Supporting Information

Achieving 17.38% efficiency of ternary organic solar cells enabled by a large-bandgap donor with noncovalent

conformational lock

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1. Design strategy



Scheme 1. Design strategy and chemical structure of BTBR-2F.

2. Materials and Instruments

All materials and solvents were purchased from Tianjin Kemiou, Alfa Aesar Co., Ltd. and used without further purification. Compound Y6, PM6 and BDTT were purchased from eFlexPV Ltd., and Hyper Inc. Nuclear magnetic resonance (NMR) spectra of the materials were collected on Bruker AVANCE spectrometer, deuterated chloroform (CDCl₃) was used as the solvent and tetramethylsilane (TMS) as the internal reference. Mass spectrometry (MS) data were measured on a Brooker solanX 70 FT-MS with ESI as the ion source. The photophysical and electronchemical properties of the materials were measured on UV-visible-near infrared spectrograph (Agilent Cary 60 spectrometer) and electrochemistry workstation (CHI660A, Chenhua Shanghai), respectively. The thermogravimetric analyses (TGA) and differential scanning calorimetric (DSC) measurements were carried out on a TA TGA 50 and a DSC Q10 differential scanning calorimeter instrument under nitrogen gas flow with a 20 °C min⁻¹ and a 10 °C min⁻¹ heating rate, respectively. The DSC samples were prepared by scraping and collecting the annealed blend films from ITO glass, which were prepared by coating and drying the blend solutions. Atomic force microscopy (AFM) images were characterized with a Veeco Multi-Mode 8 in a tapping mode. GIWAXS measurements were carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300K detector, and the incidence angle is 0.2°.

3. OSCs fabrication and measurement

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Electron-only devices were fabricated with the structure of ITO/ZnO/Active materials/PFN-Br/Al, and hole-only devices were fabricated with the structure of ITO/PEDOT: PSS/Active materials/MoO₃/Al. The mobilities were determined by fitting the dark current under low voltage, which is described as $J=(9/8)\varepsilon_0\varepsilon_r\mu((V^2)/(L^3))$, where J is the current, μ is the electron mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, V is the effective voltage, and L is the thickness of the blend films. The effective voltage can be obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the applied voltage (V_{appl}) , $V = V_{appl} - V_{bi} - V_s$.

Inverted OSC devices (ITO/ZnO/active layer/MoO₃/Al) were utilized for studying photovoltaic performance. The patterned ITO was carefully washed by acetone, water, ethanol and isopropanol, and then treated by UV-ozone cleaning for 15 min. A ZnO precursor solution was spin coated onto a cleaned ITO, subsequently annealed at 220°C for 30 min in the air to obtain a ZnO-covered ITO. The chloroform solution (13.2 mg mL⁻¹ in total) with 0.5 vol% of 1-CN was spin-coated on ZnO layer with 1800 rpm for 40 s to obtain a photosensitive active layer. The PM6: Y6 blend film and the ternary blend films were thermal annealed at 110 °C for 10 min. The BTBR-2F: Y6 blend film was prepared with/without 0.5 vol% of 1-CN and annealed at 160 °C for 2 min. At last, the MoO₃ layer and Al electrode were slowly evaporated onto the surface of active layer under a vacuum pressure of 2×10^{-4} Pa. The *J-V* plots were measured using a Keithley 2400 source meter, and an Oriel Sol3A solar simulator coupled with 1.5 G solar spectrum filters was used as the light source.



4. Synthesis and characterization of BTBR-2F

Scheme 2. The synthetic routes of BTBR-2F.

The synthetic routes of **BTBR-2F** are shown in **Scheme S2**. *Compound 1* is synthesized according to the reported reference.^[1] The structure of **BTBR-2F** has been characterized and confirmed by ¹H NMR, ¹³C NMR and HRMS measurement. **BTBR-2F** shows excellent solubility in common organic solvents, such as chloroform and dichloromethane.

