# **Supporting Information (SI)**

## "Fluorinated and Methylated ortho-Benzodipyrrole-Based Acceptors Suppressing Charge

Recombination and Minimizing Energy Loss in Organic Photovoltaics"

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## 1. Materials, instruments and characterization

Chemicals used in this study were purchased from commercial source and were used directly without any purification. Tetrahydrofuran (THF) were dried by solvent purification system. *N,N*-dimethylformamide (DMF) was dried by activated molecular sieves. Compound **1a**, **1b**, 1,2-dibromo-4,5-difluoro-3,6-diiodobenzene, 1,2-dibromo-3,6-diiodo-4,5-dimethylbenzene and Y6-16 were synthesized according to literatures procedures.<sup>1-5</sup> PM6 was purchased from Solarmer, Inc. Varian-400 MHz, JEOL-400 MHz and JEOL-500 MHz instrument spectrometers were used to measure <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR. Deuterated chloroform (CDCl<sub>3</sub>) with TMS as internal were used as references in NMR measurements. The mass spectra of the samples were recorded on JEOL T200-GC high resolution spectrometer using electron impact (EI) or field desorption (FD) method. UV-vis absorption spectra were measured on HP8453 UV-vis spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were conducted on a TA Q200 Instrument and a TA TGA55 Instrument under nitrogen atmosphere at heating/cooling rate of 10 °C/min. Surface topography was investigated using SPA-300HV AFM and standard tips (Tapping mode; L: 240 µm;

Resonance Frequency: 70 kHz; Spring Constant: 2 N/m).

### 2. Synthetic procedures



Scheme S1. Synthetic routes for o-BDP-based CFB and CMB.

### Synthesis of compound 3a



To a solution of starting material **1a** (3.73 g, 10 mmol) in dry THF (53 ml) was added lithium diisopropylamide (LDA, 5.25 ml, 10.5 mmol) dropwise under -78 °C. After being stirred at -78 °C for 1.5 h, SnBu<sub>3</sub>Cl (3.58 ml, 11.0 mmol) was added dropwise. The reaction solution was gradually warmed up to room temperature. After being stirred for 12 h, the mixture was quenched by pouring into water, followed by extraction with ethyl acetate (100 ml x 2) and water (200 ml). The collected organic layer was dried over anhydrous MgSO<sub>4</sub>. After removing solvent under reduced pressure, the resulting brown oil, compound **2a**, was directly used in the next step without further purification. Compound **2a** (1718.0 mg, 2.59 mmol), 1,2-dibromo-4,5-difluoro-3,6-diiodobenzene (565.5 mg, 1.08 mmol), P(*o*-tolyl)<sub>3</sub> (131.5 mg, 0.43 mmol) and Pd<sub>2</sub>(dba)<sub>3</sub> (99.0 mg, 0.11 mmol) were dissolved in dry toluene (4.5 ml) and stirred at 120 °C for 24 h. After cooling to room temperature, the mixture was extracted with ethyl acetate and water. The collected organic layer was dried over anhydrous MgSO<sub>4</sub>. After removing solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (hexane) to get the orange liquid **3a** (383.5 mg, 35%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.12(s, 2H), 2.74 (t, *J* = 7.4 Hz, 4H), 1.76 (m, 4H), 1.43-1.22 (m, 32H), 0.88 (t, *J* =

6.5 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  148.62, 139.97, 139.48, 136.13, 129.78, 127.04, 124.49, 123.03, 106.23, 31.97, 29.82, 29.72, 29.70, 29.62, 29.44, 29.43, 28.72, 25.70, 22.77, 14.19. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  –129.88; HRMS (FD, C<sub>40</sub>H<sub>48</sub>F<sub>2</sub>S<sub>4</sub>Br<sub>4</sub>): calcd, 1009.9346; found 1009.9345.

