

Supporting Information

Simple non-fused small-molecule acceptors with bithiazole core: synthesis, crystallinity and photovoltaic properties

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1. General experimental information and characterizations

All manipulations were performed under dry nitrogen flow. ^1H NMR spectra were recorded at 400 MHz and 500 MHz on Bruker Avance-400 and Bruker Avance-500 spectrometer using CDCl_3 as solvent and tetramethylsilane (TMS) as internal standard. Mass spectra (MS) were measured on a Bruker Daltonics BIFLEX III MALDI-TOF analyzer. Thermo-gravimetric analyses (TGA) were carried out on a Perkin-Elmer Diamond TG/DTA thermal analyzer at a scan rate of $10\text{ }^\circ\text{C min}^{-1}$ under nitrogen atmosphere. UV-Vis absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer. Cyclic voltammetry (CV) was conducted on a CHI630E voltammetric analyzer under nitrogen atmosphere in an anhydrous acetonitrile solution of tetrabutyl- ammonium hexafluorophosphate (Bu_4NPF_6) (0.1 M) at a scan rate of 20 mV s^{-1} . The theoretical study was performed on the 6-31G** basis set in Gaussian 09 using the density functional theory (DFT), as approximated by the B3LYP. The surface morphology of the J71: BTz-4F1 and J71: BTz-4Cl-1 blend films was investigated by an atomic force microscopy (AFM).

1.1 Synthesis of compound **2a**

Compound **1a** (1.07 g, 6.36 mmol) was dissolved in anhydrous THF (40 mL) and the solution was cooled to $-78\text{ }^\circ\text{C}$ under nitrogen atmosphere. 2.0 M of lithium diisopropyl-amide (13 mL, 25.40 mmol) was added carefully. After stirring for 2 h, 1.0 M of trimethyltin chloride (22 mL, 22.20 mmol) was added into the mixture in one portion. After 30 minutes, the reaction mixture was stirred for 12 h at room temperature. It was

then poured into water and extracted with CH₂Cl₂. The combined organic phase was dried over anhydrous MgSO₄. After removal of the solvent, compound **2a** was obtained as pale yellow solid powder (2.20 g, yield 70.0 %). ¹H NMR (400 MHz, CDCl₃) δ 7.80 (s, 2H), 0.45 (s, 18H).

1.2 Synthesis of compound **4a**

A mixture of compound **2a** (1.00 g, 2.00 mmol), Pd₂(dba)₃ (40.0 mg), P(o-tol)₃ (50.0mg) and compound **3** (1.80 g, 5.00 mmol) was dissolved in 40 mL anhydrous toluene, then stirred for 18 h at 110 °C under nitrogen atmosphere. After cooled to room temperature, the reaction solution was washed with water and extracted with CH₂Cl₂, then the combined organic phase was dried over anhydrous MgSO₄. After removal of the solvent, the crude product was purified by column chromatography eluting with PE: DCM (1:2, *V:V*) to obtain compound **4a** as bright yellow viscous solid (0.48 g, yield 33.10%). ¹H NMR (400 MHz, CDCl₃) δ 9.89 (s, 2H), 8.02 (s, 2H), 7.62 (s, 6H), 2.75 (d, *J* = 7.2 Hz, 4H), 1.72 (m, 2H), 1.25-1.22 (m, 32H), 0.87-0.84 (m, 12H).

1.3 Synthesis of BTz-4F-0

A mixture of compound **4a** (0.18 g, 0.25 mmol), compound **5** (0.32 g, 1.40 mmol) and pyridine (0.20mL) was dissolved in 25 mL anhydrous tetrahydrofuran, then stirred for 3 h at 50 °C under nitrogen atmosphere. After cooled to room temperature, the crude product was purified by column chromatography eluting with CHCl₃. Then the resulting concentrated solution was precipitated with methanol and filtered with suction, and dried under vacuum to obtain a reddish brown solid with metallic luster (0.18 g, yield 62.5%). ¹H NMR (500 MHz, CDCl₃) δ 8.83 (s, 2H), 8.57 (d, *J* = 15.9 Hz, 2H), 8.22 (s,

2H), 7.76-7.69 (m, 2H), 2.79 (d, $J = 7.1$ Hz, 4H), 1.77-1.74 (m, 2H), 1.27-1.23 (m, 32H), 0.87-0.84 (m, 12H).

