Supplementary Information

**Alkyl chain modulation of** **asymmetric hexacyclic fused acceptor synergistically with wide bandgap third component for high efficiency ternary organic solar cells**

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**Experimental Section**

**1.1 Materials.**

The PM6 (Mn =49 kDa，PDI: 2.3) was purchased from Solarmer Energy Inc. Unless otherwise stated, all materials were obtained commercially and used without further purification. The BP4F-HU, BP4F-UU, and BTP-TA were designed and synthesized by our group.

**1.2 Instruments.**

1H NMR and 13C NMR spectra were obtained on a Bruker AVANCE 400 MHz nuclear magnetic resonance (NMR) spectroscopy, using locking to the deuterated solvent (CDCl3) and using tetramethylsilane (TMS) as an internal standard. The molecular mass was confirmed using an Autoflex III matrix-assisted laser desorption ionization mass spectrometer (MALDI-TOF-MS). For the solid-state measurements, PM6, BP4F-HU, BP4F-UU, and BTP-TA solutions in chloroform were spin-coated on quartz plates. The cyclic voltammetry results were obtained with a computer-controlled CHI 660E electrochemical workstation using polymer or non-fullerene acceptor films on the platinum electrode (1.0 cm2) as the working electrode, a platinum wire as the counter electrode, and Ag/AgCl (0.1 M) as the reference electrode in an anhydrous and argon-saturated solution of 0.1 M of tetrabutylammonium hexafluorophosphate (Bu4NPF6) in acetonitrile at a scanning rate of 50 mV·s-1. The highest occupied molecular orbital (HOMO) and lowest unoccupied orbital (LUMO) energy levels were calculated from the onset oxidation potential and onset reduction potential, according to the equation *E*HOMO /LUMO = −e (4.80−*E*1/2, Fc/Fc+ +*E*onset, ox/red) (eV). UV-vis absorption spectra were recorded on the SHIMADZU UV-2600 spectrophotometer. Photoluminescence (PL) spectra of films were measured by an FLS1000 Edinburgh instruments ltd. Atomic force microscopy (AFM) images were obtained using a Veeco Dimension 3100V microscope in the tapping mode. Transmission electron microscopy (TEM) measurements were conducted using FEI Tecnai G2F20.

**1.3 SCLC measurement.**

The hole-only device for the hole mobility was fabricated with a device structure of ITO/PEDOT: PSS (20nm)/Active Layer/MoO3 (10nm)/Ag. The electron-only device for electron mobility was fabricated with a device structure of ITO/ZnO/ Active Layer /PFN-Br/Ag. Both the hole and electron mobilities by space charge limited current (SCLC) was calculated with the following Mott-Gurney equation in the SCLC region: *J* = (9/8) *ε0 εr μ* (*V2/L3*), in which *ε0* is the permittivity of the free space, *εr* is the average dielectric constant of the blend film and assumed to be 3, *L* is the thickness of the active layer, and *V* is the applied voltage.

**1.4 Synthetic Procedures**

BP4F-HU and BP4F-UU were synthesized according to the previous methods reported by our group earlier [1, 2]. End-group 1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (DTBA) were purchased from SunaTech Inc.



**Scheme S1.** Synthetic route of BTP-TA acceptor.

**Synthesis of BTP-TA.** In a 100 mL round bottom flask, compound BTP-CHO (200 mg, 0.15 mmol), and compound DTBA (290 mg, 1.47mmol) were dissolved in 20mL dry chloroform under argon, pyridine (1 mL) was added dropwise while stirring at room temperature. Then the reaction mixture was stirred at 65 ℃ for 6 hours. Next, the mixed product was concentrated by rotary evaporation. The crude product was purified on silica gel chromatography using petroleum ether/ CHCl3 (1:1, *v*/*v*) to give compound BTP-TA (0.24 g) as a dark solid in a yield of 95%.

1H NMR (400 MHz, CDCl3) (ppm): δ 9.00 (s, 2H), 4.75 (d, J = 7.5 Hz, 4H), 4.64 (dt, J = 20.3, 7.0 Hz, 8H), 3.24 (t, J = 7.7 Hz, 4H), 1.45 - 1.31 (m, 26H), 1.29 - 1.21 (m, 25H), 1.17 - 1.06 (m, 24H), 0.83 (ddd, J = 21.2, 10.7, 5.3 Hz, 30H).

