Trifluoro Alkyl Side Chains in the Non-fullerene Acceptors to Optimize the

Phase Miscibility and Vertical Distribution of Organic Solar Cells

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Experimental Section Materials and Synthesis

Compound 1 was purchased from Jiaxing Hepu Photoelectric Company. Compound 2-1 were purchased from Shanghai Kaiwei Chemical Technology Company. Compound 2-2 and compound 2-3 were purchased from J&K Scientific Company. All reagents and chemicals were purchased from J&K, Aladdin, Alfa and used as received. Solvents and other common reagents were obtained from the Tianjin KangKeDe company. Chloroform was dry before use. Unless noted, all other solvents and chemical reagents were purchased from commercial sources and used without further purification. Structural characterization such as NMR and MS were shown in Figure S8-S22.



Scheme. 1. Synthetic route of BTP-BF, BTP-OF, and BTP-DF.

Compound 3-1(BTP-N-BF): Compound 1 (352.9 mg, 0.46 mmol), 4-bromo-1,1,1-trifluorobutane(1 g, 4.88 mmol), potassium carbonate (538.7 mg, 3.76 mmol), potassium iodide (790 mg, 4.64 mmol) and 80 mL of ultra-dry N,N-dimethylformamide were added to a round bottom flask. Then the mixture was deoxygenated with argon for 15 min and the temperature was raised to 80 degrees

Celsius and reflux for 24 h. After removing the solvent from the filtrate, the residue was extracted with ethyl acetate and H₂O. The organic layers were combined and dried over anhydrous magnesium sulfate and filtered to obtain a crude product. After the solvent was distilled off under reduced pressure, the crude product was purified by column chromatography using petroleum ether/dichloromethane (v/v, 1:1) as the eluent to obtain a red solid. ¹H NMR (400 MHz, CDCl₃) δ 7.05 (s, 2H), 4.72 (t, *J* = 7.2 Hz, 4H), 2.83 (t, *J* = 7.6 Hz, 4H), 2.05 (dd, *J* = 14.5, 6.8 Hz, 6H), 1.92-1.79 (m, 9H), 0.88 (t, *J* = 6.8 Hz, 7H). MALDI-TOF MS (m/z): 994.36.

Compound 3-2 (BTP-N-OF): was synthesized by a similar procedure as compound 3-1. The final product were obtained as red solid. ¹H NMR (400 MHz, CDCl₃) δ 6.76 (s, 2H), 3.90 (s, 4H), 2.52 (t, J = 7.5 Hz, 4H), 2.13-1.93 (m, 6H), 1.46 (dd, J = 14.5, 7.0 Hz, 6H), 1.32 (d, J = 25.6 Hz, 44H), 0.90 (t, J = 6.4 Hz, 8H). MALDI-TOF MS (m/z): 1078.46.

Compound 3-3 (BTP-N-DF): was synthesized by a similar procedure as compound 3-1. The final product were obtained as red solid. ¹H NMR (400 MHz, CDCl₃) δ 8.05 (s, 1H), 6.84 (s, 1H), 4.16 (t, J = 6.7 Hz, 1H), 2.60 (t, J = 7.7 Hz, 1H), 2.08-1.96 (m, 1H), 1.74 (s, 1H), 1.68 – 1.63 (m, 1H), 1.53-1.44 (m, 1H), 1.41-1.23 (m, 9H), 0.89 (t, J = 6.7 Hz, 1H). MALDI-TOF MS (m/z): 1135.65.

Compound 4-1(BTP-BF-CHO): Compound 3-1 (400 mg, 0.41 mmol), ultra dry N,Ndimethylformamide (0.59 mL, 7.6 mmol) and phosphorus oxychloride (0.71 mL, 7.6 mmol),and 1,2dichloroethane were added into a 100 mL round bottom flask, fully degassed, exchanged for 15 minutes, and heated to 90 degrees Celsius to reflux and react for 12 h. After the reaction is over, the mixture was cooled to room temperature, and 40 mL of the sodium acetate solution (1 M/L aqueous solution) was added to it. The mixed solution was then stirred at room temperature for 30 minutes, poured into water, extracted with dichloromethane, and the organic phase was dried with MgSO₄ and concentrated under reduced pressure. The crude product was purified by silica gel chromatography using dichloromethane/petroleum ether (1:1, v/v) as the eluent to obtain BTP-BF-CHO as a dark red solid. ¹H NMR (400 MHz, CDCl₃) δ 10.07 (s, 1H), 5.29 (s, 1H), 4.77 (s, 2H), 3.11 (s, 2H), 2.11 (s, 5H), 1.87 (s, 2H), 1.25 (s, 14H), 0.87 (s, 4H). MALDI-TOF MS (m/z): 1050.35.