1.4 Synthesis of compound **2b**

Compound **1b** (0.5 g, 2.55 mmol) was dissolved in anhydrous THF (50 mL) and the solution was cooled to -78 °C under nitrogen atmosphere. 2.0 M of lithium diisopropyl-amide (3.82 mL, 7.64 mmol) was added carefully. After stirring for 2 h, 1.0 M of trimethyltin chloride (7.64 mL, 7.64 mmol) was added into the mixture in one portion. After 30 minutes, the reaction mixture was stirred for 12 h at room temperature. It was then poured into water and extracted with CH_2Cl_2 . The combined organic phase was dried over anhydrous MgSO_4 . After removal of the solvent, compound **2b** was obtained as pale yellow solid powder (0.89 g, yield 66.87 %). ^1H NMR (500 MHz, CDCl_3) δ 2.53 (s, 6H), 0.43 (s, 18H).

1.5 Synthesis of compound **4b**

A mixture of compound **2b** (0.50 g, 0.96 mmol), $\text{Pd}_2(\text{dba})_3$ (17 mg), $\text{P}(\text{o-tol})_3$ (23mg) and compound **3** (0.80 g, 2.30 mmol) was dissolved in 25 mL anhydrous toluene, then stirred for 18 h at 110 °C under nitrogen atmosphere. After cooled to room temperature, the reaction solution was washed with water and extracted with CH_2Cl_2 , then the combined organic phase was dried over anhydrous MgSO_4 . After removal of the solvent, the crude product was purified by column chromatography eluting with PE: DCM (1:2, $V:V$) to obtain compound **4b** as bright yellow viscous solid (0.33 g, yield 45.64%). ^1H NMR (500 MHz, CDCl_3) δ 9.91 (s, 2H), 7.64 (s, 2H), 2.55 (d, $J = 7.1$ Hz, 4H), 2.45 (s, 6H), 1.60 (s, 2H), 1.17 (s, 32H), 0.84 (d, $J = 5.7$ Hz, 12H).

1.6 Synthesis of BTz-4F-1

A mixture of compound **4b** (0.24 g, 0.32 mmol), compound **5** (0.29 g, 1.28 mmol) and pyridine (0.20 mL) was dissolved in 25 mL anhydrous tetrahydrofuran, then stirred for 1 h at 50 °C under nitrogen atmosphere. After cooled to room temperature, the crude product was purified by column chromatography eluting with CHCl₃. Then the resulting concentrated solution was precipitated with methanol and filtered with suction, and dried under vacuum to obtain a reddish brown solid with metallic luster (0.32 g, yield 84.0%). ¹H NMR (400 MHz, CDCl₃) δ 8.86 (s, 2H), 8.58 (dd, J = 9.8, 6.5 Hz, 2H), 7.74 (s, 4H), 2.61 (d, J = 7.1 Hz, 4H), 2.56 (s, 6H), 1.62 (s, 2H), 1.21 (d, J = 23.0 Hz, 32H), 0.84 (m, 12H). MS (MALDI-TOF) of C₆₆H₆₄F₄N₆O₂S₄ for [M]⁺: calcd. 1177.51; found: 1177.15.

1.7 Synthesis of BTz-4Cl-1

A mixture of compound **4b** (90 mg, 0.12 mmol), compound **6** (125.75 mg, 0.48 mmol) and pyridine (0.20 mL) was dissolved in 15 mL anhydrous tetrahydrofuran, then stirred for 1 h at 50 °C under nitrogen atmosphere. After cooled to room temperature, the crude product was purified by column chromatography eluting with CHCl₃. Then the resulting concentrated solution was precipitated with methanol and filtered with suction, and dried under vacuum to obtain a reddish brown solid with metallic luster (100 mg, yield 67.59%). ¹H NMR (500 MHz, CDCl₃) δ 8.88 (s, 2H), 8.81 (s, 2H), 8.00 (s, 2H), 7.75 (s, 2H), 2.62 (d, J = 7.1 Hz, 4H), 2.57 (s, 6H), 1.62 (s, 2H), 1.18 (s, 32H), 0.84 (d, J = 4.8 Hz, 12H). MS (MALDI-TOF) of C₆₆H₆₄Cl₄N₆O₂S₄ for [M]⁺: calcd. 1243.32; found: 1243.32.

