

Electronic Supplementary Information for:

**Benzotriazole based polymers with different side chains
employed as dopant-free hole-transporting materials for
high-efficiency perovskite solar cells**

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† Electronic supplementary information (ESI) available.

Materials

PbI₂ (99.999%), PbBr₂ (99.99%), FAI (99.5%), MABr (99.5%), DMF (99.9%), DMSO (99.9%), Ethyl acetate (99.9%) and chlorobenzene (99.9%) were purchased from J&K Chemistry. 4,7-bis(5-bromothiophen-2-yl)-5,6-difluoro-2-octyl-2H-benzo[d][1,2,3]triazole, 4,7-bis(5-bromothiophen-2-yl)-2-(2-ethylhexyl)-5,6-difluoro-2H-benzo[d][1,2,3]triazole, 3,3'-(2,6-bis(trimethyltin)benzothiophene)-4,8-bis(9-(2-ethylhexyl)-9H-carbazole) were purchased from SunaTech Inc. Toluene was fresh distilled from CaH₂. Other solvents and reagents were commercially available and no further purified.

Characterization and measurements

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 was measured by DSA25 contact angle instrument. 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. The atomic force microscopy (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 10⁵ 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 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.

Synthesis of PBTA-8

4,7-bis(5-bromothiophen-2-yl)-5,6-difluoro-2-octyl-2H-benzo[d][1,2,3]triazole (50.0 mg, 0.085 mmol) and 3,3'-(2,6-bis(trimethyltin)benzothiophene)-4,8-bis(9-(2-ethylhexyl)-9H-carbazole) (90.8 mg, 0.085 mmol) have been added into a flask of 25 ml, and then added the Pd(pph₃)₄ (4.0 mg, 0.0034 mmol) as the catalyst. The flask needs refilled with nitrogen. 10 ml toluene was used as the solvent, which had been nitrogen blowing ahead of time. The reaction was stirred at 100 °C for 48 h.

Afterwards, we dropped the coarse product into methyl alcohol and then extracted by Soxhlet extraction via methyl alcohol, acetone, hexane, dichloromethane, and chloroform. Collected the end-product gathered of chloroform. Finally, we obtained a rose-red membrane polymer by dried under vacuum. $M_n=14.4$ kDa, PDI=1.77. Decomposition temperature (5% weight loss) was 445 °C.

Synthesis of PBTA-26

The synthetic procedure of PBTA-26 was same as PBTA-8 by Stille polycondensation between 4,7-bis(5-bromothiophen-2-yl)-2-(2-ethylhexyl)-5,6-difluoro-2H-benzo[d][1,2,3]triazole (50 mg, 0.085 mmol) and 3,3'-(2,6-bis(trimethyltin benzothiophene)-4,8-bis(9-(2-ethylhexyl)-9H-carbazole)(2) (90.8 mg, 0.085 mmol). $M_n=23.3$ kDa, PDI=1.89. Decomposition temperature (5% weight loss) was 437 °C.

Device fabrication

The PVSCs with a structure of ITO/SnO₂/perovskite/HTM/MoO₃/Ag were studied. Indium tin oxide (ITO) conduction glass was pre-cleaned in soap DI water, DI water, acetone, and isopropanol for 30 min at 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, after the films were annealed at 150 °C for 30 min in air. The perovskite solution was prepared by dissolving PbI₂ (1.1 M), FAI (1.0 M), PbBr₂ (0.22 M), and MABr (0.2 M) in an anhydrous solvent DMF:DMSO = 4:1 (volume ratio) added CsI (1.5 M) in DMSO according to a volume ratio = 95:5. The perovskite precursor solution was spin-coated at 1000 rpm for 10 s, followed by 6000 rpm for 20 s. During the spin-coating, 100 μL ethyl acetate (EA) was dropped on the spinning substrate at 3 s before the procedure end. Then the films were annealed at 100 °C for 20 min in the glove box. The

resulting perovskite active layers presented 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 3000 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 MoO_3 and an 80 nm Ag electrode through a shadow mask, which defines active area of the devices of 0.04 cm^2 . The devices were encapsulated in glass by UV-curable resin in the glove box, then measurements and storage were carried out in air.