Compound 4-2(BTP-OF-CHO): was synthesized by a similar procedure as compound 4-1 and compound 3-1. The final product was obtained as a dark red solid. ¹H NMR (400 MHz, CDCl₃) δ 9.91 (s, 1H), 4.25 (s, 2H), 4.05 (s, 2H), 2.73 (s, 2H), 1.98 (s, 6H), 1.86 (s, 3H), 1.68 (s, 3H), 1.49 (s, 3H), 1.19 (s, 23H), 0.81 (s, 3H). MALDI-TOF MS (m/z): 1134.45.

Compound 4-3(BTP-DF-CHO): was synthesized by similar procedure as compound 4-1 and compound 3-1. The final product was obtained as a dark red solid. ¹H NMR (400 MHz, CDCl₃) δ 10.13 (s, 1H), 4.64 (s, 2H), 3.19 (s, 2H), 1.26 (s, 15H), 0.86 (d, J = 4.2 Hz, 2H). MALDI-TOF MS (m/z): 1190.51.

Compound 5-1(BTP-BF): Compound 4-1 (150 mg, 0.15 mmol), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (0.21 mg, 0.91 mmol), pyridine (5 mL), and chloroform (45 mL) were dissolved in a round bottom flask under nitrogen. The mixture was stirred at 65 degrees Celsius overnight. After cooling to room temperature, the mixture was poured into methanol and filtered. The residue was purified by column chromatography, using dichloromethane/petroleum ether (1/1, v/v) as the eluent to give a black-blue solid BTP-BF. ¹H NMR (400 MHz, CDCl₃) δ 8.94 (s, 1H), 8.51 (s, 1H), 7.71 (s, 2H), 7.65 (s, 1H), 7.52 (s, 2H), 4.88 (s, 2H), 4.31 (s, 2H), 3.10 (s, 2H), 2.47 (s, 1H), 2.32 (s, 1H), 2.19 (s, 5H), 2.02 (s, 2H), 1.26 (s, 24H), 0.88 (s, 9H). MALDI-TOF MS (m/z): 1446.36.

Compound 5-2(BTP-OF): was synthesized by a similar procedure as compound 4-1 and compound 3-1. The final product was obtained as a black-blue solid. ¹H NMR (400 MHz, CDCl₃) δ 8.62 (s, 1H), 8.36 (s, 1H), 7.55 (s, 1H), 4.63 (s, 2H), 2.92 (s, 2H), 2.09 (s, 5H), 1.74 (s, 2H), 1.61 (dd, *J* = 15.0, 7.7 Hz, 3H), 1.25 (s, 35H), 0.87 (s, 9H), 0.07 (s, 2H), 0.00 (s, 2H). MALDI-TOF MS (m/z): 1558.48.

Compound 5-3(BTP-DF): was synthesized by a similar procedure as compound 4-1 and compound 3-1. The final product was obtained as black-blue solid. ¹H NMR (400 MHz, CDCl₃)) δ 8.91 (s, 1H), 8.51 (dd, *J* = 9.4, 6.4 Hz, 1H), 7.65 (d, *J* = 14.5 Hz, 1H), 4.86 (s, 2H), 3.09 (s, 2H), 2.28 – 2.17 (m, 2H), 2.16 (s, 2H), 1.81 (s, 2H), 1.53 (s, 6H), 1.26 (s, 11H), 0.86 (d, *J* = 6.9 Hz, 3H). MALDI-TOF MS (m/z): 1614.55.

Methods

Molecular structure characterization (NMR, MS spectra, DFT).

