

**Efficiency enhancement in dopant-free perovskite solar cells by
employing fluoro-substituted electron donor-electron acceptor
type polymeric hole-transporting materials**

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Experimental section

Materials.

Compound 1 was purchased from Kaimuke Technology., compound 2, 4 and 7 were purchased from SunaTech, compound 8 was purchased from Zhiyan Technology. Toluene was fresh distilled from CaH₂. PbI₂ (99.999%), CsI₂ (99.99%), FAI (99.5%), MABr (99.5%) were purchased from Xi'an Polymer Light Technology Corp. DMF (99.9%), DMSO (99.9%), Ethyl acetate (99.9%) and chlorobenzene (99.9%) were purchased from J&K Chemistry. Other solvents and reagents were commercially available and no further purification, unless otherwise specified. 1,3-Bis(5-bromothiophen-2-yl)-5,7-bis(2-ethylhexyl)benzo[1,2-c:4,5-c']dithiophene-4,8-dione (BDD) was synthesized according to literature. Synthesis of Compound 3, 4,7-dibromo-2-(2-octyldodecyl)-2H-benzo[d][1,2,3]triazole

Synthesis

Synthesis of, 4,7-dibromo-2-(2-octyldodecyl)-2H-benzo[d][1,2,3]triazole (**3**)

Compound 1 (500.0 mg, 1.81 mmol) and K₂CO₃ (274.5 mg, 1.99 mmol) were added into anhydrous DMF (10 mL) solution, under nitrogen, compound 2 (717.9 mg, 1.99 mmol) were added dropwise into the solution. The mixture was stirred at 75°C for 24 h. After cooling to room temperature, ethyl acetate (50 mL) was added into the mixture, followed by washing with water (3×50 mL). The organic phase was dried by anhydrous MgSO₄. After evaporating the solvent, the residue was purified by column chromatography on silica gel, employing petroleum ether : CH₂Cl₂ (12:1, v/v) as the eluent to afford the final product (535.4 mg, 53.2%) as a light yellow oil. ¹H NMR (400

MHz, Chloroform-*d*) δ 7.44 (s, 2H), 4.67 (d, $J = 7.3$ Hz, 2H), 2.34 (p, $J = 6.3$ Hz, 1H), 1.40 – 1.16 (m, 32H), 0.87 (td, $J = 6.8, 3.3$ Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.66, 129.47, 110.00, 61.19, 39.04, 31.93, 31.87, 31.14, 29.78, 29.62, 29.60, 29.48, 29.43, 29.35, 29.26, 26.02, 22.71, 22.68, 14.15, 14.14.

Synthesis of 2-(2-octyldodecyl)-4,7-di(thiophen-2-yl)-2H-benzo[*d*][1,2,3]triazole (**5**)

Compound **3** (535.4 mg, 0.96 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (44.4 mg, 4% mol) were added to a 50 mL flask. Followed by a nitrogen flushing for 10 min, compound **4** (734.8 mg, 1.96 mmol) and dry toluene (10 mL) were injected to the mixture and stirred at 110°C overnight. A saturated solution of KF (20 mL) was added into the reaction and stirring for another 6h. After cooling to room temperature, the mixture was extracted with ethyl acetate (3×30 mL) followed by washing with saturated NaCl (3×50 mL), the organic phase was dried by anhydrous MgSO_4 . After evaporating the solvent, the residue was purified by column chromatography on silica gel employing petroleum ether : CH_2Cl_2 (8:1, v/v) as the eluent to afford the final product (433.0 mg, 80%) as a light yellow oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, $J = 3.6$ Hz, 2H), 7.63 (s, 2H), 7.38 (d, $J = 5.0$ Hz, 2H), 7.24 – 7.12 (m, 2H), 4.75 (d, $J = 6.6$ Hz, 2H), 2.39 – 2.25 (m, 1H), 1.43 – 1.19 (m, 32H), 0.93 – 0.82 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.00, 140.04, 128.07, 126.94, 125.50, 123.58, 122.64, 39.11, 31.93, 31.90, 31.49, 29.91, 29.67, 29.65, 29.59, 29.36, 29.33, 26.30, 22.70, 22.68, 14.13.

Synthesis of 4,7-bis(5-bromothiophen-2-yl)-2-(2-octyldodecyl)-2H-benzo[*d*][1,2,3]triazole (**6**)

Compound **5** (433.0 mg, 0.77 mmol) and NBS (281.0mg, 1.58 mmol) was added into a 50 mL flask, then charged with nitrogen for three times. CHCl₃ (20 mL) was injected to the mixture. The reaction was stirred at 0 °C for 1 h. After removing the solvent, the residue was purified by column chromatography, employing petroleum ether: CH₂Cl₂ (8:1, v/v) as the eluent to afford the final product (503.8 mg, 90.7%) as a light yellow oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 3.9 Hz, 1H), 7.50 (s, 1H), 7.11 (d, *J* = 3.9 Hz, 1H), 4.72 (d, *J* = 6.5 Hz, 1H), 2.35 – 2.24 (m, 1H), 1.29 (dd, *J* = 39.2, 7.5 Hz, 16H), 0.87 (q, *J* = 6.4 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 141.63, 141.30, 130.85, 126.86, 122.98, 122.09, 113.20, 60.04, 39.13, 31.94, 31.90, 31.47, 29.91, 29.68, 29.66, 29.64, 29.59, 29.37, 29.33, 26.27, 22.71, 22.69, 14.14.