13C NMR (101 MHz, CDCl3) (ppm): δ 178.57, 161.44, 160.12, 153.28, 147.56, 146.11, 144.93, 137.41, 136.75, 134.26, 133.09, 130.35, 113.17, 108.21, 77.37, 77.26, 77.05, 76.73, 55.47, 44.05, 43.18, 39.14, 31.94, 31.79, 31.18, 30.42, 29.87, 29.79, 29.68, 29.65, 29.57, 29.42, 29.38, 29.33, 29.23, 25.44, 22.73, 22.62, 14.17, 14.15, 12.58, 12.44, 1.05, 0.03.

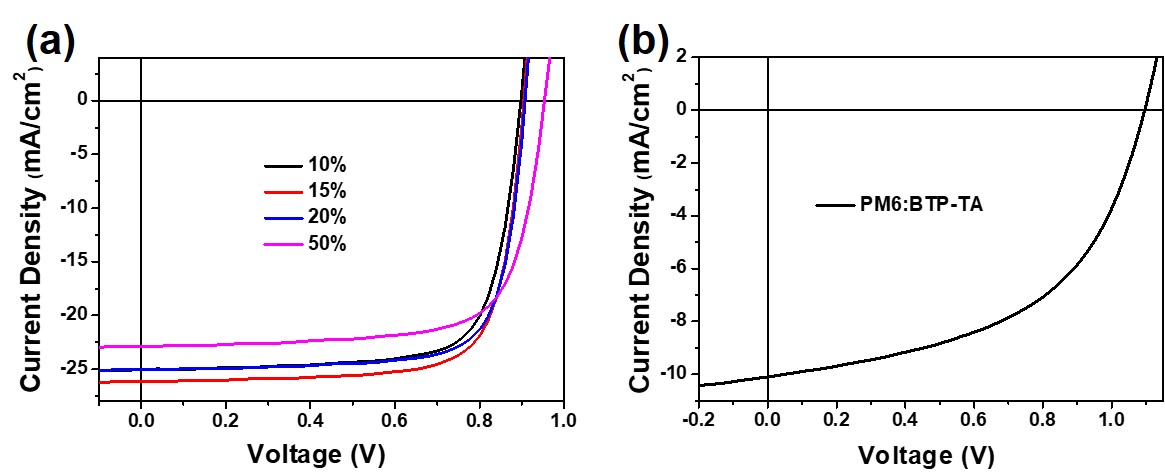
**Supplementary Figures and Tables**

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**Fig. S1.** Cyclic voltammetry of a) BP4F-HU, b) BP4F-UU, and c) BTP-TA as thin films in CH3CN/0.1M [*n*-Bu4N]+[PF6]-.

**Table S1.** Absorption properties and energy levels of three SMAs

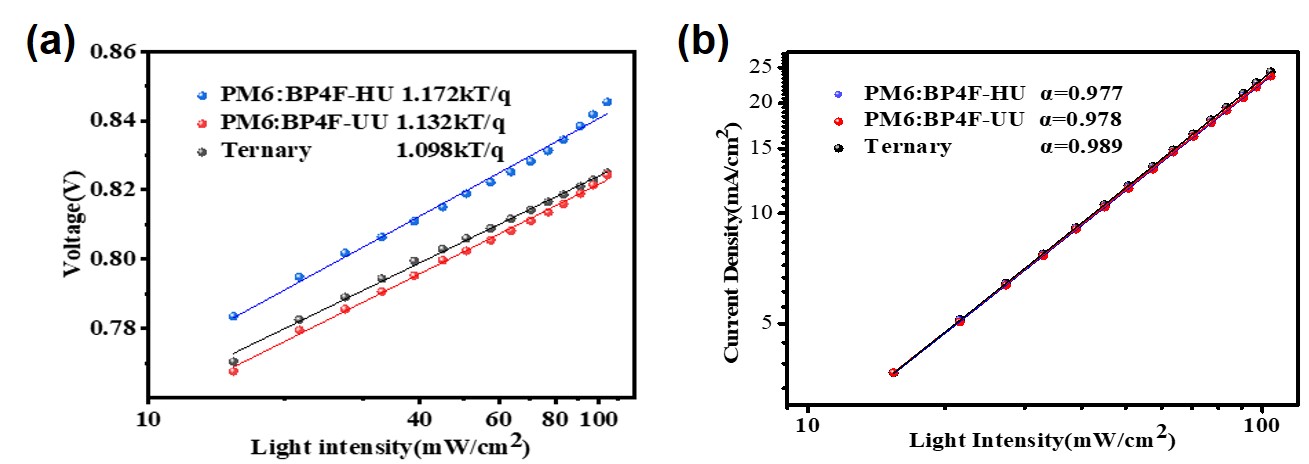
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| --- | --- | --- | --- | --- | --- | --- | --- |
| Acceptors | Solution | | Film | | *E*g (eV) | LUMO (eV) | HOMO (eV) |
| λonset (nm) | λmax (nm) | λonset (nm) | λmax (nm) |
| BP4F-HU | 771 | 717 | 880 | 787 | 1.41 | -3.82 | -5.66 |
| BP4F-UU | 764 | 717 | 871 | 793 | 1.42 | -3.86 | -5.71 |
| BTP-TA | 703 | 655 | 744 | 680 | 1.66 | -3.61 | -5.68 |