¹H NMR was obtained on a Bruker Avance III 400 NMR Spectrometer (operating at 400 MHz, using CDCl₃ as solvent using tetramethylsilane (TMS) as internal standard). The mass spectra were measured by the Bruker Microflex MALDI-TOF mass spectrometer. The HOMO and LUMO levels of donor unit, π -bridge and acceptor units were optimized by the density functional theory (DFT) at

the B3LYP/6-31G (d, p) level. To simplify the calculation, the alkyl groups were replaced by methyl. All calculations were performed in the gas phase and with Gaussian 09 program.¹

Molecular properties characterization (UV-vis spectra, CV, contact angle).

The UV-Vis absorption spectra of the solution and film were measured by the Perkin Elmer Lambda 950 spectrophotometer. The electrochemical cyclic voltammetry (CV) was conducted an electrochemical workstation (VMP3 Biologic, France) with a Pt disk coated with the blend film, a Pt plate, and an Ag⁺/Ag electrode acting as the working, counter, and reference electrodes, respectively, in a 0.1 mol/L tetrabutylammonium phosphorus hexafluoride (Bu₄NPF₆) acetonitrile solution. The experiments were calibrated with the standard ferrocene/ferrocenium (Fe) redox system and the assumption that the energy level of Fe is 4.8 eV below vacuum. The contact angle (θ) in solutions of BTP-BF, BTP-OF and BTP-DF were measured on ITO/glass substrate by using the pendant drop method with the XG-CAMB₃ standard contact angle meter.

AFM, TEM, and GIWAXs characterization.

The atom force microscopy (AFM) images were taken on a NanoScopeIIIa controller (Veeco Metrology Group/Digital Instruments, Santa Barbara, CA) using a built-in software (version V6.13R1) to capture images. The transmission electron microscopy (TEM) images were acquired using a HITACHI H-7650 electron microscope operating at an acceleration voltage of 100 kV. The grazing incidence wide-angle X-ray scattering (GIWAXS) experiments were conducted using the XEUSS SAXS/WAXS equipment.² CCL was calculated by Scherrer equation: CCL = $2\pi K$ /FWHM, where *K* is shape factor (0.9 is used here), FWHM represents the full-width at half-maximum of the peak.³

Device fabrication and measurement.

All the OSC devices were fabricated by using a conversional structure of ITO/PEDOT:PSS/active layer/PDINN/Ag, where PDINN and PEDOT:PSS were respectively used as electron-transport and hole-transport interlayer. The ITO glass substrates were cleaned sequentially under sonication with detergent, deionized water, acetone and isopropyl alcohol. After oxygen plasma cleaning for 15 min, the PEDOT:PSS layer was deposited by spin-coating under 3500 rpm for 30 seconds on top of the ITO substrate with thermal annealed for 15 minutes at 150 °C. The blended solution was prepared by mixing PTQ10 and acceptors in a 1:1.4 weight ratio into chloroform (CF) with the addition of a small amount of chloronaphthalene (0.5 %, v/v). The ETLs dissolved in methanol at a concentration

of 1 mg/ml were spun onto the blend layer at 3000 rpm for 30 seconds. Finally, 160 nm-thick Ag was deposited onto the ETLs layer under vacuum at a pressure of 3×10^{-6} . Except for the fabrication of PEDOT:PSS layer, the other processes were all carried out in a nitrogen-filled glovebox.

The current density-voltage (*J-V*) curves were obtained by a Keithley 2420 source-measure unit. The photocurrent was measured under illumination using an Oriel Newport 150 W solar simulator (AM 1.5G), and the light intensity was calibrated with a Newport reference detector (Oriel PN 91150 V). The external quantum efficiency (EQE) measurements of the devices were performed in air with an Oriel Newport system (Model 66902). The relationship of J_{sc} to the light intensity was measured by steady-state current-voltage measurement, the light intensity was modulated by neutral density filters (NDF) with different values of optical density (OD).