Synthesis of **PBCz-BTz**

Compound **7** (75 mg, 0.07 mmol) and Compound **6** (50.6 mg, 0.07 mmol) were dissolved in fresh distilled toluene (6 mL), Pd(PPh₃)₄ (3.2 mg, 4% mol) were added into the solution. After being flushed by nitrogen for 10 min, the reaction was stirred at 110°C for 48 h. After cooling to room temperature, the mixture was precipitated into methanol to afford the crude polymer. The crude polymer was purified by Soxhlet extraction via methanol, acetone, hexane and collected by chloroform. Finally, the polymer was precipitate into methanol and dry under vacuum to afford the polymer PBCz-BTz (62.0mg 81.3%). *M_n* = 15.9 kDa, PDI = 1.95, The decomposition temperatures (*T_d*) = 447 °C

Synthesis of **PBCz-FBTz**

The synthetic and purification procedure was the same as PBCz-BTz using Compound **7** (100 mg, 0.094 mmol) and Compound **8** (70.8 mg, 0.094 mmol) to afford PBCz-FBTz (106.0 mg 84.6%). $M_n = 14.3$ kDa, PDI = 2.00, The decomposition temperatures (T_d) = 445 °C

Fabrication of perovskite solar cells.

The PVSCs with a structure of ITO/SnO₂/perovskite/HTM/MoO₃/Ag were studied. Indium tin oxide (ITO) conduction glass was pre-cleaned in detergent, deionized water (DI) water, acetone, and isopropanol for 30 min for each step, then oxygen plasma treated for 15 min. Firstly, the SnO₂ solution diluted to 2.67% (1 ml stock solution add 6.5 ml DI water). Then SnO₂ solution was spin-coated at 3000 rpm for 30 s, then the films were annealed at 150 °C for 30 min in air. The perovskite solution was prepared by dissolving PbI₂ (1.1 M), FAI (0.9 M), CsI (0.1 M), and MABr (0.08 M) in an anhydrous solvent DMF:DMSO = 4:1 (volume ratio). The perovskite precursor solution was spin-coated at 1000 rpm for 10 s, followed by 5000 rpm for 25 s. During the spin coating, 200 μL chlorobenzene (CB) was dropped on the spinning substrate at 5 s before the procedure end. Then the films were annealed at 100 °C for 10 min in the glove box. The resulting perovskite active layers present the thickness around 450 nm, which was confirmed by a step meter. Afterwards, polymeric HTMs were deposited on perovskite active layer by spin-coating 45 μL 10 mg/mL CB solution at 5000 rpm for 60 s and the thickness of the polymeric HTL around 50 nm. Finally, the devices were transferred to a vacuum chamber and finished by evaporation of an 8 nm MoO₃ and an 80 nm Ag electrode through a shadow mask, which defines the active area of the devices of 0.04

cm². The devices were encapsulated in glass by UV-curable resin in the glove box, then measurements and storage were taken in air.

Instruments and characterization.

The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AVIII-400 Spectrometer. All the intermediates were tested in CDCl₃ solution and tetramethylsilane (TMS) as standard. The thermogravimetric analysis (TGA) was carried out on a Mettler-Toledo 851e/822e analysis system under nitrogen gas flowing rate of 50 mL min⁻¹ with the heating rate of 10 °C min⁻¹. Gel permeation chromatograph (GPC) with chloroform (40 °C) as eluent against polystyrene standard. Ultraviolet–visible (UV–vis) spectra were obtained from a SHIMADZU UV-2600 spectrophotometer. Water contact angle (WCA) was measured by DSA25 contact angle instrument. Steady-state photoluminescence (PL) spectra and time-resolved (TR) PL decay curves were obtained using an FLS920 fluorescence spectrometer equipped with a xenon arc lamp (Xe900), a microsecond flash lamp (μF900), and a nanosecond hydrogen flash lamp (nF920). Cyclic voltammetry (CV) experiments were performed with a Zahner IM6e electrochemical workstation. All CV measurements were carried out at room temperature with a conventional three-electrode configuration employing a glassy carbon electrode as the working electrode, a silver chloride (Ag/AgCl) electrode as the reference electrode, and a Pt wire as the counter electrode. Thin films were deposited from chlorobenzene solution onto the working electrodes. Tetrabutylammonium phosphorus hexafluoride (Bu₄NPF₆, 0.1 M) in dry CH₃CN was used as the supporting electrolyte, and the scan rate was 100 mV s⁻¹. Highest occupied molecular orbital (HOMO) energy levels were calculated from the onset oxidation potential using the equation $E_{\text{HOMO}} = -(4.80 + E_{\text{onset}} - E_{\text{FOC}})$. Lowest unoccupied molecular orbital (LUMO) energy levels are estimated from the optical band gap and HOMO

levels. AFM images were obtained using a Bruker MultiMode8 microscope in air mode and ScanAsyst software. X-ray diffraction (XRD) was measured using an X'pert3 and Empyrean in reflection mode. Current-voltage ($J-V$) curves were measured under 100 mW cm^{-2} irradiation by using the solar simulator (Newport Oriol solar 3A) and recorded with a Keithley 2400 source meter. External quantum efficiency (EQE) spectra of the solar cells were obtained by using Enlitech QE-R011 (Enlitech Co. Ltd., Taiwan) measurement system. Electrochemical impedance spectroscopy (EIS) was measured by a CHI 660 electrochemical workstation (CH Instruments Inc) in the frequency range from 10^{-1} to 10^5 Hz with a signal amplitude of 700 mV. The tests were calibrated with the standard ferrocene/ferrocenium (Fc/Fc^+) redox system with the assumption that the energy level of Fc/Fc^+ is 4.8 eV under vacuum. The steady-state PCE and current density was measured by monitoring photocurrent with a bias voltage at the maximum power point. solar simulator (Newport Oriol solar 3A) was used as the light source.