#### Synthesis of compound 4a



To a solution of compound **3a** (213.1 mg, 0.21 mmol), 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP, 107.0 mg, 0.17 mmol), Na<sup>t</sup>OBu<sub>3</sub> (184.0 mg, 1.92 mmol) and Pd<sub>2</sub>(dba)<sub>3</sub> (40.0 mg, 0.04 mmol) dissolved in of *p*-xylene (5.0 ml) was added 2-hexyldecan-1-amine (311.0 mg, 1.28 mmol). The mixture was stirred at 125 °C for 20 h. After cooling to room temperature, the mixture was extracted with ethyl acetate and water. The collected organic layer was dried over anhydrous MgSO<sub>4</sub>. After removing solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (hexane) to get the orange liquid **4a** (61.6 mg, 25%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.00 (s, 2H), 4.48 (d, *J* = 7.8 Hz, 4H), 2.78 (t, *J* = 7.7 Hz, 4H), 2.01-1.99 (m, 2H), 1.88-1.79 (m, 4H), 1.48-1.15 (m, 36H), 1.14- 0.97 (m, 20H), 0.95-0.80 (m, 30H), 0.73 (t, *J* = 7.2 Hz, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  142.55, 138.97, 137.68, 136.72, 127.20, 123.57, 119.55, 117.98, 112.28, 54.77, 31.98, 31.88, 29.74, 29.70, 29.41, 29.23, 22.74, 22.67, 22.55, 14.15, 14.14, 14.01.<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  –158.03; HRMS (FD, C<sub>72</sub>H<sub>114</sub>N<sub>2</sub>F<sub>2</sub>S<sub>4</sub>): calcd, 1172.7838; found 1172.7821.

#### Synthesis of compound 5a



To a solution of anhydrous *N*,*N*-dimethylformamide (1 ml) was added phosphorus oxychloride (0.5 ml) dropwise in iced-water bath and stirred at 0 °C for 30 min to prepare the Vilsmeier reagent. The reagent was then added dropwise to a solution of compound **4a** (117.4 mg, 0.1 mmol) in 1,2-dichloroethane (12 ml). The mixture was stirred at 80 °C for 16 h. After cooling to room temperature, the mixture was poured into water and stirred for 1 h for hydrolysis. The resulting solution was then extracted by with dichloromethane and water. The collected organic layer was dried over anhydrous MgSO<sub>4</sub>. After removing solvent under reduced pressure, the crude product was purified by column

chromatography on silica gel (hexane/DCM, v/v, 2/1) to get the orange solid **5a** (78.7 mg, 64%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.14 (s, 2H), 4.52 (d, J = 7.8 Hz, 4H), 3.17 (d, J = 7.7 Hz, 4H), 2.04-1.95 (m, 2H), 1.93-1.86 (m, 4H), 1.51-1.27 (m, 30H), 1.23-0.97 (m, 28H), 0.89 (m, 28H), 0.73 (t, J = 7.2 Hz, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  181.78, 146.54, 143.54, 138.62, 137.85, 137.40, 129.39, 128.16, 122.88, 113.17, 55.13, 31.93, 29.65, 29.62, 29.52, 29.36, 29.34, 29.18, 22.69, 22.61, 14.07, 13.93. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -156.07; HRMS (FD, C<sub>74</sub>H<sub>114</sub>F<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S<sub>4</sub>): calcd, 1228.7731; found 1228.7709.

#### Synthesis of CFB



To a solution of compound **5a** (73.8 mg, 0.06 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inded-1-ylidene)malononitrile (58.0 mg, 0.25 mmol) in chloroform/DMF (12.3 ml/2.5 ml, v/v) was added trimethylsilyl chloride (3.1 ml) dropwise. The resulting blue solution was stirred at 50 °C for 16 h. After cooling to room temperature, the mixture was extracted with dichloromethane and water. The collected organic layer was dried over anhydrous MgSO<sub>4</sub>. After removing solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (hexane/DCM, v/v, 2/1) to get the blue solid **CFB** (80.4 mg, 81%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.17 (s, 2H), 8.61-8.56 (m, 2H), 7.71 (d, *J* = 7.4 Hz, 2H), 4.66 (d, *J* = 7.8 Hz, 4H), 3.21 (t, *J* = 7.6 Hz, 4H), 2.06 (m, 2H), 1.90-1.81 (m, 4H), 1.55-1.21 (m, 32H), 1.20-0.84 (m, 54H), 0.73 (t, *J* = 7.1 Hz, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  186.08, 158.93, 154.53, 154.49, 153.80, 145.25, 139.27, 138.05, 136.73, 135.65, 135.56, 134.64, 133.44, 129.19, 126.58, 120.35, 115.07, 114.89, 114.20, 112.50, 69.15, 55.47, 31.95, 29.65, 29.37, 22.71, 22.65, 14.11, 14.09, 14.03. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -122.62 ~ -122.72 (m), -124.00 ~ -124.07 (m), -154.52 (s); HRMS (FD, C<sub>98</sub>H<sub>118</sub>N<sub>6</sub>O<sub>2</sub>F<sub>6</sub>S<sub>4</sub>): calcd, 1652.8109; found 1654.8112.