2. Devices fabrication and characterizations

Bulk heterojunction organic solar cells were fabricated with the following conventional structure: ITO/ PEDOT: PSS/active layer/PFN-Br/Al. ITO substrates were cleaned and then dried in an oven at 85°C for 12 hours. The PEDOT: PSS precursor was spin-coated onto the ITO surface at 3000 r.p.m. and thermal annealed for 15 min in air. The thickness of the ITO film are about 40 nm. Then the PEDOT: PSS-coated substrates were transferred into a nitrogen-filled glove box. Then blend solution was spin-coated on the PEDOT: PSS layer. Then evaporated 10 nm thick PFN-Br and 100 nm thick Al on the active layer. The current density-voltage ($J-V$) characteristics of the devices under illumination of AM 1.5 G solar simulator (Newport, 100 mW cm⁻², calibrated by a silicon reference cell) were measured on a computer-controlled Keithley 2420 source measure unit. The external quantum efficiencies (EQE) of organic solar cells were analyzed using a certified Newport incident photon conversion efficiency (IPCE) measurement system (Model 66902).

Optimal fabricating condition was acquired based on J71: BTz-4F-1, and then BTz-4Cl-1-based devices adopted the same condition directly without special optimization.

3. Supplementary figures and tables.

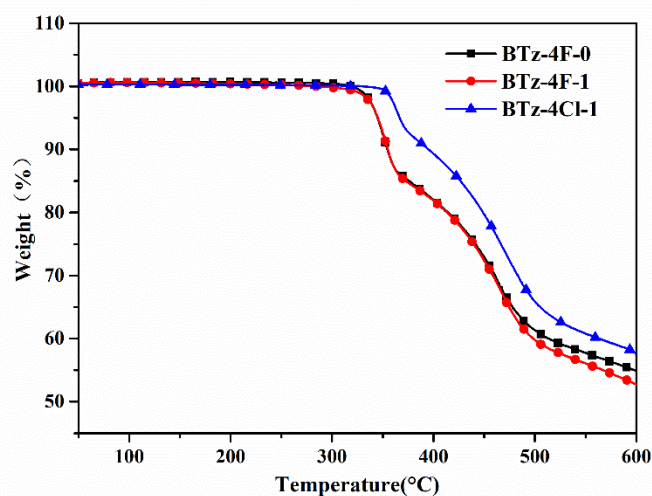


Fig. S1 TGA curve of BTz-4F-0, BTz-4F-1 and BTz-4Cl-1.

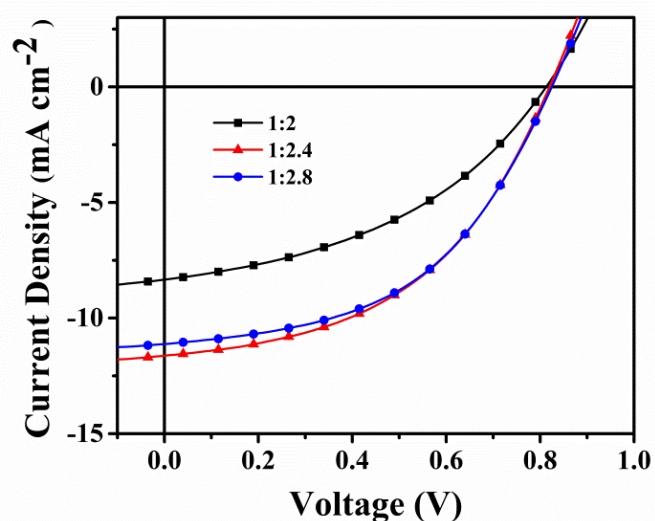


Fig. S2 J - V curve of the OSCs based on J71: BTz-4F-1 at different D/A ratios.

Table S1 Photovoltaic properties of the OSCs based on J71: BTz-4F-1 at different D/A ratios

	V_{oc} /V	J_{sc} /mA cm ⁻²	FF /%	PCE /% ^a
D/A 1:2	0.81	8.30	41.99	2.83 (2.79)
D/A 1:2.4	0.82	11.58	47.35	4.49 (4.47)
D/A 1:2.8	0.82	11.07	48.95	4.47(4.46)

^a The average PCE in parentheses were obtained from 5 devices.

