# Supporting Information

## Strategic Engineering of H-/J-Aggregation Equilibrium in Non-Fullerene Acceptors Toward High-performance Organic Photovoltaics

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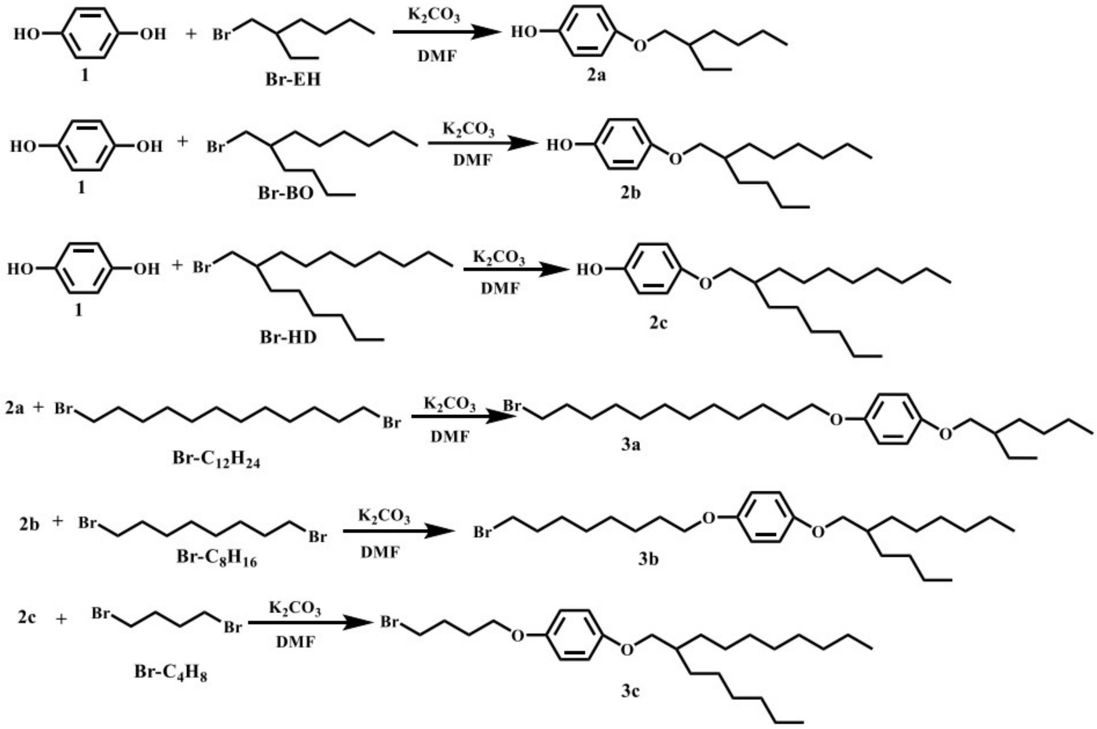
## Experimental Method

### 1.Materials

2PACz was purchased from Sigma (CNPZ20), PNDIT-F3N was purchased from eFlexPV Limited, Chloroform (anhydrous, 99.8%) was purchased from Sigma Aldrich, 1-CN was purchased from TCI, PM6 was purchased from Solarmer, Y6 was purchased from eFlexPV Limited, L8-BO was purchased from eFlexPV Limited. All materials were used directly after purchase, without any purification. SM-EH, SM-BO and SM-HD were synthesized according to following methods.



**Scheme S1.** The synthetic routes of alkyl side chain.

### Synthesis of compound 2a

Hydroquinone (compound **1**) (6 g) and potassium carbonate (15.061 g, 2 eq) were added to a 250 mL two-necked flask, then 90 mL of N, N-dimethylformamide (DMF) was added, nitrogen was pumped and vented 15 times, and the reaction was stirred in an oil bath at 50 °C for 1 h. Brominated isooctane (compound Br-EH) (11.576 g, 1.1 eq) was added to the flask at this temperature. eq) to the flask and then warmed to 60 °C with stirring overnight. The mixture was filtered to remove potassium carbonate and concentrated under reduced pressure to remove a large amount of solvent, then the concentrate was poured into 200 mL of water and extracted with dichloromethane (DCM), then dried and concentrated by rotary evaporation, and the crude product was purified by separating the impurities from the by-products on a silica gel column using dichloromethane and petroleum ether as the eluents (v/v, 1:1) to give compound **2a** (4.208 g) as a colorless liquid. $^1$H NMR (400MHz, $CDCl_3$) δ 6 .80-6.73 (m, 4H), 3.80-3.75 (m, 2H), 1.50-1.40 (m, 1H), 1.39-1.24 (m, 4H), 0.91 (q, J=7.3, 6.9 Hz, 11H).

**Synthesis of compound 2b**

To a 250 mL double-necked flask was added Compound **1** (6.059 g), potassium carbonate (15.21 g) and N, N-dimethylformamide (90 mL), and stirred in an oil bath under nitrogen atmosphere at 50 °C for 1 h. The flask was charged with 15.086 g of Compound Br-BO (2-butyl-1-bromooctane), and the temperature was raised to 60 °C with stirring overnight. The reaction mixture was filtered, and then concentrated under reduced pressure to remove a large amount of solvent, the concentrate was poured into 200 mL of water and washed and extracted three times, the combined organic phases were dried and filtered and concentrated, and then purified by silica gel column with dichloromethane and petroleum ether as eluents (v/v, 1:1) to obtain Compound **2b** (3.688 g), which was a colorless liquid.$^1$H NMR (400 MHz, $CDCl_3$) δ 6.84-6.69 (m, 4H), 3.77 (d, J=5.7 Hz, 2H), 1.73 (h, J=5.9 Hz, 1H), 1.47-1.17 (m, 17H), 0.89 (q, J=6.7 Hz, 6H).

**Synthesis of compound 2c**

Under nitrogen atmosphere, a 250 mL double-necked flask with hydroquinone (6.024 g), potassium carbonate (15.122 g) and DMF (90 mL) was placed in an oil bath and stirred at 50 °C for 1 h. The temperature was maintained at which time the bromoalkanes Br-HD, i.e., 1-bromo-2-hexyldecane (18.375 g) were added to the reaction flask, and the temperature of the oil bath was elevated to 60 °C, and the reaction was carried out overnight. After completion of the reaction, the mixture was withdrawn and filtered to collect the filtrate concentrated under reduced pressure and then washed and extracted three times, the combined organic phases were dried, filtered and concentrated, and the concentrated crude product was separated and purified by silica gel column using dichloromethane/petroleum ether as eluent (v/v,1:1) to obtain the final product compound **2c** (4.859 g). $^1$H NMR (400 MHz, $CDCl_3$) δ 6.77 (q, J= 9.1 Hz, 4H), 4.55 (s, 1H), 3.76 (d, J=5.8 Hz, 2H), 1.78-1.60 (m, 2H), 1.29 (dd, J=14.4, 7.3 Hz, 23H), 1.01-0.82 (m, 6H).

**Synthesis of compound 3a**

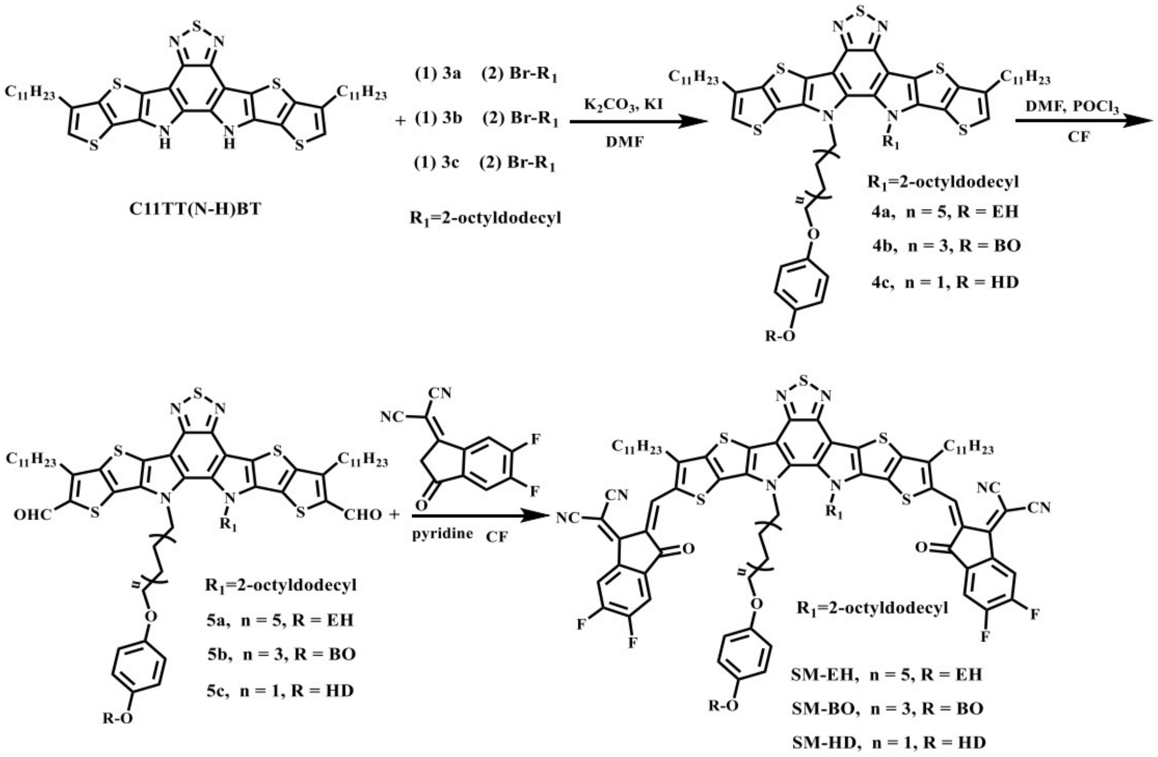
Compound **2a** (4.08 g) and potassium carbonate (5.234 g) were added to a 250 mL two-necked flask, then 60 mL DMF was added, and the air in the flask was evacuated by nitrogen pumping and venting for 12 times, and then stirred at room temperature for 1 h. To the flask was added 1,12-dibromododecane (Compound Br-$C_{12}H_{24}$) (9.316 g) under room temperature, and the flask was stirred at room temperature for 30 min and then the reaction was stirred overnight at 60 °C in an oil bath. The mixture was filtered and concentrated under reduced pressure to remove the solvent and then washed and extracted three times, the extract was dried and filtered and then evaporated to obtain the concentrated crude product, which was purified by silica gel column using dichloromethane and petroleum ether as eluents (v/v, 1:5) to obtain compound **3a** (2.052g). $^1$H NMR (600 MHz, CDCl3) δ 6.82 (s, 4H), 3.90 (t, J=6.6 Hz, 2H), 3.82-3.72 (m, 2H), 3.41 (t, J=6.9 Hz, 2H), 1.89-1.65 (m, 5H), 1.47-1.22 (m, 24H), 0.95-0.85 (m, 6H).