## Synthesis of compound 3b



To a solution of compound 1b (588 mg, 1.3 mmol) in dry THF (2.5ml) was added i-PrMgCl·LiCl (1.0

ml, 1.3 M) dropwise at 0 °C. After being stirred for 1 h, the solution was added ZnCl<sub>2</sub> (204.0 mg, 1.47 mmol) in dry THF (1.0 ml) and was stirred for 30 min to freshly prepare a zinc reagent. To another solution of 1,2-dibromo-3,6-diiodo-4,5-dimethylbenzene (258.0 mg, 0.5 mmol) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (35.2 mg, 0.05 mmol) in dry THF (1.0 ml) was added the zinc reagent dropwise. After being stirred for 18 h at 60 °C, the resulting solution was poured into water and was extracted with dichloromethane. The collected organic layer was then dried over anhydrous MgSO<sub>4</sub>. After removing solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (hexane) to get the orange liquid **3b** (156.0 mg, 31%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.07 (s, 2H), 2.74 (t, *J* = 7.6 Hz, 4H), 1.83-1.73 (m, 4H), 1.44-1.23 (m, 32H), 0.88 (t, *J* = 6.9 Hz, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  139.78, 139.16, 138.76, 138.27, 136.36, 136.13, 126.61, 121.95, 104.20, 32.01, 29.85, 29.72, 29.64, 29.45, 29.44, 28.75, 22.78, 18.93, 14.21; HRMS (FD, C<sub>42</sub>H<sub>54</sub>S<sub>4</sub>Br<sub>4</sub>): calcd, 1008.9847; found 1008.9857.

#### Synthesis of compound 4b



To a solution of compound **3b** (151.0 mg, 0.15 mmol), 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP, 77.0 mg, 0.12 mmol), Na<sup>t</sup>OBu<sub>3</sub> (135.0 mg, 1.40 mmol) and Pd<sub>2</sub>(dba)<sub>3</sub> (29.0 mg, 0.03 mmol) dissolved in *p*-xylene (3.5 ml) was added 2-hexyldecan-1-amine (225.0 mg, 0.93 mmol). The mixture was stirred at 125 °C for 20 h. After cooling to room temperature, the mixture was extracted with ethyl acetate and water. The collected organic layer was dried over anhydrous MgSO<sub>4</sub>. After removing solvent under reduced pressure, the crude product was purified by column chromatography on silica gel to get the orange liquid **4b** (36.7 mg, 21%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.93 (s, 2H), 4.46 (d, J = 7.8 Hz, 4H), 2.77 (t, J = 7.7 Hz, 4H), 2.68 (s, 6H), 2.04-1.90 (m, 2H), 1.88-1.78 (m, 4H), 1.45-1.15 (m, 36H), 1.10-0.95 (m, 20H), 0.87-0.80 (m, 30H), 0.70(t, J = 7.3 Hz, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  140.99, 137.74, 136.37, 129.06, 124.17, 123.19, 121.28, 119.76, 118.25, 54.30, 31.91, 31.84, 29.70, 29.68, 29.64, 29.61, 29.44, 29.38, 29.34, 29.23, 22.68, 22.63, 22.52, 14.11; HRMS (FD, C<sub>74</sub>H<sub>120</sub>N<sub>2</sub>S<sub>4</sub>): calcd, 1164.8340; found 1164.8321.