SCLC device Fabrication: Mobility measurements of blend films were characterized using a holeonly device configuration of ITO/PEDOT:PSS/active layer/MoO_x/Ag and electron-only device construct as ITO/ZnO/active layer/PDINN/Al in the space charge limited current regime. The mobilities were determined by fitting the dark current to the model of a single carrier SCLC, which is described by the equation:

$$J = 9\varepsilon_0 \varepsilon_r \mu V^2 / 8L^3$$

where J is the current density, L is the film thickness of the active layer, μ is the hole mobility, ε_r is the relative dielectric constant of the transport medium. It is assumed to be 3, which is typical for conjugated organic materials. ε_0 is the permittivity of free space, V is the internal voltage in the device and $V = V_{appl} - V_r - V_{bi}$, where V_{appl} is the applied voltage to the device, V_r is the voltage drop due to contact resistance and series resistance across the electrodes, and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes.

Operational Stability Test: Operational stability of the cells was performed on a multi-channel solar cell performance decay testing system ((PVLT-G8001M, Suzhou D&R Instruments Co. Ltd.) inside a N₂-filled glove box (H₂O < 10 ppm, O₂ < 10 ppm), and the cells were illuminated with a white LED light (D&R Light, L-W5300KA-150, Suzhou D&R Instruments Co. Ltd. see Figure S6, Supporting Information for the light spectrum) at a simulated one sun intensity (the initial short current equals to the J_{sc} measured under standard condition). The cell's performance was measured

by I-V sweeping from 1.2 to -0.05 V, with a step of 0.01 V. The temperature was measured from time to time and it was around 40-50 °C.

1. Supplementary Figures



Figure S1. The density functional theory (DFT) calculation of molecules.



Figure S2. Electrochemical cyclic voltammetry curves of these acceptors films measured in 0.1 mol $L^{-1}Bu_4NPF_6$ acetonitrile solutions.



Figure S3. Water and diiodomethane contact angles of the pristine donor (a, f) PTQ10 and acceptors (b, g) BTP-BF, (c, h) BTP-OF, (d, i) BTP-DF, and (e, j) Y6.



Figure S4. The out-of-plane and in-plane cuts of the pure film GIWAXS patterns.



Figure S5. Absorption spectra of PTQ10:BTP-BF, PTQ10:BTP-OF, and PTQ10:BTP-DF in blend

films.



Figure S6. Spectrum of the LED light used for aging test.



Figure S7. Normalized (a) V_{oc} , (b) J_{sc} , (c) FF, and (d) PCE decay of the PTQ10:Accepters solar cells under continuous illumination 300 h in glove box.

2. Supplementary Tables

D/A	Additive (%)	Annealing (°C)	$V_{oc}(\mathbf{V})$	J_{SC} (mA/cm ⁻²)	FF(%)	PCE(%)
1:1.3	-	100	0.70	6.97	47.44	2.22
	-	100	0.66	6.94	56.66	2.59
1.1.4	0.3%CN	100	0.72	11.72	44.60	3.78
1:1.4	0.5%CN	100	0.75	12.16	49.60	4.53
	0.7%CN	100	0.73	8.02	52.32	3.12
1:1.5	-	110	0.68	7.05	47.61	2.30

Table S1. Detailed photovoltaic performance data of the OSCs with different total concentration of donors (PTQ10) and BTP-BF in CF.

Table S2. Detailed	photovoltaic	performance	data of the	OSCs based	on PTQ10:BTP-OF.
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Ad D/A	Additive	Annealing	$V_{oc}(\mathbf{V})$	$J_{\rm sc}({\rm mA/cm}^{-2})$	FF(%)	PCE(%)
	(%)	(°C)		st		
1:1	-	-	0.75	8.44	33.74	2.14
1:1.2	-	-	0.80	22.38	47.14	8.67
1:1.3	-	-	0.81	24.56	47.77	9.67
1:1.4	-	-	0.83	25.68	59.42	12.86
	0.3%CN	-	0.80	22.40	35.23	6.33
		-	0.82	24.81	50.90	10.39
	0.50/CN	90	0.83	24.37	64.08	12.96
	0.570CIN	100	0.80	25.70	49.48	10.36
		120	0.64	13.23	32.55	2.81
	1.0%CN	-	0.7	18.01	50.02	6.59
1:1.5	-	-	0.74	14.45	34.52	3.85