**Synthesis of compound 3b**

A 250 mL double-necked vial with compound **2b** (3.574 g), potassium carbonate (3.662 g) and DMF (80 mL) was stirred at room temperature under nitrogen for 1 h. To the reaction vial was added 1,8-dibromooctane (compound Br-C8H16) (5.408 g), stirred at room temperature for 0.5 h, and then the temperature was raised to 60 °C with stirring in an oil bath, and the reaction was carried out overnight. The mixture was withdrawn and filtered to collect the filtrate and concentrated under reduced pressure and then washed and extracted three times, the combined organic phases were dried and filtered and concentrated, and the concentrated crude product was separated and purified by a silica gel column using petroleum ether/dichloromethane as the eluent (v/v, 5:1) to give the final product compound **3b** (1.868 g). $^1$H NMR (400 MHz, $CDCl_3$) δ 6.82 (s, 4H), 3.90 (t, J=6.5 Hz, 2H), 3.76 (s, 2H), 3.41 (t, J=6.8 Hz, 2H), 1.86 (p, J=6.9 Hz, 5H), 1.47-1.25 (m, 24H), 0.89 (q, J=6.8 Hz, 6H).

**Synthesis of compound 3c**

To a 250 mL double-necked flask was added compound **2c** (4.672 g), potassium carbonate (4.015 g) and DMF (90 mL), stirred at room temperature for 1 h after nitrogen pumping and venting, stirred at 50 °C in an oil bath for 1 h, and the flask was charged with compound Br-C4H8 (1,4-dibromobutane) (4.703 g), stirred at room temperature for 30 min, then warmed to 60 °C and stirred overnight. The reaction mixture was filtrated, then concentrated under reduced pressure to remove a large amount of solvent, and the organic phase obtained by washing and extracting the concentrate with water was dried with anhydrous magnesium sulfate, and then concentrated under reduced pressure to obtain the crude product, which was purified by a silica gel column to give compound **3c** (2.149 g). $^1$H NMR (400 MHz, $CDCl_3$) δ 6.82 (s, 4H), 3.94 (d, J=6.0 Hz, 2H), 3.77 (d, J=5.7 Hz, 2H), 3.49 (t, J=6.7 Hz, 2H), 2.12-1.98 (m, 2H), 1.92 (dt, J=8.8, 6.0 Hz, 2H), 1.49-1.17 (m,25H), 0.88 (t, J=6.5 Hz, 6H).



**Scheme S2.** The synthetic routes of small molecule acceptor SM-EH, SM-BO, SM-HD.

**Synthesis of compound 4a**

Compound C11TT(N-H)BT (2.512 g), potassium carbonate (3.253 g), potassium iodide (1.116 g) and N, N-dimethylformamide (90 mL) were added to a 250 mL double-necked vial, filled with nitrogen to exclude air, and stirred at 60 ℃ for 1.5 h. To the vial was added Compound **3a** (2.032 g), and the system was warmed up to 90 ℃ and stirred for 24 hours. Then 1-bromo-2-octyldodecane (Compound Br-R$_1$) (7.282 g) was added to the system and stirring was continued at this temperature for 24 hours. The reaction mixture was filtered to remove potassium carbonate and concentrated under reduced pressure, then washed and extracted to dryness, and evaporated to give the concentrated crude product, which was purified by a silica gel column (petroleum ether/dichloromethane, v/v,6:1) to give the orange-colored solid compound **4a** (1.37 g).$^1$H NMR (600 MHz, CDCl$_3$) δ 7.00 (s, 2H), 6.80 (s, 4H), 4.63-4.54 (m). 4.63-4.54 (m, 4H), 3.87 (t, J=6.6 Hz, 2H), 3.77 (dd, J=5.8, 2.6 Hz, 2H), 2.80 (td, J=7.9, 3.2 Hz, 4H), 1.91-1.81 (m, 6H), 1.70 (dt, =13.4, 6.7 Hz, 3H), 1.49 (dd , J=14.0, 7.1 Hz, 1H), 1.43 (q, J=5.1, 3.2 Hz, 8H), 1.37 (t, J=7.4 Hz, 8H), 1.32-1.24 (m, 39H), 1.17 (ddd, J=15.0, 11.5, 6.7 Hz, 12H), 1.04 (dt, J=9.1, 7.0 Hz, 7H), 0.97 (t, J=7.2 Hz, 4H), 0.93-0.85 (m, 24H), 0.82 (t, J=7.3 Hz, 4H).

**Synthesis of compound 4b**

Compound C11TT(N-H)BT (2.301 g), potassium carbonate (2.986 g), potassium iodide (0.992 g) were added to a 250 mL double-necked flask, and the reactants were dissolved with 80 mL of N,N-dimethylformamide, and the reaction flask was pumped and deflated 18 times and then stirred in an oil bath at 60 °C for 1.5 h. To the double-necked flask was added Compound **3b** (1.868 g), and the temperature was raised to 90 °C for 24 h. Then 6.67 g of compound Br-$R_1$ (1-bromo-2-octyldodecane) was added and stirred for 24 h. The mixture was filtered to remove the carbon dioxide. The mixture was filtered to remove potassium carbonate and concentrated under reduced pressure to remove a large amount of solvent, then the concentrate was poured into 200 mL of water and extracted with dichloromethane, the extract was dried, filtered and concentrated under reduced pressure to obtain the crude product, which was purified by separating the impurities and by-products through a silica gel column using dichloromethane and petroleum ether as the eluent (v/v,1:4) to obtain the orange-colored compound **4b** (1.648 g). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.00 (d, J=4.2 Hz, 2H), 6.81-6.78 (m, 2H), 6.78-6.75 (m, 2H), 4.65-4.56 (m, 4H), 3.76 (t, J=5.9 Hz, 4H), 2.83-2.79 (m, 4H), 1.91- 1.82 (m, 6H), 1.46-1.41 (m, 6H), 1.37 (qd, J=7.1, 2.2 Hz, 6H), 1.29 (qq, J=16.4, 9.2, 7.3 Hz, 47H), 1.16 (dtd, J=13.5, 9.6, 9.1, 6.2 Hz, 11H), 1.08-0.96 (m 12H), 0.89 (dq, J=13.6, 6.9 Hz, 24H), 0.83 (t, J=7.3 Hz, 4H).

**Synthesis of compound 4c**

A 250 mL reaction flask containing compound C11TT(N-H)BT (1.963 g), potassium carbonate (2.542 g), potassium iodide (0.872 g) and DMF (70 mL) was stirred at 60 °C for 1.5 h under nitrogen protection, then compound **3c** (1.604 g) dissolved in 10 mL of DMF was added, and stirred at 90 °C for 24 h. After that condition, 1-bromo-2-octyldodecane (5.69 g) was added and stirred for 24 h at 90 °C, keeping this condition. The mixture was concentrated under reduced pressure, extracted 3 times with DCM and dried and extracted, the filtrate was concentrated under reduced pressure and the crude product was purified by petroleum ether/dichloromethane (v/v, 6:1) through silica gel column to give 1.762 g of compound **4c**. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.01 (s, 2H), 6.73-6.57 (m, 4H), 4.75 (t, J= 7.3 Hz, 2H), 4.58 (d, J=7.7 Hz, 2H), 3.77-3.62 (m, 4H), 2.88-2.73 (m, 4H), 2.08 (h, J=7.6, 7.1 Hz, 3H), 1.86 (t, J=7.6 Hz, 4H), 1.53 (t, J=7.0 Hz, 2H), 1.42 (dt J=22.9, 7.4 Hz, 10H), 1.34-1.24 (m, 54H), 1.17 (q, J=7.4 Hz, 6H), 1.06-0.93 (m, 12H), 0.88 (td, J=6.9, 3.1 Hz, 24H), 0.83 (t, J=7.3 Hz, 4H).

**Synthesis of compound 5a**

Compound **4a** (1.01 g) was added to a 500 mL two-necked flask, then ultra-dry N,N-dimethylformamide (8.5 mL) and chloroform (60 mL) were added, and the reaction system was stirred in an ice-water bath with nitrogen and air exhaust, and then phosphorus triclopyr (4.5 mL) was added dropwise in the same conditions, stirred in the ice-water bath for 30 min, and then heated up to 60 °C to stir the reaction overnight.

The reaction was quenched by adding saturated potassium carbonate solution (170 mL) to the vial at 0 °C, stirred until the solution changed color, washed and extracted and dried, then concentrated under reduced pressure
, and purified by column chromatography (eluent dichloromethane/petroleum ether, v/v=1/1) to obtain compound **5a** (0.787 g) as a red solid. $^1$H NMR (600 MHz, $CDCl_3$) δ 10.13 (d, J=3.1 Hz, J=3.1 Hz, $^1$H NMR) δ 10.13 (d, J=3.1 Hz, J=3.1 Hz, J=3.1 Hz, J=3.1 Hz). J=3.1 Hz, 2H), 6.80 (s, 4H), 4.70-4.55 (m, 4H), 3.87 (t, J=6.6 Hz, 2H), 3.77 (dd, J=5.8, 2.6 Hz, 2H), 3.19 (t, J=7.8 Hz, 4H), 1.91 (dp, J=12.7, 7.2 Hz, 6H), 1.69 (tq, J=15.2, 9.1, 8.0 Hz, 4H), 1.50-1.41 (m, 7H), 1.37 (td, J=8.3, 7.9, 4.2 Hz, 8H), 1.32-1.23 (m, 34H), 1.21-1.09 (m, 18H), 1.06-1.00 (m, 7H), 0.99-0.84 (m , 29H), 0.81 (t, J=7.3 Hz, 4H).

