)	18.8 ± 0.3 (18.9)	0.682 ± 0.005 (0.688)	10.7 ± 0.1 (10.8)
	5 min	0.833 ± 0.005 (0.839)	19.5 ± 0.3 (20.1)	0.692 ± 0.008 (0.702)	11.2 ± 0.4 (11.8)
	10 min	0.833 ± 0.003 (0.837)	19.5 ± 0.3 (19.4)	0.662 ± 0.008 (0.675)	10.8 ± 0.2 (11.0)

Table S5 Summary of the GIWAXS parameters for the π−π stacking in the out-of-plane direction of the PBDB-T:TTTP2−5 blends.

blend[a]	out-of-plane			
	q (Å^{-1})	d (Å)	FWHM	CL (Å)
PBDB-T:TTTP2	1.71	3.67	0.226	25.0
PBDB-T:TTTP3	1.70	3.70	0.280	20.2
PBDB-T:TTTP4	1.74	3.61	0.286	19.8
PBDB-T:TTTP5	1.71	3.67	0.271	20.9

[a] The π−π stacking peak of the PBDB-T:TTTP1 blend was absent.

Notes and references

S1. S. Dai, F. Zhao, Q. Zhang, T. K. Lau, T. Li, K. Liu, Q. Ling, C. Wang, X. Lu, W. You and X. Zhan, *J. Am. Chem. Soc.*, 2017, **139**, 1336-1343.

S2. R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650-654.

S3. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.

S4. G. G. Malliaras, J. R. Salem, P. J. Brock and C. Scott, *Phys. Rev. B*, 1998, **58**, 13411-13414.

S5. U. Rau, B. Blank, T. C. M. Müller and T. Kirchartz, *Phys. Rev. Appl.*, 2017, **7**, 044016.

S6. U. Rau, *Phys. Rev. B*, 2007, **76**, 085303.