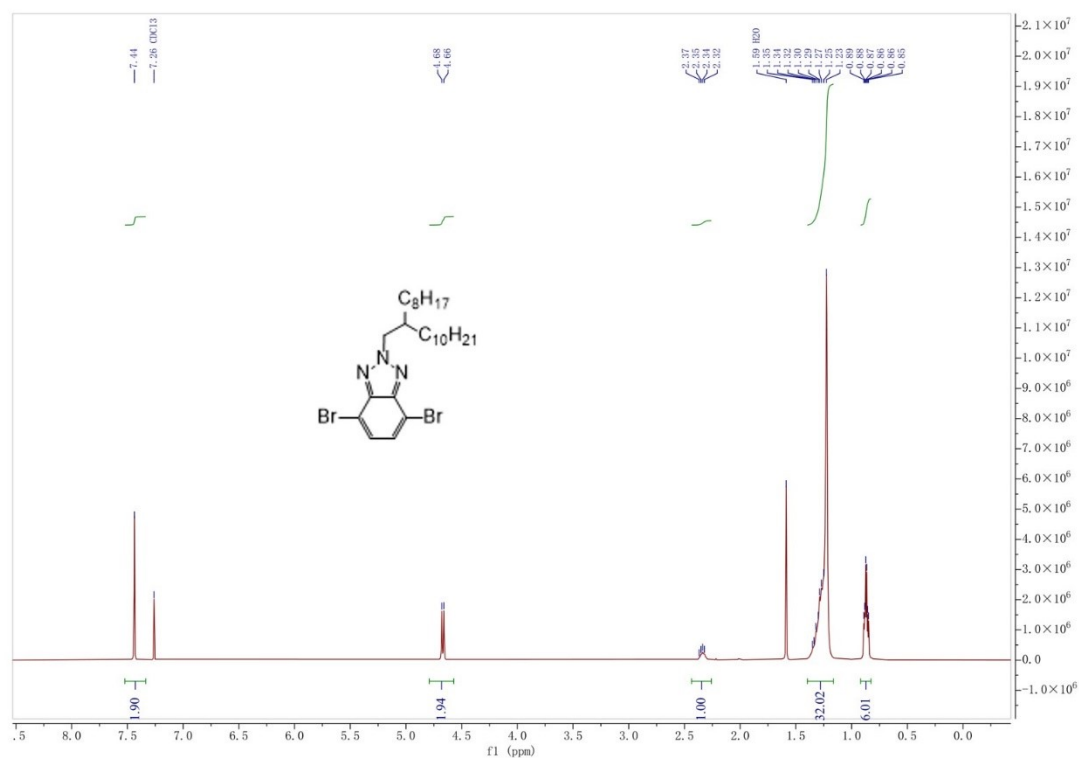


Fig. S1 ^1H NMR spectrum of compound 3

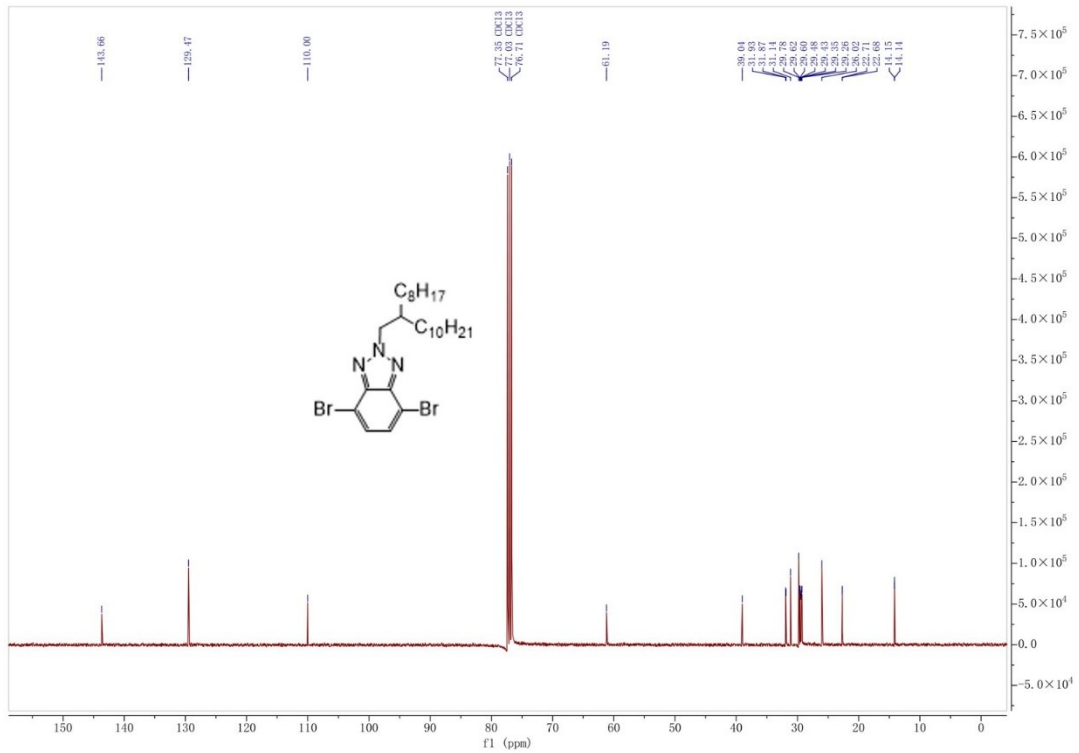


Fig. S2 ^{13}C NMR spectrum of compound 3

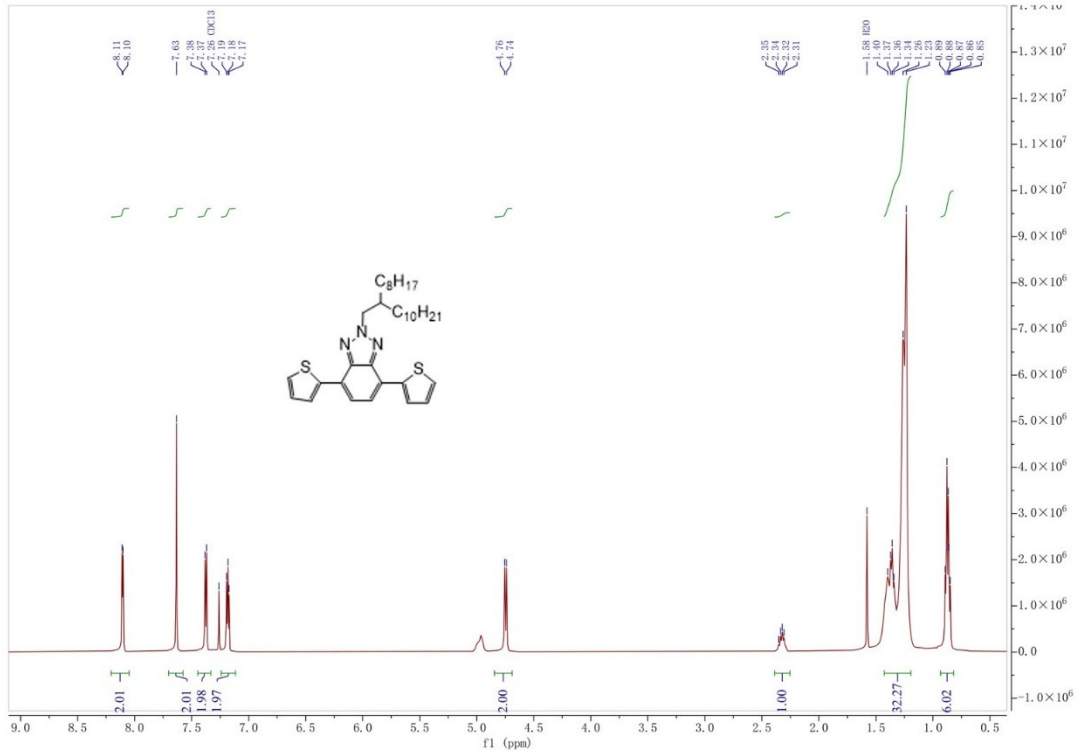


Fig. S3 ^1H NMR spectrum of compound 5

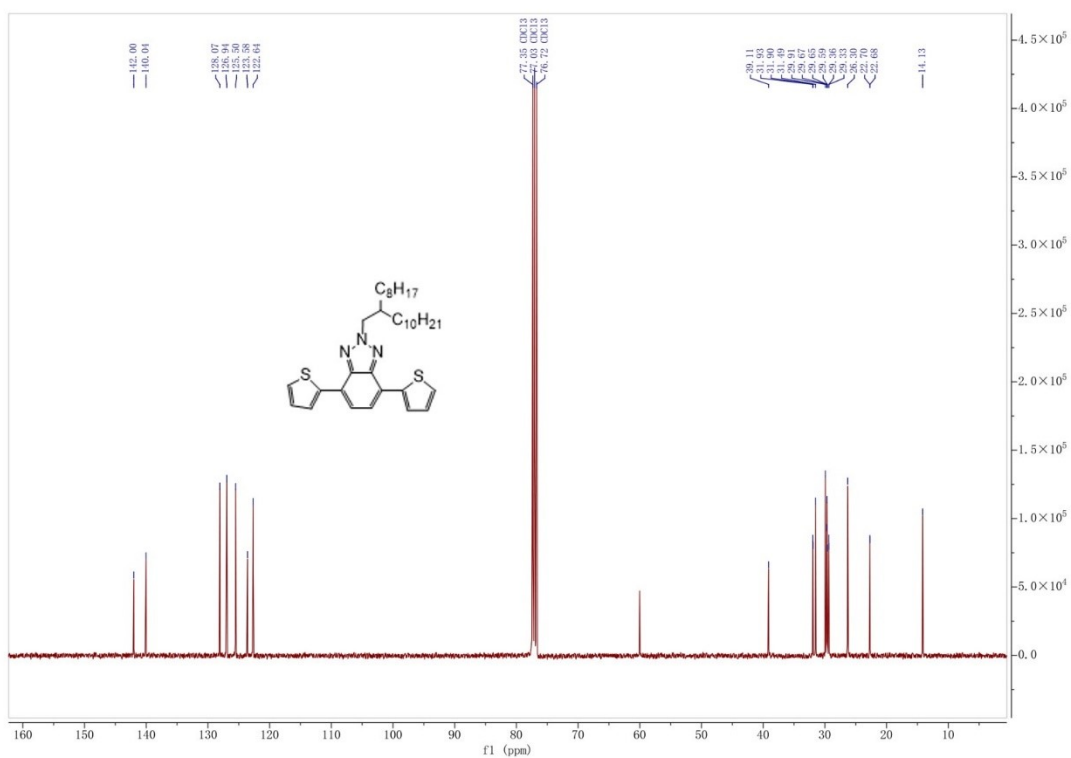


Fig. S4 ^{13}C NMR spectrum of compound 5

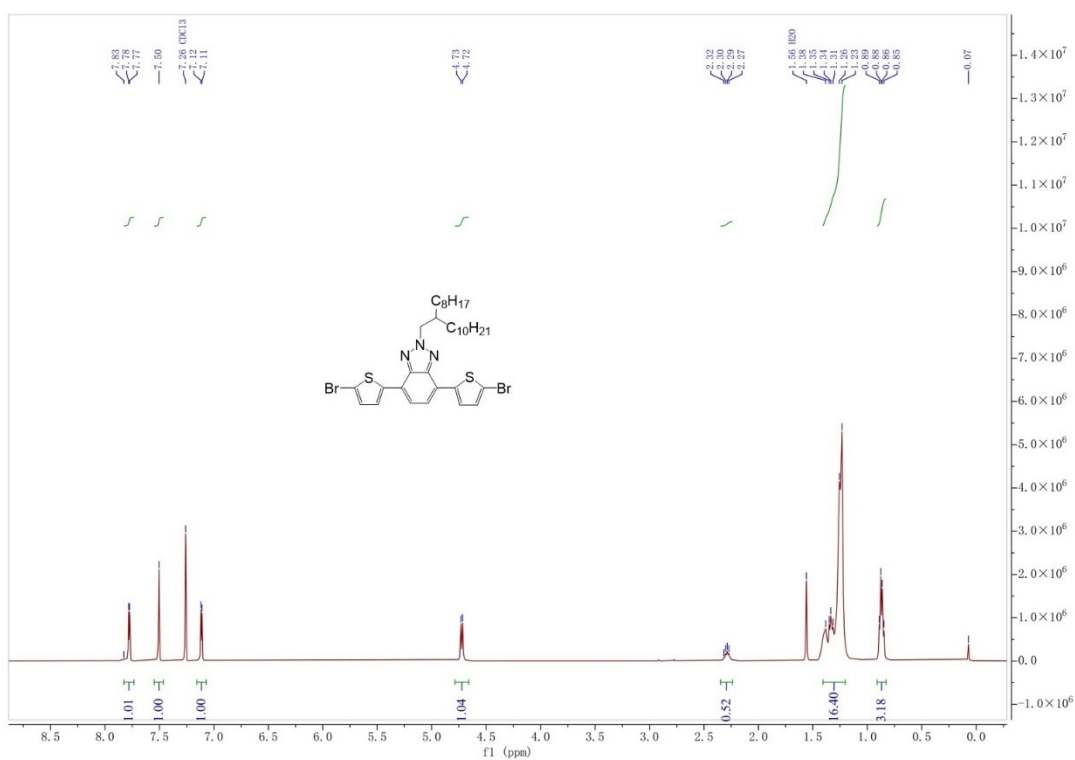


Fig. S5 ^1H NMR spectrum of compound 6