**Synthesis of compound 5b**

To a 250 mL two-necked flask was added compound **4b** (0.928 g), anhydrous DMF (7.5 mL), followed by chloroform (60 mL), nitrogen protection and air venting, and stirring in an ice-water bath while trichlorophosphorus (4 mL) was added slowly dropwise, followed by stirring for 30 min, and the mixture was heated at reflux and reacted at this temperature overnight. The reaction was quenched by the addition of saturated potassium carbonate solution (140 mL) under the condition of ice bath and stirred until the solution turned into orange color and the quench was complete. The crude product was extracted twice with dichloromethane in water, dried and concentrated under reduced pressure. The crude product was purified by column chromatography to afford compound **5b** (0.463 g).$^1$H NMR (400 MHz, $CDCl_3$) δ 10.12 (d, J=6.4 Hz, 2H), 6.77 (q, J=9.2 Hz, 4H), 4.75-4.53 (m, 4H), 3.82-3.72 (m, 4H), 3.16 (td, J=7.8, 4.4 H). 7.8, 4.4 Hz, 4H), 1.92 (h, J=8.2, 7.8 Hz, 6H), 1.78-1.66 (m, 3H), 1.60 (p, J=6.7 Hz, 2H), 1.45 (q, J=7.6 Hz, 6H), 1.29 (dd, J=14.6, 6.1 Hz, 58H), 1.17-1.09 (m 6H), 0.99-0.85 (m, 28H), 0.84-0.76 (m, 7H).

**Synthesis of compound 5c**

Compound **4c** (1.018 g) was added to a 500 mL two-necked flask, 8 mL of anhydrous DMF was added, 40 mL of chloroform was added, and the reaction mixture was stirred in an ice-water bath by charging nitrogen to exclude the air for 10 min, and then phosphorous trichloride (4.6 mL) was added dropwise at this condition, and then stirred for 30 min at this temperature, and the mixture was heated to reflux stirring and the reaction was carried out overnight. The reaction was burst by adding saturated potassium carbonate solution (140 mL) to the reaction system at 0 °C, stirred until the solution changed color (about 8 h), the organic phase was collected by washing and extraction, dried and filtered, and the solution was further concentrated under reduced pressure and purified by column chromatography to give a red solid as compound **5a** (0.452 g). $^1$H NMR (600 MHz, $CDCl_3$) δ 10.14 (s 2H), 6.71-6.54 (m, 4H), 4.79 (t, J=7.4 Hz, 2H), 4.61 (d, J=7.8 Hz, 2H), 3.72 (dd, J=8.2, 5.7 Hz, 4H), 3.19 (t, J=7.8 Hz, 4H), 2.07 (dt, J=22.9, 6.9 Hz, 3H), 1.92 (dt, J=15.4, 7.8 Hz, 4H), 1.56 (d, J=7.6 Hz, 2H), 1.47 (q, J=7.9 Hz, 4H), 1.38 (p, J=6.9 Hz, 6H), 1.27 (dd, J=13.7, 5.8 Hz, 50H), 1.15 (dtq, J=15.9, 8.1, 4.0. 3.5 Hz, 8H), 1.02 (ddd, J=11.7, 7.5, 4.1 Hz, 7H), 0.96 (dd, J=12.4, 5.5 Hz, 5H), 0.91-0.85 (m, 24H), 0.81 (t, J=7.3 Hz, 4H).

**Synthesis of compound SM-EH**

Compound **5a** (0.207 g) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile (0.164 g), and chloroform (20 mL) were added to a 100 mL two-necked flask, and the flask was evacuated by pumping and venting 20 times, and ultra-dry pyridine (0.8 mL) was added slowly by dropwise addition while stirring at 0 °C, and the reaction was stirred under these conditions for 1 The reaction was stirred overnight at 60 °C in an oil bath. The reaction was extracted twice with water-washed dichloromethane, and the organic phase was dried and filtered, concentrated under reduced pressure, separated and purified by a short silica gel column using petroleum ether/dichloromethane (v/v,2/1) as eluent, and then further purified by back-dropping, and the drying chamber was placed at 60 °C overnight to obtain a dark blue solid, i.e., the small molecule receptor **SM-EH** (0.157 g). $^1$H NMR (600 MHz, $CDCl_3$ ) δ 8.91 (s, 1H), 8.64 (s, 1H), 8.49 (dd, J=9.8, 6.4 Hz, 1H), 8.41 (dd, J=9.8, 6.3 Hz, 1H), 7.60 (dt, J=20.6, 7.3 Hz, 2H), 6.81-6.70 (m, 4H), 4.77 (t, J=8.3 Hz, 2H ), 4.62 (d, J=7.8 Hz, 2H), 3.84-3.70 (m, 4H), 3.01 (dt, J=29.5, 8.1 Hz, 4H), 2.30 (s, 2H), 2.01 (p, J=7.0 Hz, 1H), 1.81 (q, J=7.8 Hz, 2H), 1.76-1.65 (m, 7H), 1.58 (s, 6H 1.58 (s, 6H), 1.48 (dq, J=18.0, 5.8, 4.1 Hz, 7H), 1.39 (dtt, J=15.1, 7.7, 4.0 Hz, 9H), 1.35-1.22 (m, 42H), 1.20-1.15 (m, 2H), 1.08 (dp, J=18.4, 6.8 Hz, 10H), 0.93-0.85 (m, 20H), 0.80 (t, J=7.3 Hz, 4H), 0.75 (t, J=7.3 Hz, 4H).

**Synthesis of compound SM-BO**

Compound **5b** (0.14 g) and fluorinated end-group (2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile) (0.134 g) were added to a 100 mL two-necked flask and dissolved in 20 mL of chloroform, and then stirred at 0 °C with the nitrogen evacuated to remove the air from the reaction system, and then pyridine (0.5 mL) was slowly added dropwise at 0 °C under the condition, and then the reaction mix was stirred for 1 hour. Then the reaction mixture was heated to reflux and stirred overnight. After the reaction was completed, the mixture was poured into 100 mL of water and extracted with dichloromethane, and the extracted lower organic liquid was dried and filtered by magnesium sulfate, and then the solvent was removed by decompression, and purified by column chromatography using petroleum ether/dichloromethane (v/v,2/1) as eluent, and in order to further improve the purity, the product was centrifuged with methanol back-drop for 3 times, and then dried in an oven at 60 °C to obtain **SM-BO** (0.135 g). $^1$H NMR (600 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.69 (s, 1H), 8.51 (dd, J=9.8, 6.4 Hz, 1H), 8.40 (dd, J=9.8, 6.4 Hz, 1H), 7.61 (dd, J=18.2, 7.3 Hz, 2H), 6.72-6.61 (m, 4H), 4.79 (t, J=4H), 6.72-6.61 (m, 4H). 4.79 (t, J=8.2 Hz, 2H), 4.64 (d, J=7.8 Hz, 2H), 3.79-3.71 (m, 4H), 3.05 (dt, J=26.8, 8.1 Hz, 4H), 2.23 (d, J=13.5 Hz, 2H), 2.05-2.00 (m, 1H), 1.84-1.69 (m, 8H) , 1.49 (q, J=7.5, 7.1 Hz, 10H), 1.33-1.23 (m, 50H), 1.18 (p, J=7.1 Hz, 4H), 1.14-1.04 (m, 11H), 0.88 (tt, J=7.1, 3.8 Hz, 20H), 0.78 (dt, J=32.3, 7.2 Hz, 10H).

**Synthesis of compound SM-HD**

Compound **5c** (0.2 g) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile (0.189 g) were added to a 100 mL reaction flask, chloroform (20 mL) was added and placed in an ice-water bath with stirring, and ultra-dry pyridine (0.7 mL) was added drop-wise, which at this time was 0 °C to maintain this state condition with stirring for 1 h. Then the reaction was heated in oil bath reflux, the reaction stirred overnight. After washing and extracting, it was dried and concentrated in vacuum. The preliminary product was purified by column chromatography, and the purity was further improved by back-drop centrifugation in methanol for three times to obtain the final product, **SM-HD** (0.19 g), which was a small molecule receptor with a dark blue color.$^1$H NMR (600 MHz, $CDCl_3$) δ 8.90 (s, 1H), 8.52 (dt, J=9.7, 5.7 Hz, 2H), 8.38 (dd, J=9.8, 6.3 Hz, 1H), 8.38 (dd, J=9.8, 6.3 Hz, 2H), and 8.38 (dd, J=9.8, 6.3 Hz, 2H). 6.3 Hz, 1H), 7.63 (t, J=7.4 Hz, 1H), 7.37 (t, J=7.3 Hz, 1H), 6.98-6.85 (dd, J=8.8,8.5 Hz, 4H), 4.95 (s, 2H), 4.63 (d, J=7.7 Hz, 2H), 4.24 (s, 2H), 3.70 (d, J=5.7 Hz, 2H), 2.97 (dt, J=34.5, 8.1 Hz, 4H), 2.61-2.52 (m, 2H), 2.30-2.22 (m, 2H), 2.00-1.93 (m, 1H), 1.84-1.62 (m, 6H), 1.54-1.41 (m, 5H), 1.36-1.22 (m, 57H), 1.16 (p, J=7.7 Hz, 2H), 1.16 (p, J=7.7 Hz, 2H), 1.16 (p, J=7.7 Hz, 2H), 1.16 (p, J=7.7 Hz, 2H) 1.16 (p, J=7.2 Hz, 3H), 1.06 (ddq, J=22.9, 15.3, 7.3 Hz, 10H), 0.90-0.84 (m, 20H), 0.77 (dt, J=38.0, 7.3 Hz, 10H).

## 2.Measurements:

### Optical measurements:

The UV-visible spectrum was taken in UV-VIS-NIR spectrophotometer (AGILENT Cary 7000). Steady state photoluminescence (PL) spectra were acquired by a spectrometer (FLS1000). Fluorescence decay dynamics are acquired by TCSPC. The excitation wavelength is 400 nm, with laser power of 76 μW.

### Cyclic voltammetry (CV):

CV measurement was carried out on a Zahner IM6e electrochemical workstation with three electrodes, employing a glassy carbon disc as the working electrode, Pt wire as the counter electrode, and Ag/Ag+ electrode as the reference electrode at a scanning rate of 100 mV/s under a nitrogen atmosphere. Tetrabutylammoniumhexafluorophosphate (Bu4NPF6, 0.1 mol/L) dissolved in acetonitrile (HPLC grade) was adopted as the supporting electrolyte. PM6 and two acceptors were drop-cast the electrode from chloroform solutions to form thin films. Potentials were referenced to the ferrocene/ferroncenium (Fc/Fc+) redoxcouple by using ferrocene as the external standards in acetonitrile solutions.

### Atomic force microscopy (AFM):

AFM height and phase images were taken by Bruker Multimode 8. The samples for AFM were fabricated on ITO.