4.1. Synthesis of compound 2

Anhydrous THF (10 mL) was added to a dried 250 mL flask under a nitrogen atmosphere. After the solution was cooled to -78 °C, n-butyllithium (2M in THF, 1.55 mL, 3.10 mmol) was added slowly. Subsequently, a solution of compound 1 (1.561 g. 3.10 mmol) in THF (50 mL) was added via syringe over 30 minutes. After dimethylformamide (1.2 mL) was added via syringe, this mixture was stirred for 2 h at -78 °C and warmed to room temperature, and 60 mL diluted hydrochloric acid (1 mol L⁻¹) was added. Volatile solvents were removed under vacuum, and the residue was partitioned between ethyl acetate and brine (200 mL each). The layers were separated, and the aqueous phase was washed once with diethyl ether. The combined organic phase was washed once with brine, dried over MgSO₄, filtered and concentrated under vacuum to obtain a crude product. Finally, the crude product was purified by silica gel chromatography to obtain 1.285 g of compound 2 as a yellow solid with a yield of 78% (petroleum ether /dichloromethane=5/1, v/v).¹H NMR (400 MHz, CDCl₃) δ =10.04 (s, 1H), 7.37-7.42 (m, 4H), 7.01 (s, 1H), 2.96 (t, J = 7.6 Hz, 2H), 2.62 (t, J = 7.8 Hz, 2H), 1.62-1.70 (m, 4H), 1.28-1.34 (m, 20H), 0.86-0.90 (t, J = 6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 181.97, 156.62, 154.15, 153.26, 144.46, 144.13, 137.43, 134.93, 129.91, 128.88, 124.13, 122.07, 120.16, 115.46, 115.19, 31.84, 31.47, 30.57, 29.35, 28.59, 22.68, 22.65, 14.11.





Figure S1. ¹H NMR spectrum of compound 2 in CDCl₃.



Figure S2. ¹³C NMR spectrum of compound 2 in CDCl₃.

4.2. Synthesis of **DFB-2T**

N-bromosuccinimide (NBS, 0.483 g, 2.71 mmol) was added to the solution containing 25 mL chloroform, 25 mL of acetic acid, and *compound 2* (1.200 g, 2.26 mmol) under ice bath. After ice was naturally melted, the mixture was stirred at room temperature under dark for one night. Then the mixture was washed with sodium bicarbonate solution, extracted with dichloromethane (3 x 30 mL), and dried over anhydrous magnesium sulphate (MgSO₄). The solvent was removed by a rotate

evaporator and the residue was purified by silica gel chromatography (petroleum ether/dichloromethane, v/v = 5:1) to yield **DFB-2T** as a yellow solid (1.103 g, yield 80%). ¹H NMR (400 MHz, CDCl₃) δ =10.05 (s, 1H), 7.41-7.44 (m, 1H), 7.38 (s, 1H), 7.31-7.35 (m, 1H), 7.22 (s, 1H), 2.97 (t, *J* = 7.6 Hz, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 1.71-1.73 (m, 2H), 1.59-1.64 (m, 2H), 1.28-1.33 (m, 20H), 0.88 (t, *J* = 6.4 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 182.05, 156.63, 154.16, 153.32, 143.91, 143.16, 137.53, 134.54, 130.02, 128.13, 123.19, 120.71, 115.53, 114.54, 111.60, 31.83, 31.48, 29.57, 29.34, 28.57, 22.68, 22.65, 14.11.





Figure S3. ¹H NMR spectrum of DFB-2T in CDCl₃.



Figure S4. ¹³C NMR spectrum of DFB-2T in CDCl₃.