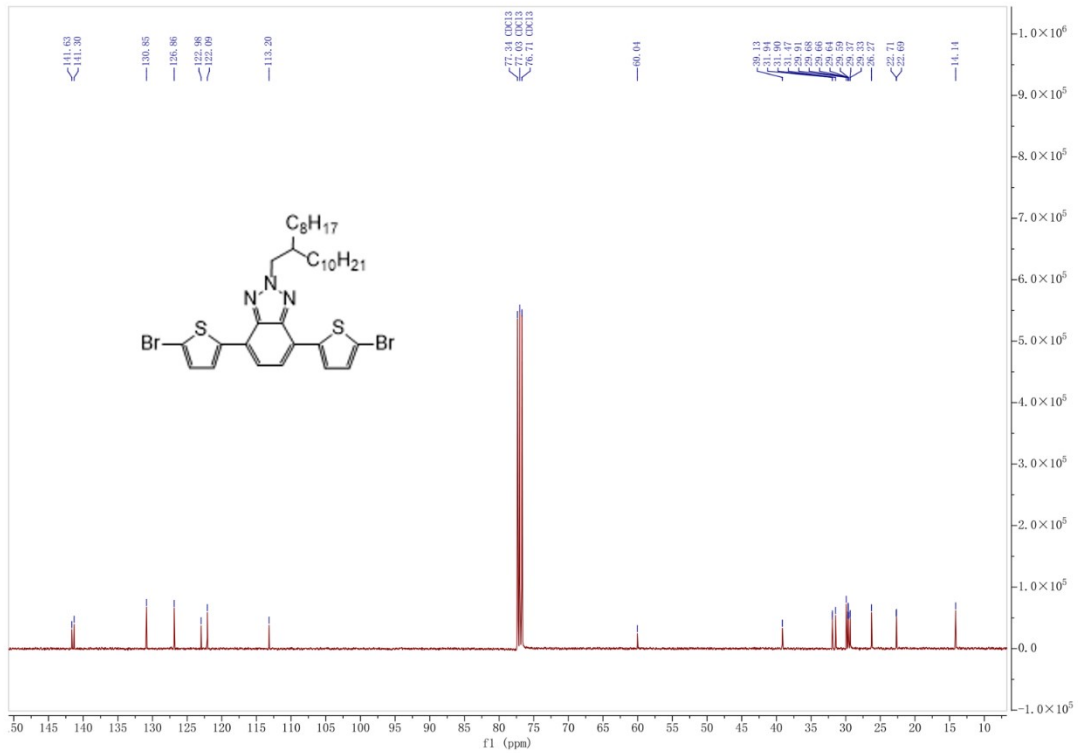


Fig. S6 ^{13}C NMR spectrum of compound 6

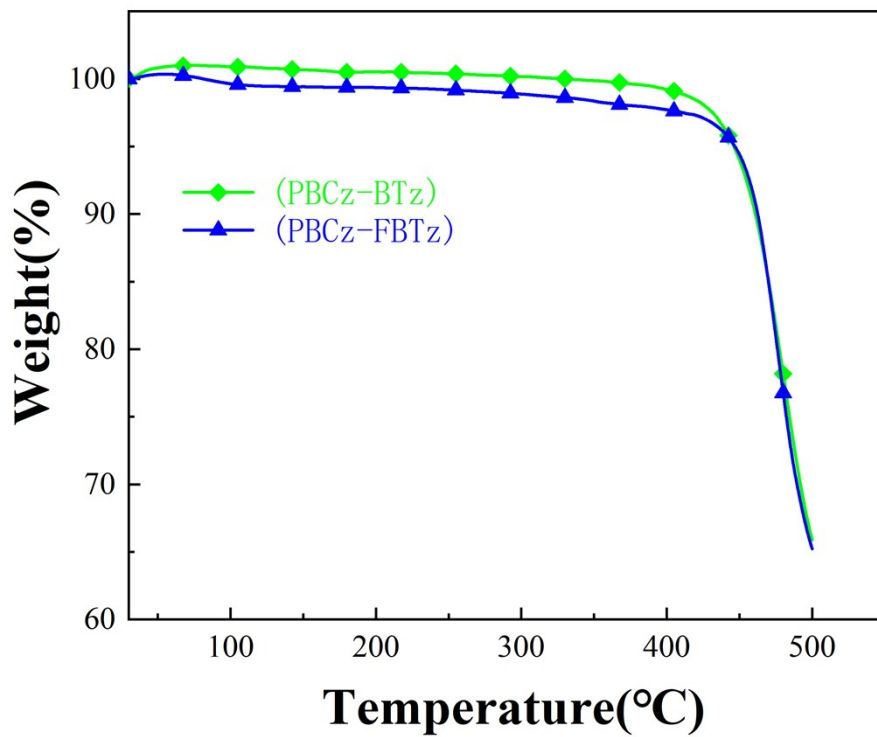


Fig. S7 TGA curves of PBCz-BTz and PBCz-FBTz

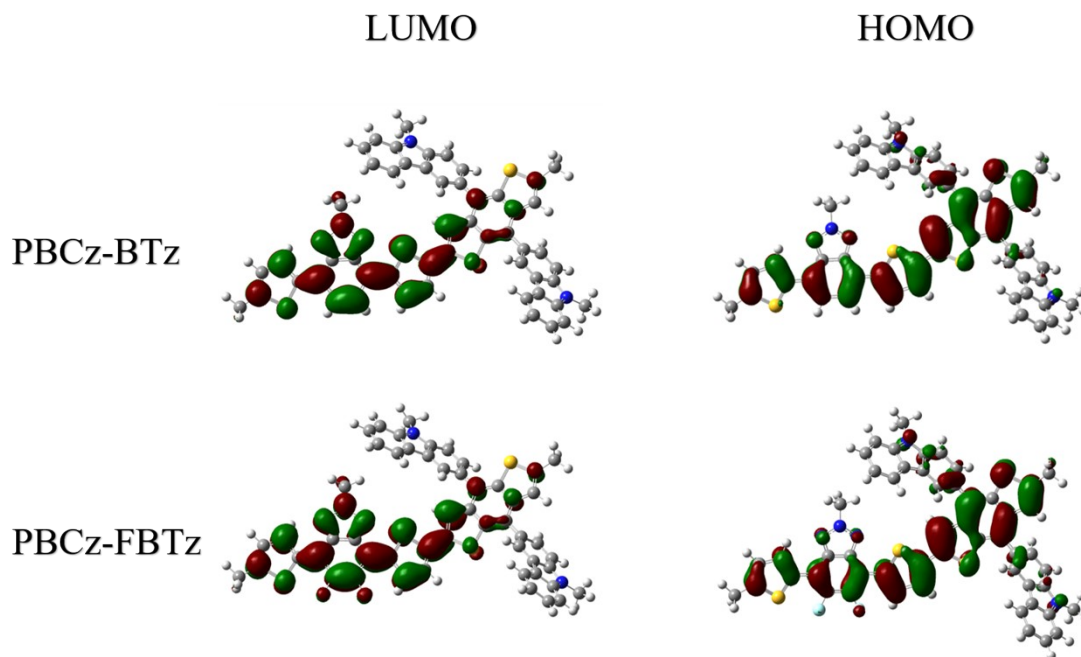


Fig. S8 The molecular orbital spatial distribution of PBCz-BTz and PBCz-FBTz

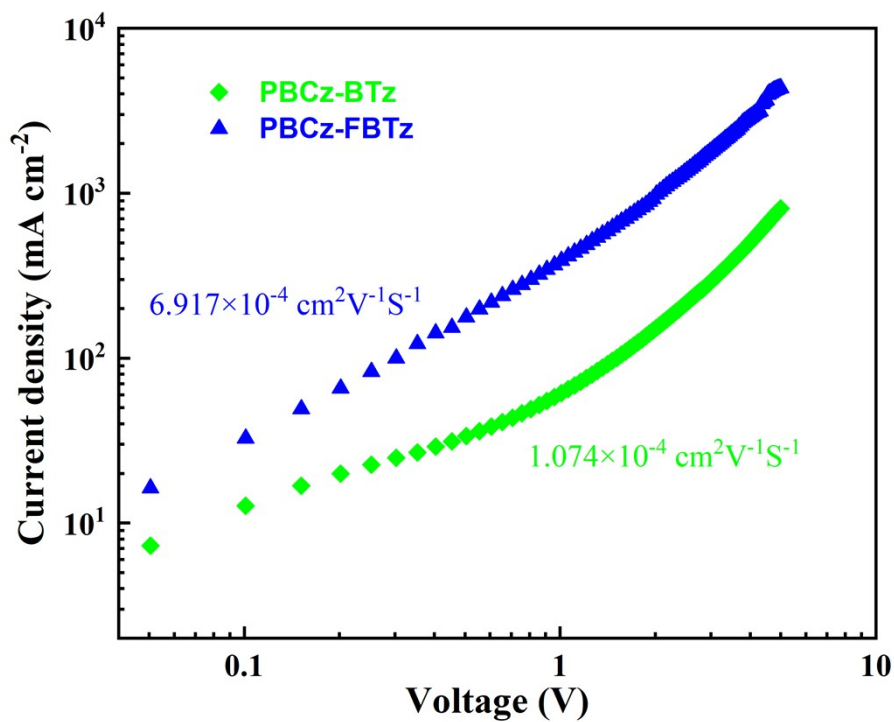


Fig. S9 SCLC curves of PBCz-BTz and PBCz-FBTz

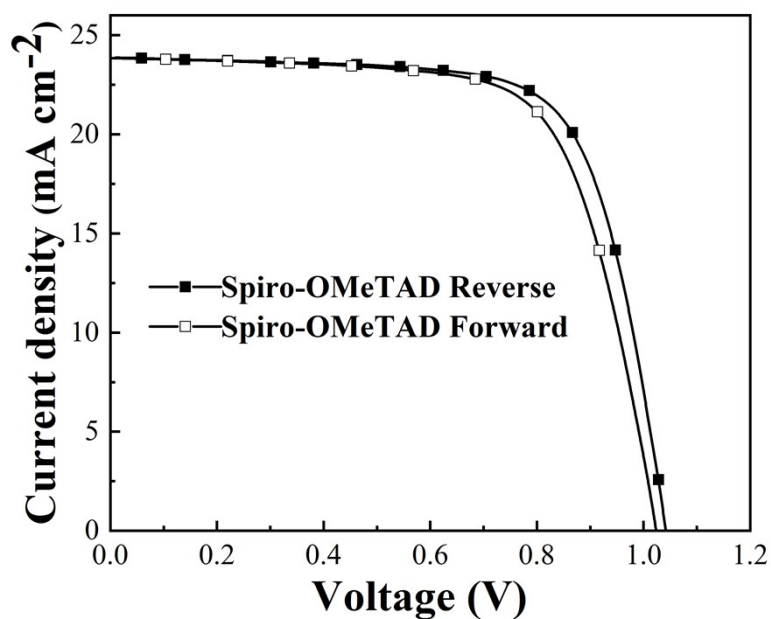