### Transmission electron microscopy (TEM):

TEM and DF-TEM images were recorded by using transmission electron microscope (HT-7700, JEOL 2100 and JEOL 2100F). The samples for TEM were fabricated on ITO.

### Grazing incidence wide-angle X-ray scattering (GIWAXS) characterization:

GIWAXS patterns were collect on XEUSS SAXS/WAXS system with incidence angle of 0.2o, the samples for GIWAXS were fabricated on silicon substrate.

### Devices fabrication and testing:

The device with a conventional glass/ITO/2PACz/D:A/PNDIT-F3N/Ag. The prepatterned ITO glasses were cleaned by detergent, deionized water and isopropyl alcohol in ultrasonic bath for 30 minutes, respectively. After blow-drying by high-purity nitrogen, the ITO-coated glass substrates were treated by UV-ozone for 25 minutes.

The preparation method for the 2PACz hole transport layer is as follows:

1.Transfer the processed ITO-coated glass to the $N_2$-filled glove box.

2.2PACz was dissolved in EtOH with concentration of 0.3mg/mL.

3.The solution was deposition on ITO by spin coating at 3000 rpm for 30 seconds, and thermal annealed at 100°C for 5 min.

4.To remove any potential residual contaminants or improve surface wettability, the 2PACz-coated substrate was rinsed by spin-coating EtOH (30 μL) at 4000 rpm for 30 seconds.

5.Followed by a brief drying step.

Then the active layer was deposition by spin coating method in $N_2$-filled glove box. The active layer films were prepared from chloroform (CF) solvent with 0-1% 1-chloronaphthalene (1-CN) or 8-12mg/mL DCBB used as additive. The concentration of donor is from 6 to 8 mg/ml, the ratio of donor and acceptor was 1:1.2. The speed of spin coating was adjusted ranging from 4500 to 3000 mm/s to optimized. Subsequently, the active layers were heated at 110°C for 10 min. The methanol solution (contain 0.5% acetic acid) of PNDIT-F3N (0.5 mg/ml) was spin-coating on the active layer at 2600 rpm. Finally, 100 nm Ag layer was thermally deposited under the vacuum condition of $1\text{x}10^{-4}$ Pa as top argentum electrode. The typical active area is 4.0 $\text{mm}^2$.

Device current density-voltage (*J-V*) characteristics were recorded using the Keithley 2400 Source Measure Unit. The photocurrent was tested under AM 1.5G illumination at 100 $\text{mWcm}^{-2}$ by a solar simulator (SCISUN, Lightsky Technology Co). The forward scan was adopted to test the J-V curves, the scan step is 0.02 V and the delay time is 1ms. The scan mode is sweep. The light intensity was calibrated by standard Si solar cell (LRC-KG2, Lightsky Technology Co). The EQE spectra were measured by using a solar-cell spectral-response measurement system (QE-R3011, EnliTech).

**Space-charge-limited-current (SCLC) mobility measurement:**

Single carrier devices were fabricated, and the dark *J-V* characteristics measured in the space charge limited (SCLC) regime following the references. The structure of hole only devices was ITO/2PACz/active layer/$MoO_3$ (5 nm)/Ag(100nm). For the electron only devices, the structure was ITO/ZnO/active layer/PNDIT-F3N/Ag (100 nm) where the Ag were evaporated. The J-V characteristics of both hole-only and electron-only devices can fit to SCLC relation:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu V^2}{8d^3} \qquad (1)$$

Where J is the current density, d is the film thickness of the active layer, μ is the charge carrier mobility, $\varepsilon_r$ is the relative dielectric constant of the transport medium, and $\varepsilon_0$ is the permittivity of free space.

**Femtosecond transient absorption (TA) spectrum:**

A Ti: sapphire amplifier (Coherent Co.) supplied laser beams centered at 800 nm with pulse duration of 25 fs, pulse repetition rate of 1 kHz, and a maximum pulse energy of 4 mJ. The output of the amplifier was split into two streams of pulses with a beam splitter. Residual stream was directed into an ultrafast spectroscopic system (Helios pump-probe system (Ultrafast Systems) to generate the white light continuum probe beam. The film samples for TA measurements are prepared on the quartz plates. The TA samples are annealed in nitrogen glove box at 110°C for 10 min.

**Density functional theory (DFT) calculations：**

Density functional theory (DFT) calculations were carried out using Gaussian 09 programs[1] throughout this manuscript. Geometric optimizations were performed using the B3LYP functional. The standard 6-31G(d) basis set for all atoms was used.

**Table S1** The summarized optical properties and energy level of materials.

| Materials | $\lambda^{sol}_{max}$ (nm) | $\lambda^{film}_{max}$ (nm) | $\lambda^{film}_{shoulder}$ (nm) | $\lambda^{film}_{onset}$ (nm) | $E^{g}_{opt}$ (eV) | HOMO (eV) | LUMO (eV) | $E^{g}_{CV}$ (eV) |
|---|---|---|---|---|---|---|---|---|
| PM6 | 577 | 617 | - | 777 | 1.596 | -5.33 | -3.51 | 1.81 |
| Y6 | 733 | 831 | 745 | 1001 | 1.239 | -5.62 | -3.94 | 1.68 |
| SM-EH | 733 | 824 | 722 | 989 | 1.254 | -5.68 | -3.95 | 1.73 |
| SM-BO | 733 | 820 | 718 | 971 | 1.278 | -5.70 | -3.95 | 1.75 |
| SM-HD | 733 | 801 | 717 | 961 | 1.290 | -5.71 | -3.99 | 1.72 |

**Table S2** Summarized photovoltaic parameters of PM6:SMs OSCs

| Active layer | $V_{OC}$ (V) | $J_{SC}$ (mA cm$^{-2}$) | FF (%) | PCE (%) |
|---|---|---|---|---|
| PM6:SM-EH | 0.931 | 19.8 | 57.82 | 10.65 |
| PM6:SM-BO | 0.938 | 20.4 | 62.13 | 11.89 |
| PM6:SM-HD | 0.939 | 21.1 | 58.54 | 11.60 |

**Table S3** The summarized parameters of devices photovoltaic parameters with different weight ratio.

| Materials(A2) | PM6:Y6:A2 | $V_{OC}$ (V) | $J_{SC}$ (mA·cm$^{-2}$) | FF (%) | PCE (%) |
|---|---|---|---|---|---|
| - | 1:1.2 | 0.838 | 26.3 | 77.09 | 16.99 |
| SM-EH | 1:1.1:0.1 | 0.839 | 27.2 | 77.79 | 17.86 |
|  | 1:1:0.2 | 0.841 | 26.4 | 74.50 | 16.54 |
|  | 1:0:1.2 | 0.931 | 19.8 | 57.82 | 10.65 |
| SM-BO | 1:1.1:0.1 | 0.844 | 27.5 | 77.82 | 18.06 |
|  | 1:1:0.2 | 0.838 | 26.7 | 76.14 | 17.03 |
|  | 1:0:1.2 | 0.938 | 20.4 | 62.13 | 11.89 |
| SM-HD | 1:1.1:0.1 | 0.846 | 27.2 | 77.45 | 17.82 |
|  | 1:1:0.2 | 0.842 | 26.5 | 75.97 | 16.95 |
|  | 1:0:1.2 | 0.939 | 22.1 | 58.54 | 12.14 |

**Table S4** The summarized parameters of devices photovoltaic parameters with different active layer thickness.

| Active layer | Thickness (nm) | $V_{OC}$ (V) | $J_{SC}$ (mA cm$^{-2}$) | *FF* (%) | PCE (%) |
|---|---|---|---|---|---|
| PM6:Y6:SM-BO | 160 | 0.833 | 27.2 | 74.16 | 16.80 |
| | 140 | 0.836 | 27.6 | 77.33 | 17.86 |
| | 120 | 0.841 | 27.6 | 77.40 | 18.03 |
| | 100 | 0.844 | 27.5 | 77.82 | 18.06 |
| | 80 | 0.844 | 27.2 | 77.65 | 17.76 |
| | 60 | 0.845 | 26.5 | 76.93 | 17.23 |
| PM6:L8-BO:SM-BO | 160 | 0.881 | 28.1 | 78.82 | 19.37 |
| | 140 | 0.884 | 27.9 | 79.06 | 19.22 |
| | 120 | 0.891 | 27.5 | 79.10 | 19.38 |
| | 100 | 0.893 | 28.1 | 79.23 | 19.88 |
| | 80 | 0.898 | 28.1 | 79.21 | 19.98 |
| | 60 | 0.888 | 27.2 | 79.42 | 19.18 |

**Efficiency-distributed histograms of the binary and ternary devices of PM6:Y6 yields.**

Error bars represent standard error of the mean (n = 20). Box-and whisker plot showing the distribution of data. The minimum value is indicated by the lower whisker, while the maximum value is shown by the upper whisker. The box represents the interquartile range, with the first quartile at the lower edge, the median as the line inside the box, and the third quartile at the upper edge. Outliers are represented as individual points beyond the whiskers.

**Table S5** The summarized parameters of optimal binary and ternary devices.

| Active Layer | $J_{ph}$ (mA/cm$^2$) | $J_{max}$ (mA/cm$^2$) | $J_{sat}$ (mA/cm$^2$) | $\eta_{diss}$ | $\eta_{col}$ |
|---|---|---|---|---|---|
| PM6:Y6 | 27.00 | 23.72 | 27.54 | 0.9806 | 0.8614 |
| PM6:Y6:SM-EH | 26.43 | 23.61 | 27.00 | 0.9789 | 0.8743 |
| PM6:Y6:SM-BO | 27.76 | 25.37 | 28.29 | 0.9812 | 0.8966 |
| PM6:Y6:SM-HD | 26.56 | 24.11 | 27.27 | 0.9742 | 0.8841 |

**Table S6** The charge mobility of the active layer.

| Active Layer | $\mu_h$ ($10^{-4}$*cm$^2$V$^{-1}$s$^{-1}$) | $\mu_e$ ($10^{-4}$*cm$^2$V$^{-1}$s$^{-1}$) | $\mu_h$:$\mu_e$ |
|---|---|---|---|
| PM6:Y6 | 6.2 | 3.5 | 1.77:1 |
| PM6:Y6:SM-EH | 6.7 | 4.7 | 1.43:1 |
| PM6:Y6:SM-BO | 11.5 | 10.7 | 1.07:1 |
| PM6:Y6:SM-HD | 7.6 | 8.1 | 0.94:1 |

**Table S7** Summarized photovoltaic parameters of binary and ternary OSCs for PM6:BTP-ec9-based and PM6:N3-based devices.

| Active layer | $V_{OC}$ (V) * | $J_{SC}$ (mA·cm$^{-2}$) * | $J_{cal}$ (mA·cm$^{-2}$) | FF (%)* | PCE (%)* |
|---|---|---|---|---|---|
| PM6:ec9 | 0.856<br>(0.854±0.005) | 28.3<br>(28.2±0.1) | 27.47 | 77.17<br>(77.15±0.32) | 18.69<br>(18.52±0.46) |
| PM6:ec9:SM-BO | 0.864<br>(0.8356±0.003) | 28.9<br>(28.7±0.2) | 27.78 | 77.81<br>(77.65±0.16) | 19.45<br>(19.20±0.31) |
| PM6:N3 | 0.850<br>(0.847±0.004) | 27.20<br>(27.1±0.1) | 26.29 | 77.45<br>(76.65±0.80) | 17.60<br>(17.25±0.35) |
| PM6:N3:SM-BO | 0.856<br>(0.853±0.003) | 27.80<br>(27.6±0.2) | 26.71 | 78.00<br>(77.32±0.68) | 18.52<br>(18.10±0.42) |

* Average PCE and its standard deviation (in parentheses) are calculated from over 20 independently fabricated devices for each condition.