4.3. Synthesis of BDTB-2F-CHO

DFB-2T (305 mg, 0.500 mmol), **BDTT** (181 mg, 0.200 mmol), and Pd(PPh₃)₄ (23 mg, 0.020 mmol) were dissolved in deoxygenated toluene. The reaction mixture was refluxed for 24 h and then extracted with dichloromethane. The collected organic layer was dried over anhydrous MgSO₄. After removal of the solvent under reduced pressure, the residue was purified by silica gel chromatography (petroleum ether/dichloromethane, v/v = 2:1) as eluent and then recrystallized from methyl alcohol to give a red product **BDTB-2F-CHO** (199.65 mg, 61%). ¹H NMR (400 MHz, chloroform-*d*) δ =10.03 (s, 2H), 7.68 (s, 2H), 7.35-7.40 (m, 10H), 6.93 (d, *J* = 3.6 Hz, 2H), 2.95 (t, *J* = 7.6 Hz, 4H), 2.89 (d, *J* = 6.8 Hz, 4H), 2.84 (t, *J* = 7.8 Hz, 4H), 1.57-1.73 (m, 10H), 1.28–1.33 (m, 56H), 0.87-0.90 (m, 24H).¹³C NMR (100 MHz, CDCl₃) δ 181.96, 156.62, 154.15, 153.62, 153.25, 145.98, 143.98, 141.84, 139.01, 137.43, 136.90, 136.81, 136.59, 133.99, 132.91, 130.84, 129.97, 127.85, 125.50, 123.42, 121.82, 120.44, 115.73, 115.11, 41.52, 34.33, 32.57, 31.93, 31.84, 31.46, 30.58, 29.72, 29.65, 29.47, 29.36, 29.20, 28.96, 28.59, 25.76, 25.58, 23.64, 23.07, 22.71, 22.65, 14.18, 14.12, 14.09, 10.93.

Figure S5. ¹H NMR spectrum of BDTB-2F-CHO in CDCl₃.

Figure S6. ¹³C NMR spectrum of BDTB-2F-CHO in CDCl₃.

4.4. Synthesis of **BTBR-2F**

Under nitrogen atmosphere, a mixture solution of **BDTB-2F-CHO** (180 mg, 0.110 mmol), 3-ethyl-2-thioxothiazolidin-4-one (46 mg, 0.290 mmol), pyridine (0.5 mL), and chloroform (25 mL) was added to a 50 mL round bottom flask and then refluxed for 24 h. After cooling to room temperature, the mixture was poured into methanol (80 mL) and then filtered. The residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/chloroform, v/v = 1:1) to give a dark red solid (150 mg, 71%). ¹H NMR (400 MHz, chloroform-*d*) δ 7.87 (s, 2H), 7.61 (s, 2H), 7.27-7.38 (m, 10H), 6.94 (d, *J* = 4.0 Hz, 2H), 4.15-4.17 (m, 4H), 2.93 (d, *J* = 6.8 Hz, 4H), 2.76-2.79 (m, 8H), 1.64-1.73 (m, 10H), 1.28–1.33 (m, 62H), 0.87-0.90 (m, 24H). ¹³C NMR (100 MHz, CDCl₃) δ 192.02, 167.24, 156.14, 155.88, 153.68, 153.43, 150.55, 145.63, 141.97, 141.32, 138.36, 136.89, 136.58, 136.45, 133.65, 132.85, 130.65, 129.39, 127.90, 125.41, 122.91, 122.51, 120.96, 120.33, 120.01, 114.71, 114.47, 41.51, 39.81, 34.35, 32.62, 32.03, 31.88, 31.12, 30.38, 30.08, 29.91, 29.62, 29.52, 29.44, 29.29, 28.99, 25.71,

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23.17, 23.14, 22.81, 22.79, 22.69, 14.26, 14.18, 14.13, 12.30, 10.96. HRMS m/z of $C_{106}H_{128}F_4N_2O_2S_{12}$ for [M+Na]⁺: calcd. 1945.6510; found: 1945.6502.

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 chemical shift(ppm)

Figure S8. ¹³C NMR spectrum of BTBR-2F in CDCl₃.

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Figure S9. HRMS spectrum of BTBR-2F.

5. Thermal stability and Cyclic voltammetry

Figure S10. TGA curves of BTBR-2F with a heating rate of 20 °C min⁻¹ under N_2 atmosphere.

Figure S11. Cyclic voltammogram of PM6, BTBR-2F, and Fc/Fc⁺.

6. The *J*-*V* curves of the OSCs

Figure S12. J-V curves of the binary and ternary OSCs

6. Physical properties of materials

Figure S13. 2D-GIWAXS images of (a) PM6 and (b) Y6 thin films.

Figure S14. The GISAXS intensity profiles of PM6: Y6 blend film and the ternary blend film with 20% BTBR-2F along the in-plane direction.