## Synthesis of compound 5b



To a solution of anhydrous *N*,*N*-dimethylformamide (1 ml) was added phosphorus oxychloride (0.5 ml) dropwise in iced-water bath. The mixture was stirred at 0 °C for 30 min to prepare the Vilsmeier reagent. The reagent was then added dropwise to a solution of compound **4b** (104.9 mg, 0.09 mmol) in 1,2-dichloroethane (10.5 ml). The mixture was stirred at 80 °C for 16 h. After cooling to room temperature, the mixture was poured into water and stirred for 1 h for hydrolysis. The resulting solution was then extracted by with dichloromethane and water. The collected organic layer was dried over anhydrous MgSO<sub>4</sub>. After removing solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (hexane/DCM, v/v, 2/1) to get the orange solid **5b** (68.2 mg, 62%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.11 (s, 2H), 4.51 (d, *J* = 7.6 Hz, 4H), 3.16 (t, *J* = 7.7 Hz, 4H), 2.71 (s, 6H), 1.91 (m, 6H), 1.50-1.15 (m, 34H), 1.14-0.95 (m, 22H), 0.88-0.81 (m, 30H), 0.71 (t, *J* = 7.2 Hz, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  181.65, 146.64, 142.23, 137.51, 136.27, 130.35, 130.22, 126.70, 123.88, 121.19, 54.53, 53.42, 31.91, 31.83, 29.69, 29.66, 29.62, 29.53, 29.37, 29.34, 29.23, 22.69, 22.63, 22.54, 14.12, 14.01; HRMS (FD, C<sub>76</sub>H<sub>120</sub>N<sub>2</sub>O<sub>2</sub>S<sub>4</sub>): calcd, 1220.8238; found 1220.8246.

#### Synthesis of CMB



To a solution of compound **5b** (36.7 mg, 0.03 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inded-1-ylidene)malononitrile (31.0 mg, 0.13 mmol) in chloroform/DMF (3.3 ml/0.7 ml, v/v) was added trimethylsilyl chloride (0.84 ml) dropwise. The resulting blue solution was stirred at 50 °C for 16 h. After cooling to room temperature, the mixture was extracted with dichloromethane and water. The collected organic layer was dried over anhydrous MgSO<sub>4</sub>. After removing solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (hexane/ dichloromethane, v/v, 2/1) to get the blue solid **CMB** (41.5 mg, 84%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 9.15 (s, 2H), 8.57 (dd, J = 9.8, 6.3 Hz, 2H), 7.69 (t, J = 7.5 Hz, 2H), 4.63 (d, J = 7.5 Hz, 4H), 3.25-3.19 (m, 4H), 2.72 (s, 6H), 2.05-1.95 (m, 2H), 1.92-1.81 (m, 4H), 1.55-1.23 (m, 36H), 1.19-0.91 (m, 30H), 0.90-0.75 (m, 20H), 0.70 (t, J = 7.1 Hz, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  186.03, 159.09, 155.39, 153.91, 144.58, 138.55, 136.88, 136.67, 135.31, 134.53, 133.14, 131.85, 131.04, 125.14, 122.51, 119.27, 115.20, 114.98, 114.82, 112.38, 67.90, 55.01, 38.79, 31.93, 31.91, 31.61, 31.35, 30.59, 29.84, 29.79, 29.68, 29.65, 29.53, 29.45, 29.38, 29.36, 29.29, 25.56, 25.48, 22.69, 22.65, 22.56, 15.92, 14.11, 14.06; HRMS (FD, C<sub>100</sub>H<sub>124</sub>N<sub>6</sub>O<sub>2</sub>F<sub>4</sub>S<sub>4</sub>): calcd, 1644.8610; found 1644.8606.

#### 3. TGA measurement results



Figure. S1. TGA measurements of CMB, CFB and Y6-16.