**Energy Loss Analysis.**

The total energy loss ($E_{\mathrm{loss}}$) of photovoltaic devices can be decomposed into three components based on the following derivation Equation (1)：

$$E_{loss} = E_g - qV_{OC}\#$$
$$= \left(E_g - qV_{OC}^{SQ}\right) + \left(qV_{OC}^{SQ} - qV_{OC}^{rad}\right) + \left(qV_{OC}^{rad} - qV_{OC}\right)\#$$
$$= \Delta E_1 + \Delta E_2 + \Delta E_3\#(1)$$

where $E$g denotes the photovoltaic bandgap of the active layer films, which was estimated from the derivative curves of the EQE spectra (d$EQE$/d$E$). $\Delta E_1$ represents the intrinsic radiative energy loss governed by the Shockley-Queisser (SQ) limit. $\Delta E_2$ corresponds to the additional radiative loss below the bandgap, which arises from the nonstep-function absorption characteristics of the active layer

The third component $\Delta E_3$ is the non-radiative energy loss, which was calculated using Equation (2) based on electroluminescence (EL) measurements ：

$$\Delta E_3 = - k_B T ln\left(EQE_{EL}\right)\#(2)$$

Here, $k_B$ is the Boltzmann constant, T is the absolute temperature (298 K), and $EQE_{EL}$ is the external quantum efficiency of electroluminescence.

**Table S8.** Detailed energy loss of these binary and ternary devices.

| Devices | $E_g$ (eV) | $V_{OC}$ (V) | $V_{loss}$ (V) | $V_{OC}^{SQ}$ (V) | $V_{OC}^{rad}$ (V) | $\Delta E_1$ (eV) | $\Delta E_2$ (eV) | $\Delta E_3$ (eV) | $EQE_{EL}$ (%) |
|---|---|---|---|---|---|---|---|---|---|
| PM6:Y6 | 1.398 | 0.838 | 0.56 | 1.137 | 1.074 | 0.261 | 0.063 | 0.236 | 0.0108 |
| PM6:Y6:SM-EH | 1.401 | 0.839 | 0.562 | 1.14 | 1.075 | 0.261 | 0.065 | 0.236 | 0.0108 |
| PM6:Y6:SM-BO | 1.404 | 0.844 | 0.56 | 1.143 | 1.078 | 0.261 | 0.065 | 0.234 | 0.0117 |
| PM6:Y6:SM-HD | 1.406 | 0.846 | 0.56 | 1.144 | 1.079 | 0.262 | 0.065 | 0.233 | 0.0122 |

**Surface Tension Calculation:**

The contact angles of two different solvent (water and Glycerol) on neat films of polymer donor PM6, three small molecular acceptors SM-EH, SM-BO, SM-HD and Y6 were used to calculate the surface tension by Wu model. The detailed calculation process is described below:

$$\gamma_{Water}(\cos\theta+1)=\frac{4\gamma_{Water}^{d}\gamma^{d}}{\gamma_{Water}^{d}+\gamma^{d}}+\frac{4\gamma_{Water}^{p}\gamma^{p}}{\gamma_{Water}^{p}+\gamma^{p}}$$

$$\gamma_{Glycerol}(\cos\theta+1)=\frac{4\gamma_{Glycerol}^{d}\gamma^{d}}{\gamma_{Glycerol}^{d}+\gamma^{d}}+\frac{4\gamma_{Glycerol}^{p}\gamma^{p}}{\gamma_{Glycerol}^{p}+\gamma^{p}}$$

$$\gamma=\gamma^{d}+\gamma^{p}$$

Where is the contact angle of films and $\gamma$ is the surface tension of the films which is the sum of dispersion ($\gamma_d$) and polarity ($\gamma_p$) components. The $\gamma_{Water}$ and $\gamma_{Glycerol}$ are the surface tensions of the water and glycerol. The Compatibility between different materials can be deduced from the empirical formula of Flory-Huggins parameter.

$$\chi\propto\left(\sqrt{\gamma_A}-\sqrt{\gamma_B}\right)^2$$

To investigate the location of three small molecular acceptors in the ternary blend, the wetting coefficient ($\omega$) of the SM-EH, SM-BO, SM-HD is calculated following the equation of Young's equation:

$$\omega_{A_2}=\frac{\gamma^{A_1/A_2}-\gamma^{D/A_2}}{\gamma^{D/A_1}}$$

Where $\gamma_{A1/A2}$ is the interfacial tension between A1 and A2. If $\omega_{A2}>1$, component A2 will lie in the domain of component D; if $\omega_{A2}<-1$, component A2 will lie in the domain of component A1; if $-1<\omega_{A2}<1$, component A2 will be located at the interfaces of D and A1. The $\gamma_{A1/A2}$ can be calculated according to the Neumann equation:

$$\gamma^{A_1/A_2}=\gamma^{A_1}+\gamma^{A_2}-2\sqrt{\gamma^{A_1}\gamma^{A_2}}e^{[-\beta(\gamma^{A_1}-\gamma^{A_2})^2]}$$

Where $\beta$ is 0.000115 $m^4mJ^{-2}$.

**Table S9** Summarized parameters for the surface energy characteristics of the films.

| Materials | $\theta_{water}$ (deg) | $\theta_{Glycerol}$ (deg) | γ (mN $m^{-1}$) | $\chi_{D\text{-}A}$ | $\chi_{A1\text{-}A2}$ | $\omega_{A2}$ |
|---|---|---|---|---|---|---|
| PM6 | 103.5 | 93.3 | 15.365 | - | - | - |
| Y6 | 93.2 | 80.2 | 24.023 | 0.963 | - | - |
| SM-EH | 100.2 | 86.4 | 21.506 | 0.515 | 0.070 | -0.441 |
| SM-BO | 99.5 | 88.1 | 18.671 | 0.161 | 0.100 | 0.211 |
| SM-HD | 101.5 | 89 | 19.052 | 0.198 | 0.002 | -0.077 |

**Table S10** The summarized crystalline parameters of neat and blend film.

| Materials | (100)IP | | | | (010)OOP | | | |
|---|---|---|---|---|---|---|---|---|
| | q (Å$^{-1}$) | d-spacing (Å) | FWHM (Å$^{-1}$) | CCL (Å) | q (Å$^{-1}$) | d-spacing (Å) | FWHM (Å$^{-1}$) | CCL (Å) |
| SM-EH | 0.225 | 27.966 | 0.045 | 124.943 | 1.697 | 3.703 | 0.245 | 23.095 |
| SM-BO | 0.229 | 27.473 | 0.053 | 106.111 | 1.740 | 3.611 | 0.245 | 23.085 |
| SM-HD | 0.246 | 25.584 | 0.060 | 94.651 | 1.784 | 3.521 | 0.258 | 21.947 |
| PM6:Y6 | 0.299 | 21.034 | 0.055 | 103.108 | 1.740 | 3.611 | 0.254 | 22.223 |
| PM6:Y6:SM-EH | 0.304 | 20.662 | 0.061 | 92.342 | 1.740 | 3.611 | 0.263 | 21.480 |
| PM6:Y6:SM-BO | 0.288 | 21.796 | 0.077 | 73.413 | 1.740 | 3.611 | 0.265 | 21.329 |
| PM6:Y6:SM-HD | 0.293 | 21.411 | 0.082 | 69.311 | 1.740 | 3.611 | 0.276 | 20.461 |