Figure S15. DSC curves of PM6, BTBR-2F, PM6:BTBR-2F (4: 1 by weight) (a) and Y6:BTBR-2F blend (5: 1 by weight) (b) in the cooling process, (c) DSC curve of ternary blend (20 wt% BTBR-2F content).

Figure S16. $J^{1/2}$ -V curves of the (a) hole-only and (b) electron-only devices based on PM6: BTBR-2F: Y6 films with different weight ratios of BTBR-2F.

Figure S17. Photoluminescence spectra of PM6 neat film, BTBR-2F neat film, PM6: Y6 (1:1), PM6: BTBR-2F (4:1) binary blends and PM6: BTBR-2F: Y6 (0.8:0.2:1) ternary blend excited at 600 nm.

Sample	$q_z(Å^{-1})$	CCL (Å)	intensity	
PM6:Y6 (0% BTBR-2F)	0.28, 1.74	22.4, 3.6	9.269, 7.036	
PM6:Y6:BTBR-2F (20% BTBR-2F)	0.285, 1.75	22.0, 3.6	11.903, 7.045	
BTBR-2F:Y6 (100% BTBR-2F)	0.295, 1.75	21.3, 3.6	10.311, 2.705	
BTBR-2F	0.355, 0.70	17.7, 9.0	150.660, 6.666	
DMC	0.315, 0.95,	19.9, 6.6,	(1 796 2 062 4 971	
PMO	1.70	3.7	01.780, 5.905, 4.871	
Y6	1.755	3.6	6.329	

Table S1. Data of the peak analysis of GIWAXS in the OOP direction.

Table S2. Data of the peak analysis of GIWAXS in the IP direction.

Sample		(Λ^{-1})	CCL	intensity	
	Sampe	$\mathbf{q}_{xy}(\mathbf{A})$	(Å)	mensity	
	PM6:Y6 (0% BTBR-2F)	0.295	21.3	8.838	
	PM6:Y6:BTBR-2F (20% BTBR-2F)	0.295	21.3	8.643	
	BTBR-2F:Y6 (100% BTBR-2F)	0.29	21.7	7.094	
	BTBR-2F	0.315, 1.71	19.9, 3.7	2.490, 2.905	
	PM6	0.285	22.0	7.240	
	Y6	0.28	22.4	3.561	

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	Water	EG	a, d	ar ^p	Surface		
	contact	contact	γ 1	γ 1-	tension ^a	$\chi^{b}_{PM6:X}$	$\chi_{BTBR-2F:X}$
	angle[°]	angle[°]	[mN m ⁻]	[mN m ⁻]	[mN m ⁻¹]		
PM6	93.25	72.00	17.57	4.28	21.84	-	0.006 K
BTBR-2F	93.75	71.50	18.92	4.35	22.60	0.006 K	-
¥6	89.5	64.25	23.20	3.97	27.17	0.290 K	0.210 K

 Table S3. The parameters of surface energies.

(a) Surface tension was calculated by Owens-Wendt-Kaelble 's model: $\gamma_L(1 + \cos \theta)$

 $= 2(\sqrt{\gamma_L^d \gamma_S^d} + \sqrt{\gamma_L^p \gamma_S^p}).$ (b)The χ value was calculated by formula: $\chi_{A:D}$ = K $(\sqrt{\gamma_A} - \sqrt{\gamma_D})2$.

BTBR-2F content	$\mu_{\rm h}$	μ_{e}	/
[wt%]	$(10^{-4} \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1})$	$(10^{-4} \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1})$	$\mu_{\rm h}/\mu_{\rm e}$
0	4.18	2.75	1.52
10	7.76	4.59	1.69
20	8.13	7.70	1.05
30	5.43	4.84	1.12
50	2.88	2.01	1.43
100 ^a	0.31	0.21	1.48

Table S4. Charge mobilities of the binary and ternary SCLC devices.

(a) Thermal annealing at 160 °C for 2 min without 1-CN.

References:

[1] Liu, Guang Run, Weng, Chao, Yin, Pan, Tan, Song Ting, Shen, Ping, Impact of the number of fluorine atoms on crystalline, physicochemical and photovoltaic properties of low bandgap copolymers based on 1,4-dithienylphenylene and diketopyrrolopyrrole, Polymer, 2017, 125, 217-226.