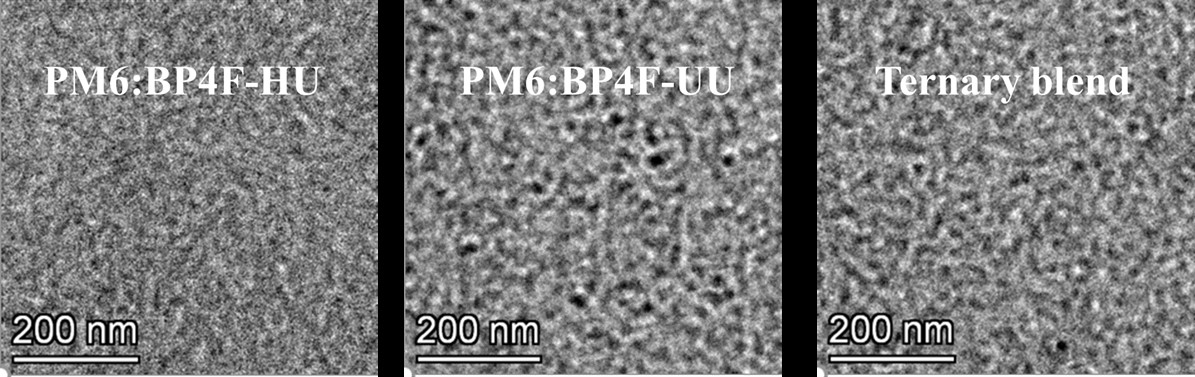
**Fig. S2.** a) *J*-*V* curves of ternary OSCs with different ratio of BTP-TA. b) *J*-*V* curve of PM6:BTP-TA devices.

**Table S2.** Photovoltaic parameters of the ternary OSCs based on PM6:BP4F-UU: BTP-TA blends with various BTP-TA ratios

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| BTP-TA Ratio (wt%) | *V*oc (V) | *J*sc (mA cm-2) | *FF* (%) | PCE (%) |
| 0% | 0.878 | 24.03 | 74.95 | 15.82 |
| 10 % | 0.898 | 25.03 | 74.58 | 16.77 |
| 15% | 0.905 | 26.14 | 75.38 | 17.83 |
| 50% | 0.908 | 24.99 | 76.11 | 17.26 |
| 20 % | 0.953 | 22.88 | 72.59 | 15.84 |
| 100% | 1.096 | 10.1 | 51.14 | 5.66 |



**Fig. S3.** a) Light intensity-dependent of *V*oc. f) Light intensity-dependent of *J*sc.



**Fig. S4.** TEM images of binary and optimized ternary blend films.

**NMR spectrum figures**

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| **Fig. S5.** 1H NMR spectrum of BP4F-HU |
| **Fig. S6.** 13C NMR spectrum of BP4F-HU |
| **Fig. S7.** 1H NMR spectrum of BP4F-UU |
| **Fig. S8.** 13C NMR spectrum of BP4F-UU |
| **Fig. S9.** Mass spectrometry of BP4F-HU |
| **Fig. S10.** Mass spectrometry of BP4F-UU |
| **Fig. S11.** 1H NMR spectrum of BTP-TA |
| **Fig. S12.** 13C NMR spectrum of BTP-TA |

**References**

[1] Cai, F., H. Peng, H. Chen, J. Yuan, J. Hai, T.-K. Lau, J. Wang, Y. Hu, W. Liu, X. Lu, and Y. Zou, An asymmetric small molecule acceptor for organic solar cells with a short circuit current density over 24 mA cm-2*.* *J. Mater. Chem. A*, 2020, 8(31), p. 15984-15991.

[2] Cai, F., C. Zhu, J. Yuan, Z. Li, L. Meng, W. Liu, H. Peng, L. Jiang, Y. Li, and Y. Zou, Efficient organic solar cells based on a new "Y-series" non-fullerene acceptor with an asymmetric electron-deficient-core*.* *Chem. Commun.* , 2020, 56(31), p. 4340-4343.