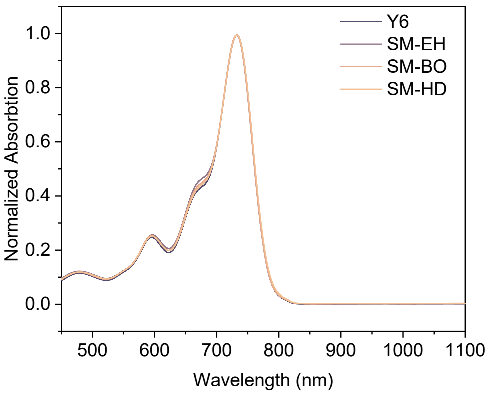


**Figure S1** The UV-vis absorption spectra of materials in solution.

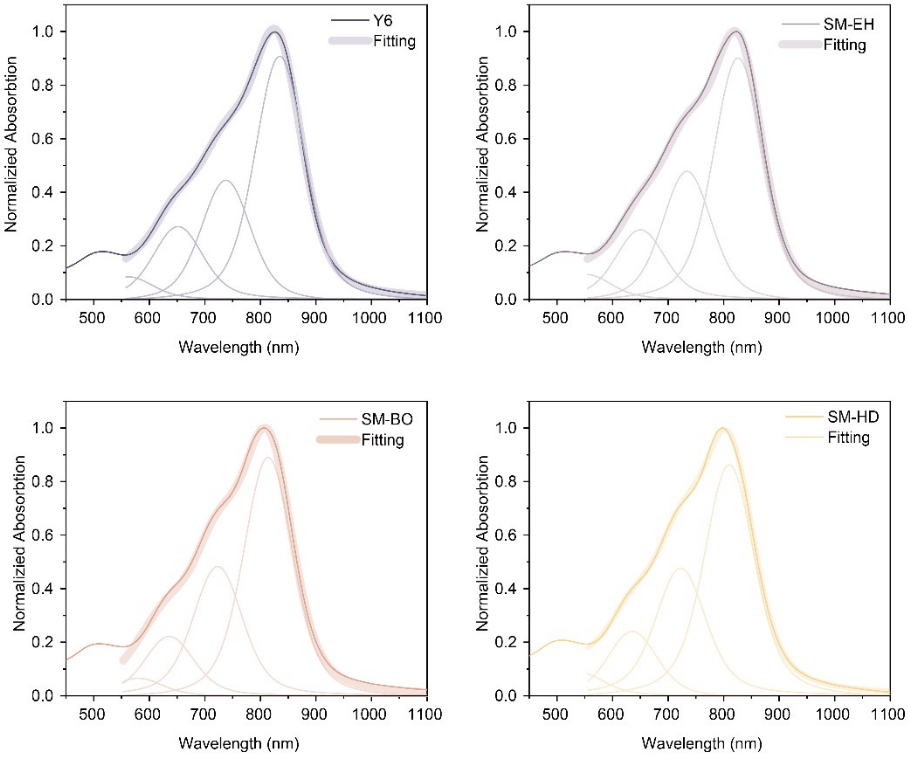


**Figure S2** Theoretical absorption spectra with Gaussian curves.

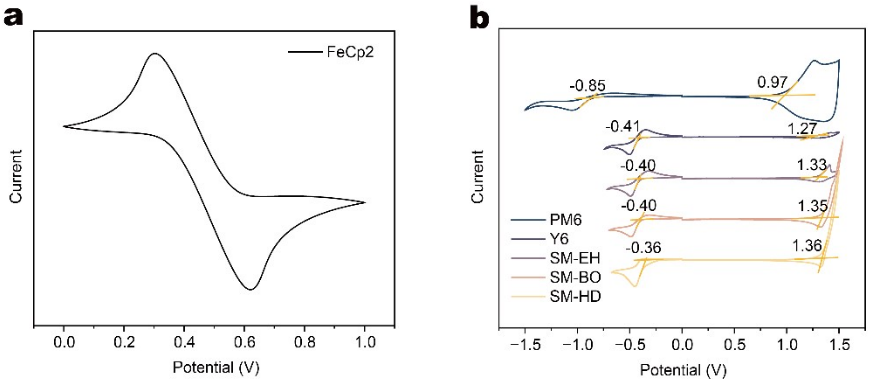


**Figure S3** Cyclic voltammograms of a) ferrocene/ ferrocenium; b) PM6, Y6 and SMAs.

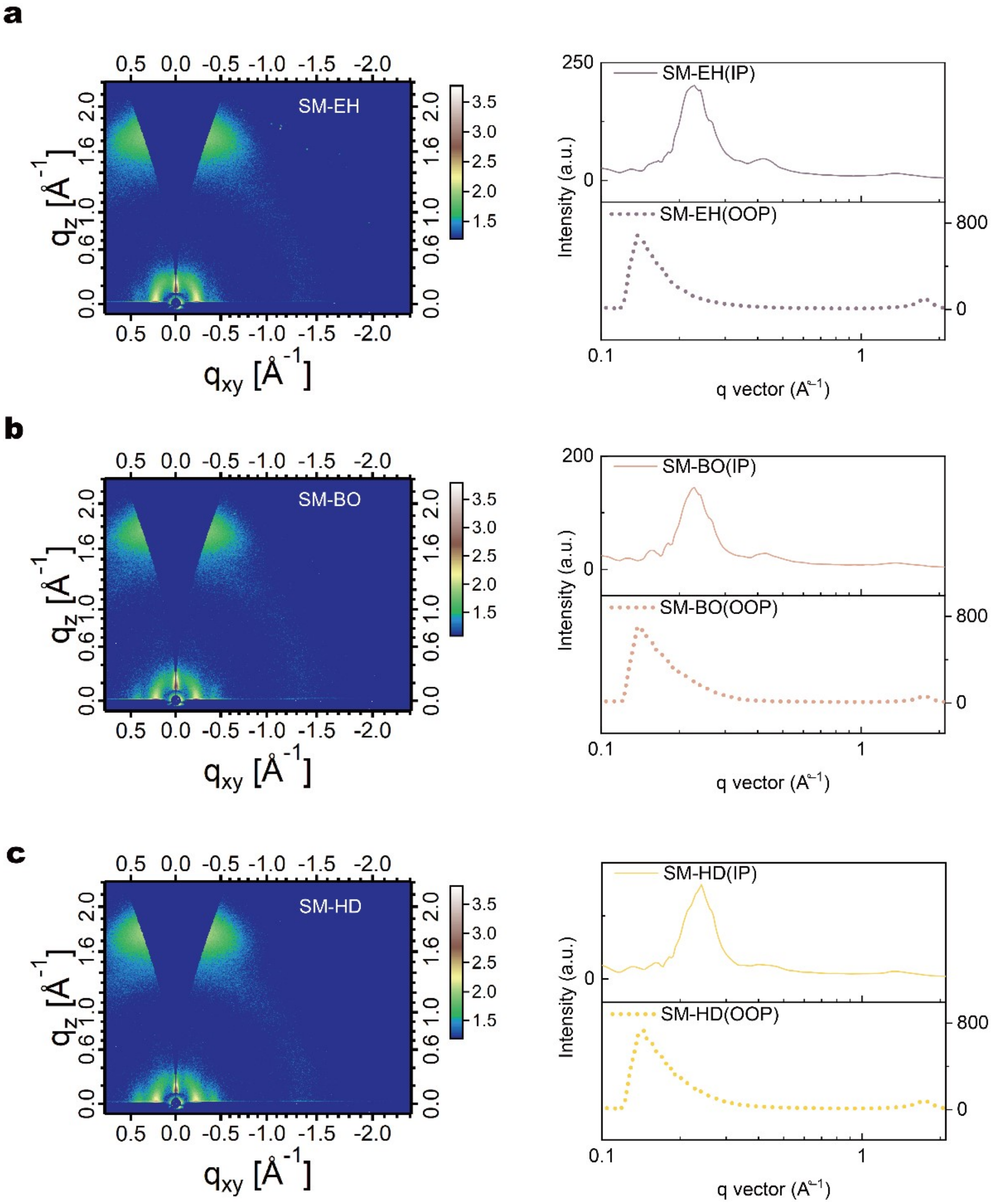


**Figure S4** GIWAXS patterns and OOP/IP cuts of the materials.

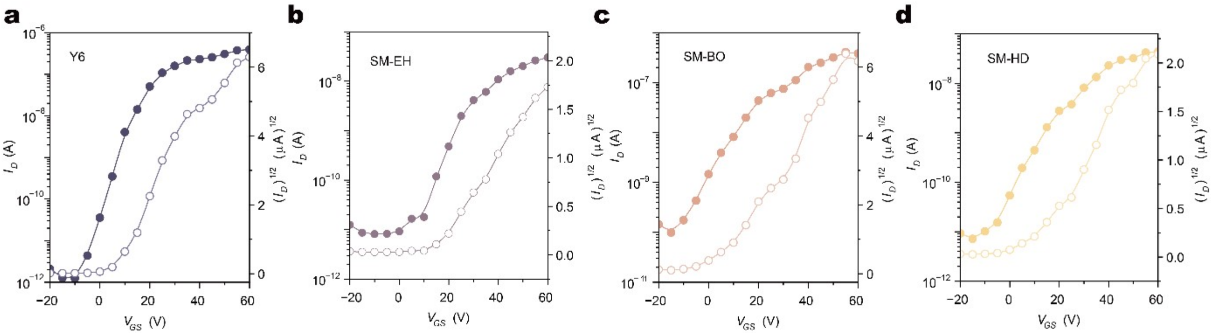


**Figure S5** The field-effect transistor (FET) measurements on Y6 and the SMA films

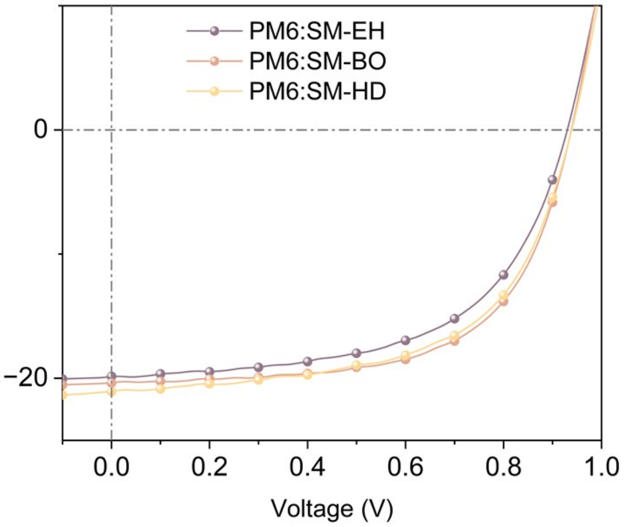


**Figure S6** The *J-V* curves of binary devices.

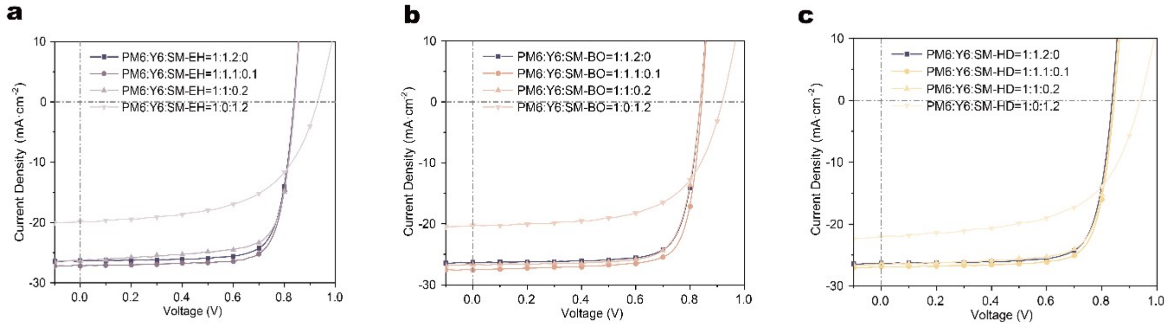


**Figure S7** The *J-V* curves of ternary devices with different weight ratio. a) PM6:Y6:SM-EH. b) PM6:Y6:SM-BO. c) PM6:Y6:SM-HD