#### 4. Cyclic voltammetry (CV) characteristics

CV was measured on a CH instruments electrochemical analyzer. A carbon glass was used as the working electrode and an Ag/AgCl electrode as the reference electrode. Solution of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile was used as electrolyte. Ferrocence, whose HOMO energy level is  $-4.8 \ eV$  with respect to zero vacuum level, was used as standard to calibrate. The HOMO energy levels were obtained from the equation  $E_{\text{HOMO}} = -|E_{\text{ox}}^{\text{onset}} - E_{\text{onset}} + 4.8| \ eV$ . The LUMO energy levels were obtained from the equation  $E_{\text{LUMO}} = -|E_{\text{red}}^{\text{onset}} - E_{\text{onset}} + E_{\text{onset}} + 4.8| \ eV$ .



**Figure. S2.** Cyclic voltammogram of (a) CMB, (b) Y6-16 and (c) CFB in thin films at a scan rate of 100 mVs<sup>-1</sup>.

## 5. Density functional theory (DFT) calculation of frontier molecular orbitals

DFT calculation were conducted by Gaussian 09 suite15 at the B3LYP/6-311G(d,p) level. All alkyl side chains were simplified to methyl group in the computational model compounds.



**Figure S3.** Frontier molecular orbital plots of (a)Y6-16, (b) AQx-2, (c) Y6-Se and (d) Y11-M and their (e) electrostatic potential plots calculated by DFT at B3LYP/6-311G(d,p) level.



**Figure S4.** Top views of optimized structure of CMB, Y6-16 and CFB calculated by DFT at B3LYP/6-311G(d,p) level. Dipole moment, S-O distance and torsion angle ( $\Phi$ ) were also denoted. The atomic species C labeled by gray, N by blue, O by red, F by cyan, and S by yellow.

#### 6. Single crystal growth and the crystallographic data

#### 6.1 Single crystal growth

Solutions of 1.6 mg of desired NFAs dissolved in 2.0 mL of chloroform were separately prepared in 4 mL vials and capped with aluminum foil with a hole punched using a 18G needle in the middle. The capped 4 mL vials were separately transferred into 20 mL vials which contained 2.5 mL of acetonitrile. All the resulting vials were tightly sealed, stored in dark and left standing. After one to two weeks, the crystal clusters would form in each vial.

#### 6.2 Crystallographic data

The single crystals of the NFAs were mounted on a CryoLoop with Parabar 10312 oil for the single-crystal X-ray diffraction experiments at -73 °C. The crystal size is 0.438 x 0.190 x 0.038 mm<sup>3</sup> for CMB and 0.577 x 0.188 x 0.110 mm<sup>3</sup> for CFB. The single-crystal X-ray diffraction data of CMB and CFB were individually collected in-house on a Bruker D8 Venture diffractometer equipped with a Mo-target (K $\alpha$  = 0.71073 Å) microfocus X-ray generators and a PHOTON-II CMOS detector. The temperature was adjusted with a nitrogen flow (Oxford Cryosystems, 800+ series). After collection, the cell refinement and the data integration were carried out by Bruker SAINT<sup>6</sup> software package using a narrow-frame algorithm and were corrected for absorption effects using the Multi-Scan method (SADABS)<sup>7</sup>. Moreover, the molecular structure was solved by SHELXT (Sheldrick 2015) and refined by SHELXL-2019/1 (Sheldrick, 2019)<sup>8</sup>. The final anisotropic full-matrix least-squares method<sup>8</sup> was used to refine on F<sup>2</sup> with variables parameters to determine crystal structure. All calculations were performed using the APEX4<sup>9</sup> software package. The crystallographic data of CMB and CFB are listed in Table S1, respectively.

Identification code	CMB	CFB
Empirical formula	$C_{100}H_{124}F_4N_6O_2S_4\\$	$C_{98}H_{118}F_6N_6O_2S_4$
CCDC number	2391712	2391682
Formula weight	1646.28	1654.22
Temperature/K	200(2)	200(2)
Wavelength/Å	1.54178	0.71073
Crystal system	Triclinic	Monoclinic

Table S1. The crystallographic data of CMB and CFB.