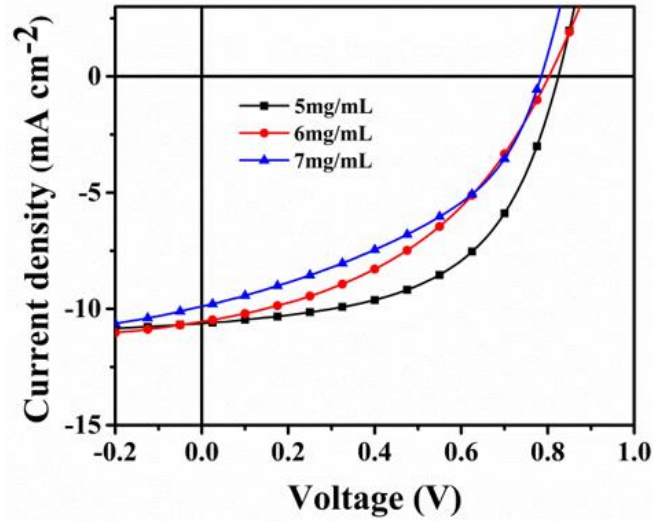


Fig. S3 J - V curve of the OSCs based on J71: BTz-4F-1 at different donor concentration.

Table S2 Photovoltaic properties of the OSCs based on J71: BTz-4F-1 at different donor concentration

	V_{oc} /V	J_{sc} / mA cm^{-2}	FF /%	PCE /% ^a	
J71 in CF(mg/mL)	5	0.82	10.59	54.51	4.76 (4.74)
	6	0.80	10.87	42.47	3.59 (3.56)
	7	0.78	9.88	42.85	3.32 (3.28)

^a The average PCE in parentheses were obtained from 5 devices.

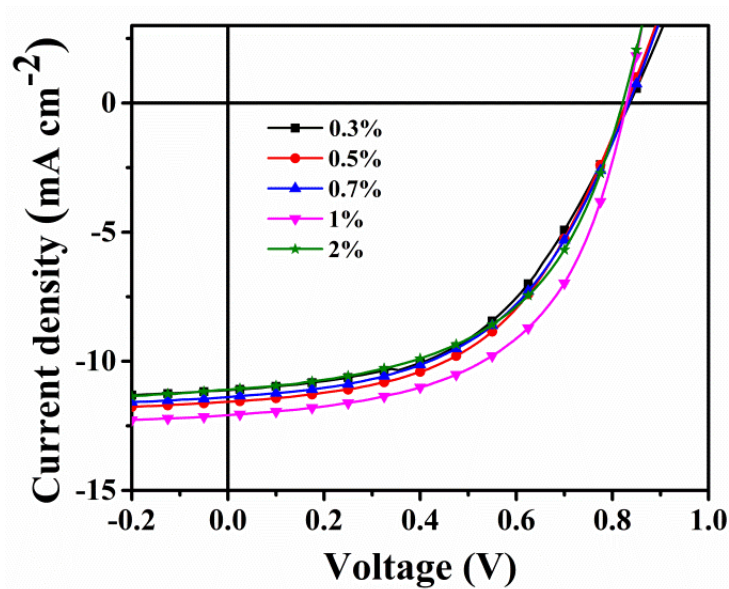


Fig. S4 J - V curve of the OSCs based on J71: BTz-4F-1 at different amount of DIO additive

Table S3 Photovoltaic properties of the OSCs based on J71: BTz-4F-1 at different amount of DIO additive

	V_{oc} /V	J_{sc} /mA cm ⁻²	FF /%	PCE /% ^a	
DIO	0.3%	0.84	11.08	50.12	4.64 (4.60)
	0.5%	0.83	11.54	50.92	4.87(4.85)
	0.7%	0.83	11.35	50.13	4.74 (4.72)
	1%	0.84	12.28	55.30	5.72 (5.66)
	2%	0.82	11.07	52.25	4.75 (4.72)

^a The average PCE in parentheses were obtained from 5 devices.

Fig. S5 Structure characterization of the BTz-4F-0, BTz-4F-1 and BTz-4Cl-1.