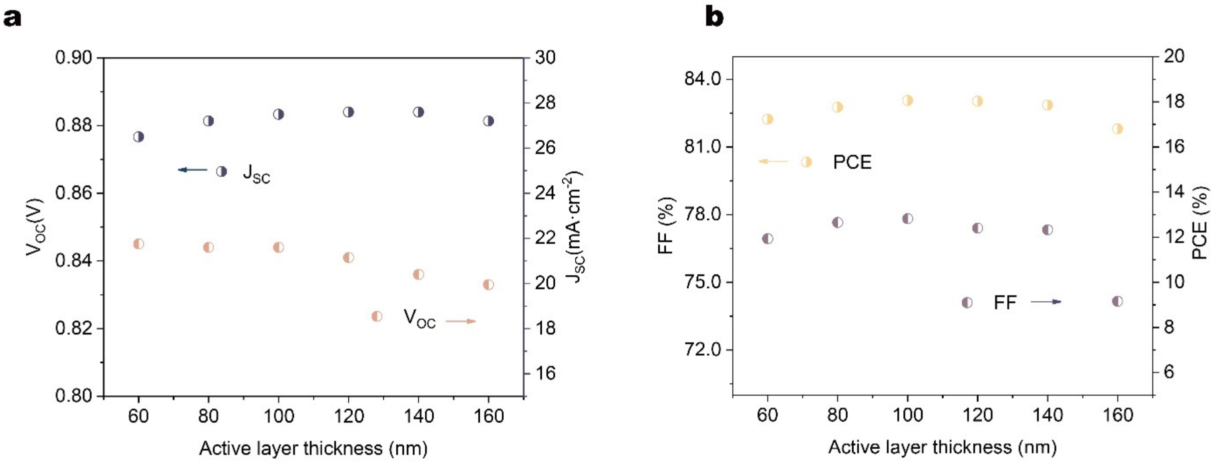


**Figure S8** a) The plot of the $J_{SC}$ and $V_{OC}$ versus the active layer thickness ranging from 60 to 160 nm; b) The plot of the PCE and FF versus the active layer thickness ranging from 60 to 160 nm.

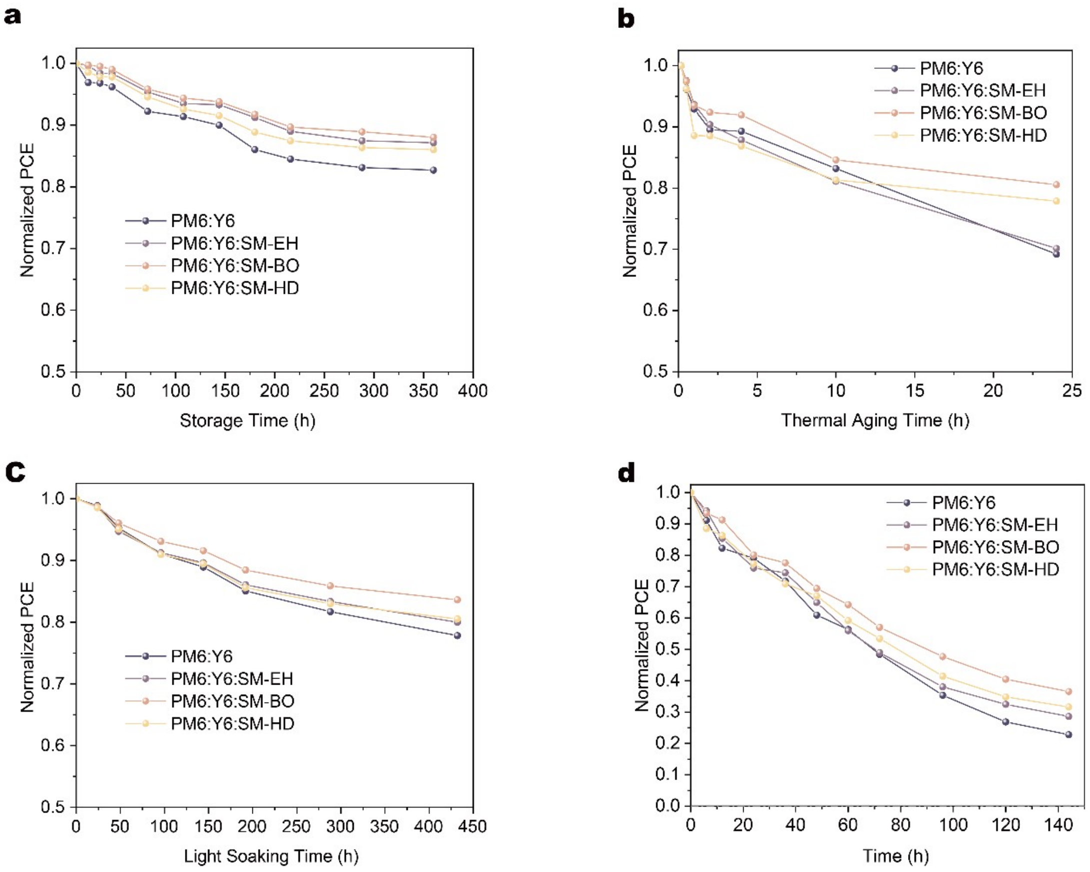


**Figure S9** a) The stability for ternary and binary devices under dark and nitrogen condition. b) The thermal stability for ternary and binary devices, which are heated at 110°C. c) The light soaking stability for ternary and binary devices under illumination at 100 mW cm$^{-2}$ by a LED simulator. d) The Damp heat stability for ternary and binary devices under 85℃ and 85% RH. All devices were encapsulated in a glovebox prior to testing.

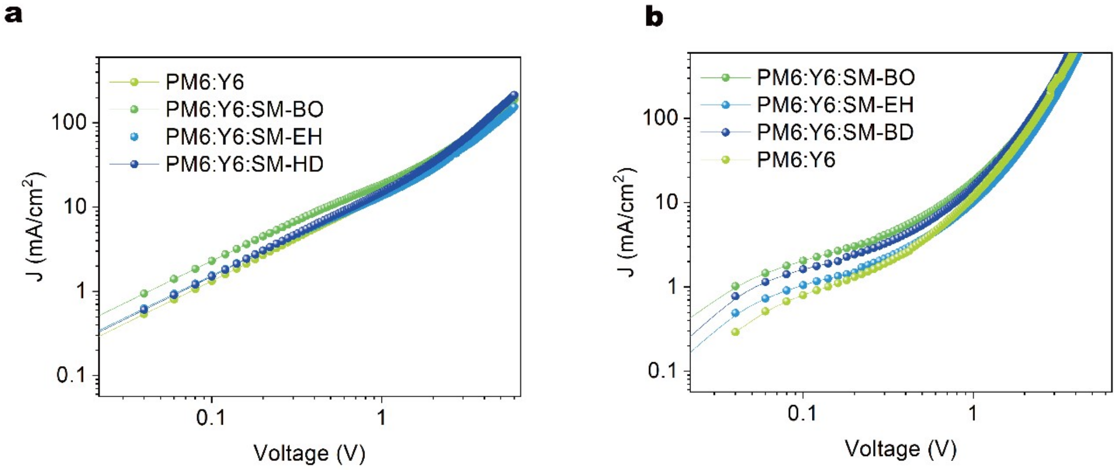


**Figure S10** The charge mobility of binary and ternary devices with a) hole-only devices and b) electron-only devices, measured by SCLC method.

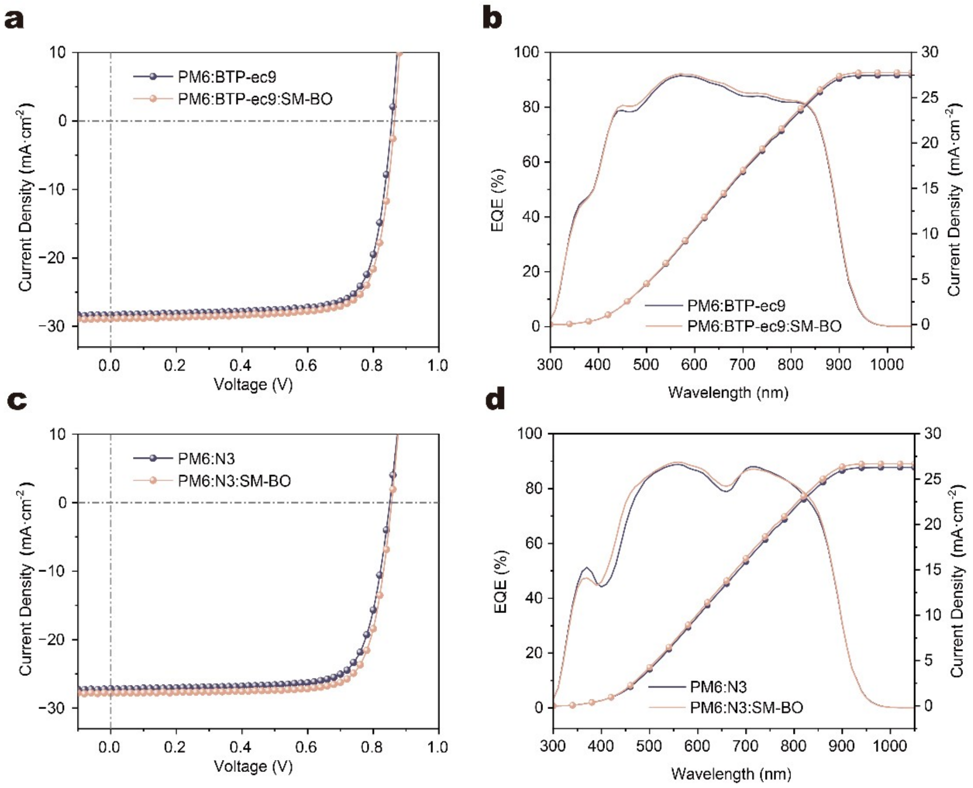


**Figure S11 The performances of the binary and ternary devices of PM6:BTP-ec9 and PM6:N3.** a, b) The *J–V* curves of binary and ternary of PM6:BTP-ec9 yields and the EQE spectra of the corresponding devices. c, d) The J–V curves of binary and ternary of PM6:N3 yields and the EQE spectra of the corresponding devices.