Space group	P-1	C2/c
a/Å	21.2230(4)	25.2111(8)
b/Å	21.3687(5)	22.7564(8)
c/Å	32.1128(6)	33.5239(11)
$\alpha / ^{\circ}$	91.9510(10)	90
β/°	91.3666(8	108.2920(11)
$\gamma/^{\circ}$	103.5864(10)	90
Volume/Å <sup>3</sup>	14140.1(5)	18261.3(11)
Z	6	8
Density/Mg/m <sup>3</sup>	1.160	1.203
Absorption coefficient/mm <sup>-1</sup>	1.383	0.167
F(000)	5292	7056
Crystal size/mm <sup>3</sup>	0.438 x 0.190 x 0.038	0.577 x 0.188 x 0.110
heta range for data collection/°	2.143 to 69.997	1.901 to 25.249
	-25<=h<=25,	-23<=h<=30,
Index ranges	-26<=k<=26,	-27<=k<=27,
	-39<=]<=35	-39<=]<=4()
Reflections collected	99898	48466
Independent reflections	53485 [R(int) = 0.0326]	16533 [R(int) = 0.0596]
Completeness to $\theta = 25.242^{\circ}$	99.8 %	99.9 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9805 and 0.8377	0.9705 and 0.8111
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	53485 / 1446 / 2822	16533 / 828 / 1043
Goodness-of-fit on F <sup>2</sup>	1.675	1.141
Final R indices [I>2sigma(I)]	R1 = 0.1717, wR2 = 0.4293	R1 = 0.1997, wR2 = 0.4729
R indices (all data)	R1 = 0.2203, wR2 = 0.4806	R1 = 0.3081, wR2 = 0.5593
Extinction coefficient	n/a	n/a
Largest diff. peak and hole/ e.Å-3	1.263 and -0.902 e.Å <sup>-3</sup>	1.227 and -0.762 e.Å <sup>-3</sup>



**Figure S5.** Two-dimensional (2D) brickwork packing of (a) CMB and (b) CFB, with the correponding  $\pi$ - $\pi$  stacking distances specified in different dimeric modes.

## 7. Device fabrication and optimization

All the devices were fabricated as the follow procedures: The ITO-coated glass was treated with UV-ozone for 25 min, spin-coated with ZnO solution, then backed at 180 °C for 25 min. The PM6:NFA blends were dissolved in chloroform, *o*-xylene, and chlorobenzene for 1 h at 45 °C, 6 h at 60 °C and 22 h at 60 °C, respectively. The blend solutions were spin-coated on top of the ZnO/ITO substrate as active layer. The resulting substrates were thermally annealed at different temperature for 10 min, followed by thermal vapor deposition of MoO<sub>3</sub> layer (7 nm) and silver anode (150 nm) at a pressure below  $10^{-6}$  torr. The devices without encapsulation were characterized in ambient condition. Current-voltage characteristics were measured by a Keithley 2400 SMU under the irradiation of AM 1.5G San-Yi solar simulator with JIS AAA spectrum. EQE spectra were measured using a lock-in amplifier with a current preamplifier under short-circuit conditions with illumination by monochromatic light from a 250 W quartz-halogen lamp (Osram) passing through a monochromator (Spectral Products CM110).

Annealing temperature [°C]	Processing solvent	$V_{ m oc}\left[{ m V} ight]$	$J_{\rm sc} [{ m mA~cm^{-2}}]$	FF [%]	PCE [%]
25	chloroform	0.91	22.46	69.27	14.09
100	chloroform	0.89	24.40	68.06	14.77
110	chloroform	0.90	23.61	73.70	15.61
120	chloroform	0.90	23.62	74.05	15.75
130	chloroform	0.90	24.32	74.76	16.20
140	chloroform	0.90	25.06	69.73	15.57
150	chloroform	0.89	25.07	69.47	15.47
130	o-xylene	0.89	24.00	77.45	16.55