D/A	Additive	Annealing	$V_{-}(\mathbf{V})$	$I (mA/cm^{-2})$	FF(%)	PCE(%)
Dir	(%)	(°C)	00	Sc (million)	11(/0)	101(/0)
	0.4%CN	95	0.82	26.06	66.55	14.21
		90	0.82	26.17	67.33	14.58
1.1.25	0.5%CN	95	0.83	26.47	68.91	15.14
1:1.35		100	0.84	26.80	65.41	14.68
		105	0.85	25.24	67.08	14.43
	0.6%CN	95	0.82	20.61	40.36	7.01
1:1.4	0.5%CN	100	0.85	25.48	65.52	14.26
	0.7%CN	100	0.84	25.97	65.68	14.44
1:1.45	0.5%CN	100	0.82	24.89	67.41	13.88

Table S3. Detailed photovoltaic performance data of the OSCs based on PTQ10:BTP-DF.

Table S4. The hole mobility and electron mobility of the films with PTQ10 as donor.

Acceptor materials	μ_e $(cm^2V^{-1}s^{-1})$	μ_h ($cm^2V^{-1}s^{-1}$)	$\mu_{h/}\mu_{e}$
Y6	1.91×10 ⁻⁴	5.35×10 ⁻⁴	2.80
BTP-BF	1.37×10-4	5.43×10 ⁻⁴	3.96
BTP-OF	1.75×10 ⁻⁴	5.20×10 ⁻⁴	2.97
BTP-DF	2.11×10 ⁻⁴	5.80×10 ⁻⁴	2.75

Table S5. Inverted devices with ITO/ZnO/PTQ10:Acceptor/MoO₃/Ag.

Active layer	V _{oc} (V)	FF (%)	J _{sc} (mA cm ⁻²)	PCE (%)
PTQ10:BTP-BF	0.71	41.63	7.82	2.31
PTQ10:BTP-OF	0.84	57.10	22.12	10.61
PTQ10:BTP-DF	0.83	65.65	24.85	13.54

Table S6. Lamellar distances, π - π stacking distances, and coherence length of the films (calculated from Scherrer equation: CCL¹/₄2 π K/ Δ q, where Δ q is the full width at half maximum of the peak and *K* is a shape factor [K¹/₄1.0 was used here]).

Films	CCL [100] [Å]	CCL [010] [Å]	d [100] [Å]	d [010] [Å]
PTQ10:BTP-BF	69.68	24.02	22.83	3.58
PTQ10:BTP-OF	93.96	31.92	23.65	3.57
PTQ10:BTP-DF	106.11	33.94	23.60	3.56



3. Spectral Charts of ¹H NMR and MS

Figure S8. ¹H NMR spectrum of 3-1 (BTP-N-BF) in CDCl₃.



Figure S9. ¹H NMR spectrum of 3-2 (BTP-N-OF) in CDCl₃.



Figure S10. ¹H NMR spectrum of 3-3 (BTP-N-DF) in CDCl₃.



Figure S11. ¹H NMR spectrum of 4-1 (BTP-BF-CHO) in CDCl₃.



Figure S12. ¹H NMR spectrum of 4-2 (BTP-OF-CHO) in CDCl₃.



Figure S13. ¹H NMR spectrum of 4-3 (BTP-DF-CHO) in CDCl₃



Figure S14. ¹H NMR spectrum of 5-1 (BTP-BF) in CDCl₃.



Figure S15. ¹³C NMR spectrum of 5-1 (BTP-BF) in CDCl₃



Figure S16. ¹H NMR spectrum of 5-2 (BTP-OF) in CDCl₃.



Figure S17. ¹³C NMR spectrum of 5-2 (BTP-OF) in CDCl₃.



Figure S18. ¹HNMR spectrum of 5-3 (BTP-DF) in CDCl₃.



Figure S19. ¹³C NMR spectrum of 5-3 (BTP-DF) in CDCl₃.



Figure S20. The high resolution mass spectrum (MALDI-TOF) of compound 5-1 (BTP-BF).



Figure S21. The high resolution mass spectrum (MALDI-TOF) of compound 5-2 (BTP-OF).



Figure S22. The high resolution mass spectrum (MALDI-TOF) of compound 5-3 (BTP-DF).

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