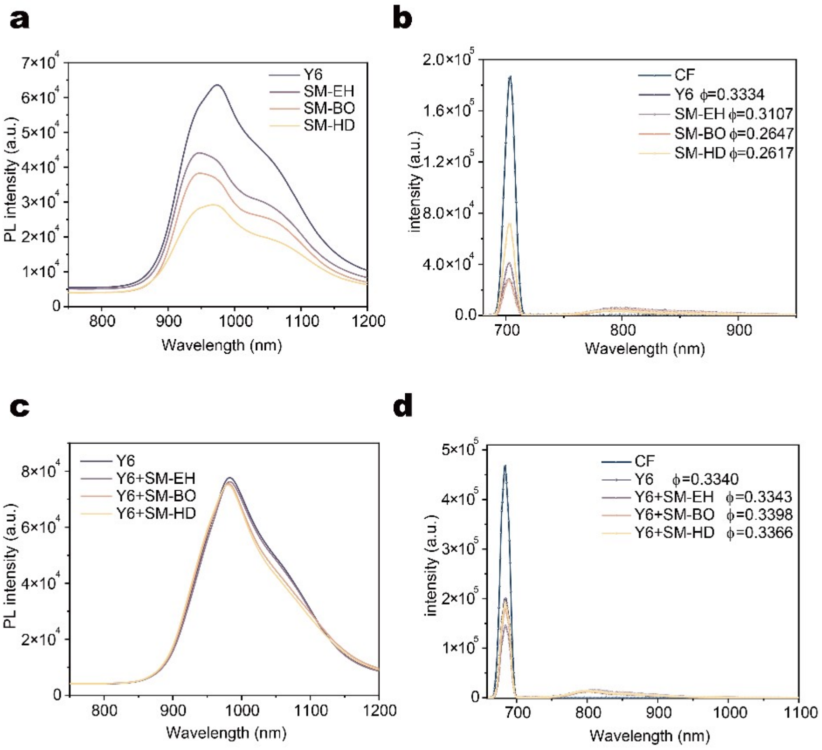


**Figure S12** a) The PL spectra and b) PL quenching efficiency for single-component acceptor film. c) The PL spectra and d) PL quenching efficiency for hybrid acceptor film.

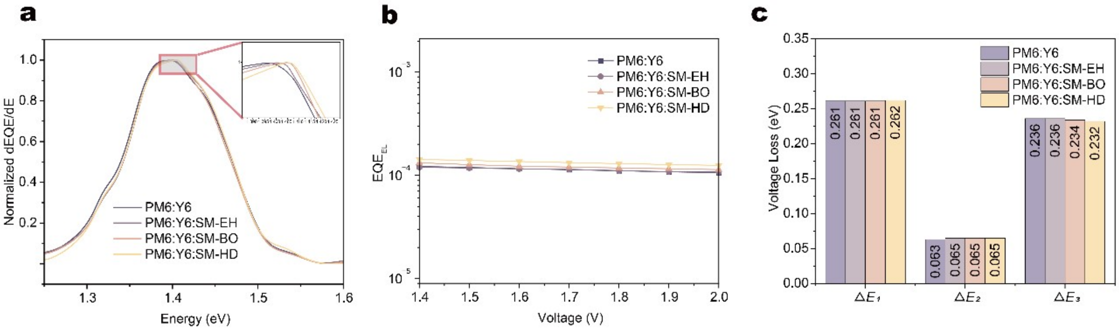


**Figure S13 Energy Loss Analysis.** a) Determination of the $E_g$ of the binary and ternary devices via the derivatives of the EQE spectra. b) The $EQE_{EL}$ curves of the binary and ternary devices of PM6:Y6 yields. c) The summary of energy losses of the binary and ternary devices of PM6:Y6 yields.

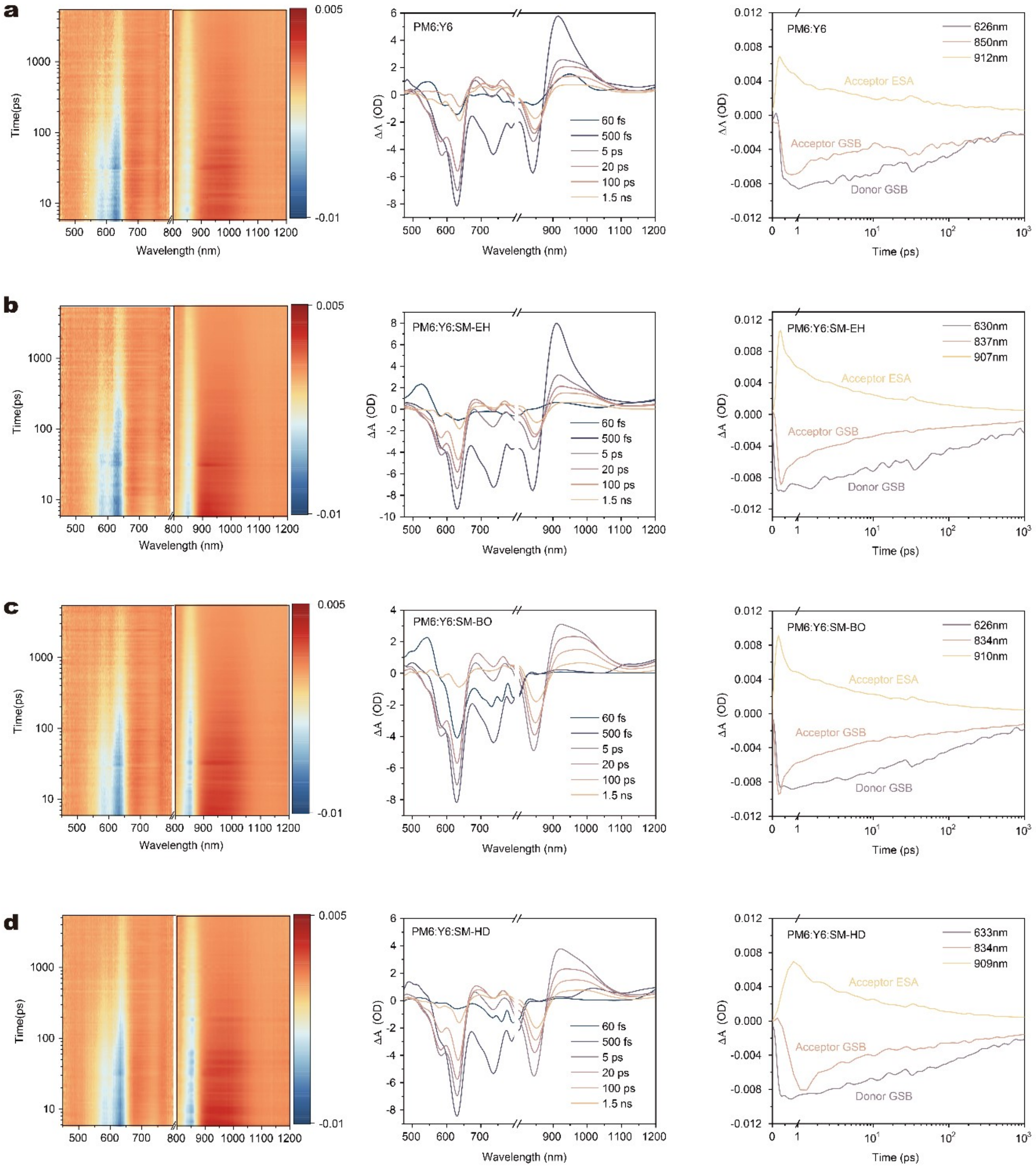


**Figure S14** The 2D TA spectra, the TA spectra at different delay times, and the TA dynamics (in the visible region) of acceptor GSB and acceptor ESA signals for (a), (b), (c), and (d) films. The TA spectra were measured under the pump laser at 800 nm.

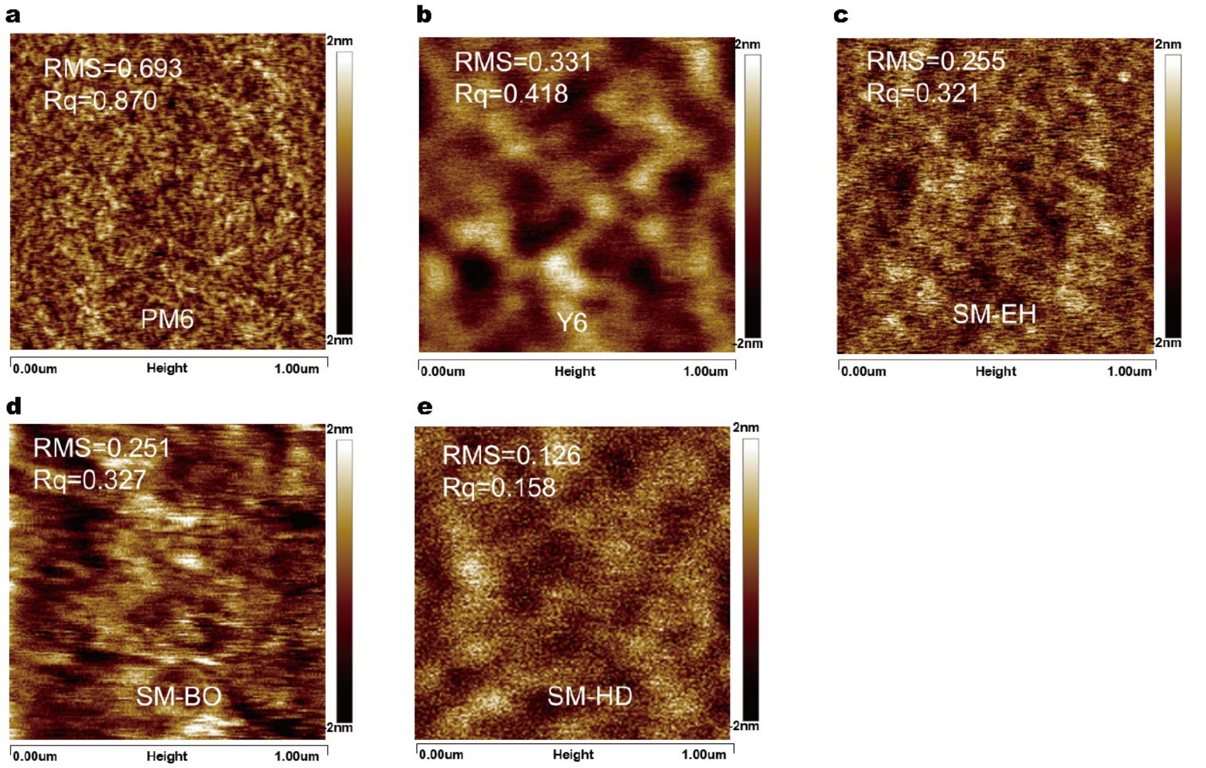


**Figure S15** The AFM height images of a) PM6, b) Y6, c) SM-EH, d) SM-BO and e) SM-HD.

[1] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B., et al. Gaussian 09, revision C.01, Gaussian, Inc., Wallingford CT, **2010**.