Fig. S10 J - V curves of the PVSCs based on Spiro-OMeTAD

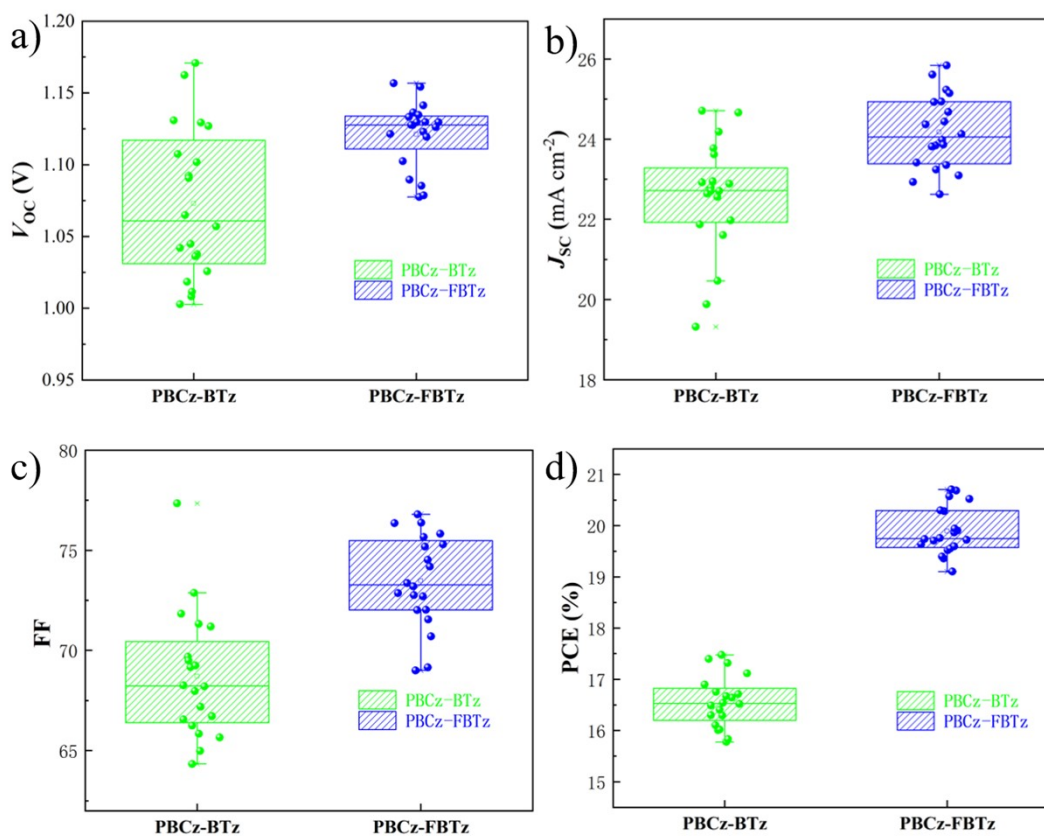


Fig. S11. Distribution of a) V_{OC} , b) J_{SC} , c) FF, and d) PCE of PVSCs from 20 PBCz-BTz and PBCz-FBTz based PVSC devices.

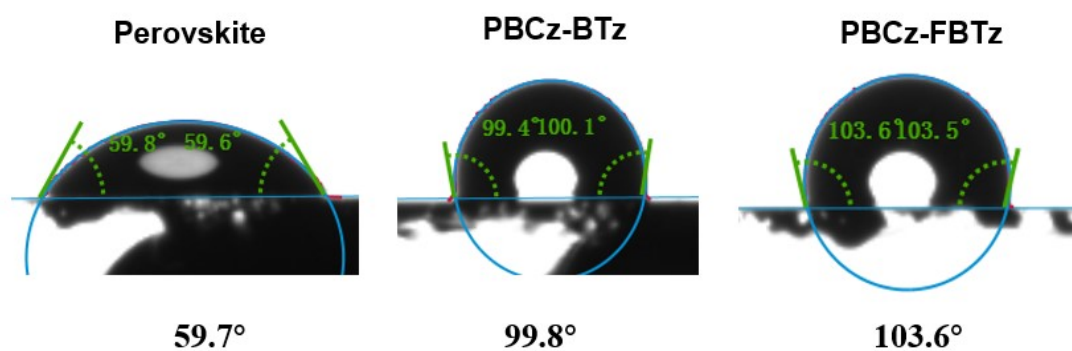


Fig. S12 Water contact angle of pristine perovskite film, PBCz-BTz/perovskite and PBCz-FBTz/perovskite

Table S1 synthetic cost for PBCz-FBTz (1 g)