**Table S2.** OPV parameters for PM6:CFB (1:1.2 wt%) devices under different annealing temperatures.

Ratio (D:A1:A2)	Processing solvent	Annealing temperature [°C]	$V_{ m oc}\left[{ m V} ight]$	$J_{ m sc}$ [mA cm <sup>-2</sup> ]	FF [%]	PCE [%]
1:0.9:0.3	o-xylene	130	0.845	26.47	74.71	16.69
1:0.6:0.6	o-xylene	130	0.862	27.32	75.61	17.83
1:0.3:0.9	o-xylene	130	0.873	26.68	73.65	17.18
1:0.6:0.6	o-xylene	140	0.862	26.86	74.10	17.13

Table S3. OPV parameters for PM6:Y6-16:CFB ternary devices under different acceptor ratio.

**Table S4.** OPV parameters for PM6:CMB (1:1.2 wt%) devices under different annealing temperatures.

Annealing	Processing		$I  [m \land am^{-2}]$	EE [0/]	DCE [0/1	
temperature [°C]	solvent		$J_{\rm sc}$ [IIIA CIII -]	FF [70]	ICE [70]	
130	chloroform	0.91	24.68	67.97	15.20	
140	chloroform	0.90	25.94	68.87	16.12	
150	chloroform	0.91	24.46	67.56	14.99	
130	o-xylene	0.89	26.50	68.83	16.29	
140	o-xylene	0.90	26.32	69.50	16.40	
150	o-xylene	0.89	26.31	67.50	15.88	

Table S5. OPV parameters for PM6:Y6-16:CMB ternary devices under different acceptor ratio.

Ratio Processing		Annealing		$J_{ m sc}$		
(D:A 1:A 2)	solvent	temperature	$V_{\rm oc}$ [V]	[mA	FF [%]	PCE [%]
(D.AI.A2)	solvent	[°C]		cm <sup>-2</sup> ]		
1:0.9:0.3	o-xylene	140	0.844	26.69	73.41	16.59
1:0.6:0.6	o-xylene	140	0.861	27.18	72.44	16.97
1:0.3:0.9	o-xylene	140	0.879	26.33	71.61	16.54
1:0.6:0.6	o-xylene	150	0.870	26.81	73.03	17.03
1:0.6:0.6	o-xylene	160	0.875	26.76	74.71	17.44
1:0.6:0.6	o-xylene	170	0.872	25.47	73.74	16.34



**Figure S6.** (a)  $J_{sc}$  versus light intensity, (b)  $V_{oc}$  versus light intensity, (c)  $J_{ph}$  versus  $V_{eff}$  spectra and (d) hole and electron mobilities for optimized PM6:CMB:Y6-16 and PM6:CFB:Y6-16 devices.

## 8. Space-charge limited current (SCLC) characteristics

The hole-only and electron-only devices were fabricated by employing the following device structure: ITO/PEDOT:PSS/active layer/Au for holes and ITO/ZnO/active layer/Al for electrons. The mobilities were obtained by taking current-voltage curves and fitting the results to the equation listed below:

 $J = \frac{9\varepsilon_0 \varepsilon_r \mu V^2}{8L^3}$ 

where J is the current density,  $\varepsilon_0$  the vacuum permittivity,  $\varepsilon_r$  the relative dielectric constant,  $\mu$  the mobility, V the voltage, and L the film thickness.<sup>10</sup>

## 9. Transient photocurrent and Transient photovoltage measurements

Transient photocurrent (TPC) and Transient photovoltage (TPV) measurements were measured by the characterization platform Paios (Fluxim AG). The exponential decay fitting<sup>11</sup> of the raw data would yield extraction time (from TPC) and carrier life time (from TPV).