Chemicals	Reagent (g)	Solvent (mL)	Price per unit (¥ g ⁻¹ /¥ L ⁻¹)	Cost (¥)
Compound 7	0.944		1300	1227.2
Compound 8	0.668		900	601.2
Pd(PPh ₃) ₄	0.055		90	4.9
Toluene		50	26	1.3
Methanol		200	12	2.4
Acetone		200	28	5.6
Hexane		200	26	5.2
Chloroform		200	32	6.4
Total				1854.2
				(\$ 259.2)

Table S2 synthetic cost for spiro-OMeTAD (1 mL)

Chemicals	Reagent (mg)	Solvent (mL)	Price per unit (¥ g ⁻¹ /¥ L ⁻¹)	Cost (¥)
spiro-OMeTAD	72.3		600	43.38
t-BP		0.028	79	2.21
LiTFSI	9.1		32	0.29
KF209	6		400	2.4
Chlorobenzene		1	1380	1.38
Total				49.7
				(\$ 6.95)

Table S3 synthetic cost for PBCz-FBTz (1 mL)

Chemicals	Reagent (mg)	Solvent (mL)	Price per unit (¥ g ⁻¹ /¥ L ⁻¹)	Cost (¥)
PBCz-FBTz	10		1854.2	18.5
Chlorobenzene		1	1380	1.4
Total				19.9
				(\$ 2.78)

Table S4 fitting parameters for TRPL of the perovskite films covered with different HTM

Sample	τ_1 (ns)	τ_2 (ns)	A_1 (%)	A_2 (%)	τ_{ave} (ns)
Perovskite	1.81	131.54	13.07	86.96	131.27
Perovskite/PBCz-BTz	1.41	116.25	48.60	51.04	114.94
Perovskite/PBCz-FBTz	1.71	84.26	3.93	96.07	84.19

Table S5 fitted data from Nyquist plots of the PVSCs with different HTM

HTM	$R_{\text{rec}} (\Omega)$	$R_s (\Omega)$	CPE (μF)
PBCz-BTz	8.57×10^5	108.3	2.10
PBCz-FBTz	1.22×10^6	87.06	2.07