**Figure S7**. (a) Transient photocurrent curves (dots) and relative fitting curves (solid lines) and (h) Transient photovoltage curves (circles) and relative fitting curves (solid lines) for optimized ternary devices.

blends	Charge extraction time [µs]	Carrier life time [µs]
PM6:Y6-16	0.39	44.4
PM6:CFB	0.34	46.2
PM6:CMB	0.37	36.7
PM6:Y6-16:CFB	0.35	60.6
PM6:Y6-16:CMB	0.37	50.8

**Table S6.** Charge extraction time and carrier life time of the OPVs extracted from TPC and TPV measurements.

## 10. Energy loss analysis

FTPS-EQE was measured by using an integrated system PECT-600 (Enli Technology Co., Ltd., Taiwan) to record the spectra of binary and ternary OPV. As for EL and EQE<sub>EL</sub> measurments, another integrated system, ELCT-3010 (Enli Technology Co., Ltd., Taiwan) was used to record the spectra by applying external voltage (0-5 V) through the corresponding OPV cells. The cross-point of normalized FTPS-EQE and EL spectra could yield  $E_g$ ,<sup>12, 13</sup> while the Gaussian fitting in low energy part of the two spectra would determine  $E_{CT}$ .<sup>14, 15</sup> EQE<sub>EL</sub> spectra could be used to obtain  $\Delta E_{nr}$  through the equation  $\Delta E_{nr} = (kT/q)\ln(1/EQE_{EL})$ .<sup>16</sup> Finally, the exponential fitting of normalized FTPS-EQE spectra in low energy region could be used to estimate Urbach energy.<sup>17</sup>



**Figure S8.** Normalized FTPS-EQE and EL spectra of (a) PM6:Y6-16:CFB and (b) PM6:Y6-16:CMB blend films. The fitting curves were depicted in dash lines, and the cross-point of the fitting curves determined the ECT value, which were also indicated in the figures.



**Figure S9.** Normalized FTPS-EQE spectra with exponential fitting results of (a) PM6:Y6-16, (b) PM6:CFB, (c) PM6:CMB, (d) PM6:Y6-16:CFB, and (e) PM6:Y6-16:CMB blend films.

#### 11. Morphology analysis

Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were conduct by the 25A1 coherent X-ray scattering beamline of the Taiwan Photon Source (TPS). 2D GIWAXS patterns were collected with an Eiger X 1M detector, and the corresponding 1D scattering profiles were extracted from the selected zones along the in-plane  $(q_{xy})$  and out-of-plane  $(q_z)$  directions. The mircobeam (ca. a couple tens of  $\mu$ m) incident angle was set to 0.05°; the sample-to-detector distance was 70.0 mm. 2D GIWAXS patterns were further converted to the scattering vector space, with  $q_{xy}$  and  $q_z$  representing the scattering vector components respectively along the in-plane and out-of-plane directions; after the conversion, there is a missing wedge of no diffraction information available in the vertical direction of each 2D GIWAXS pattern.<sup>18</sup> Surface topography was investigated using Veeco diInnova AFM and standard tips (Tapping mode; L: 240  $\mu$ m; Resonance Frequency: 70 kHz; Spring Constant: 2 N/m). Contact angle measurements were conduct through OCA25 with water and diethylene glycol (DEG).



Figure S10. Contact angle test results of neat film of PM6, CFB, Y6-16 and CMB.

film	H_O [°]	DEG [°]	γ <sup>a)</sup> [mN/m]	$\chi_{_{ m D-A}}^{~~b)}$ [a.u.]	$\chi_{A-A}^{c)}$ [a.u.]
PM6	100.5	71.3	24.97	-	-
CFB	98.7	65.9	30.11	0.24 K	0.01 K
Y6-16	97.0	63.5	31.23	0.35 K	-
CMB	96.7	62.0	32.96	0.55 K	0.02 K

Table S7. Contact angle measurement results of PM6, CFB, Y6-16 and CMB.

<sup>a)</sup>Surface tension of the neat film; <sup>b)</sup>Flory-Huggins interactive parameters between PM6 and NFAs.  $\chi_{D-A} = (\sqrt{\gamma_{PM6}} - \sqrt{\gamma_{NFA}})^2$ , where K is a constant; <sup>c)</sup>Flory-Huggins interactive parameters between Y6-16 and NFAs.  $\chi_{D-A} = (\sqrt{\gamma_{Y6-16}} - \sqrt{\gamma_{NFA}})^2$ , where K is a constant.

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Figure S15. <sup>13</sup>C NMR of compound 4a.

























Figure S28. <sup>13</sup>C NMR of compound 5b.