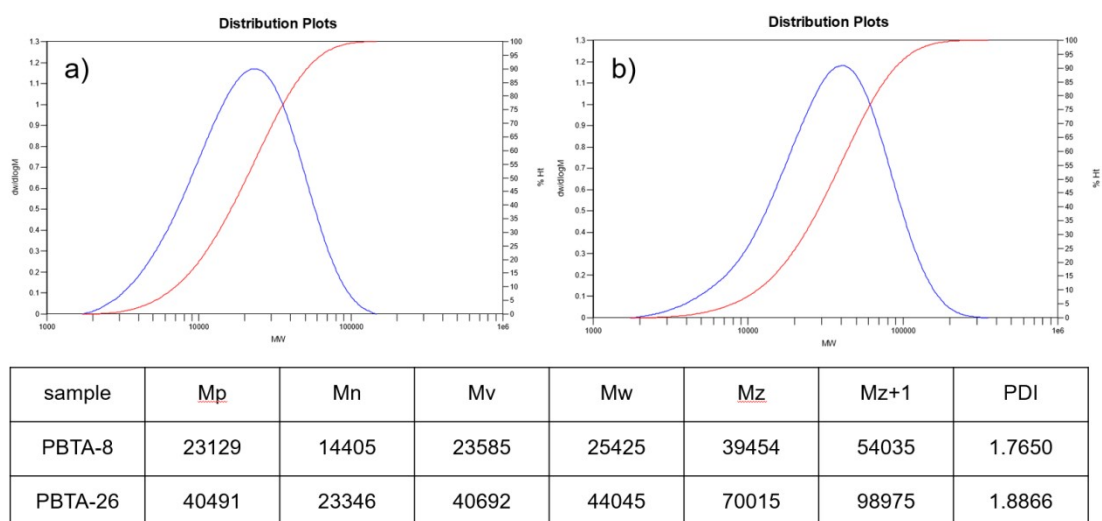


Fig. S1 GPC curves and detailed data for a) PBTA-8, b) PBTA-26.

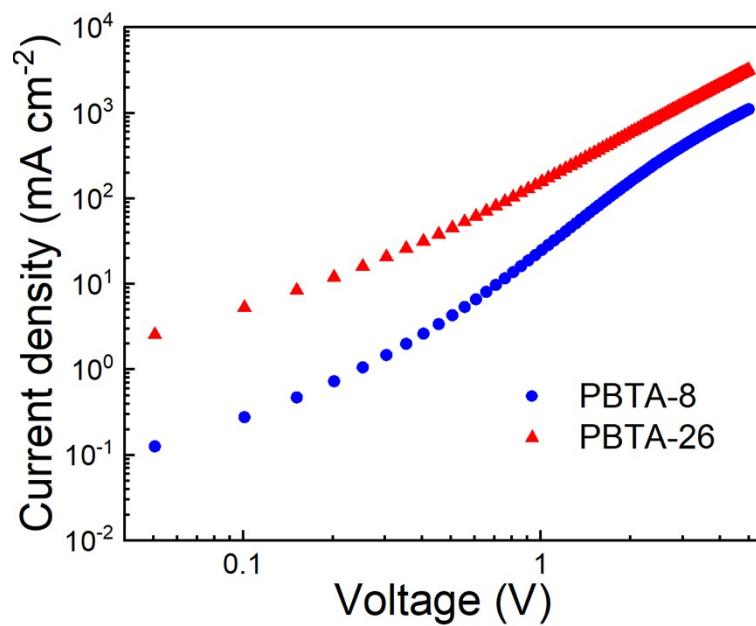


Fig. S2 J - V curves for the hole-only devices with a device structure of ITO/PEDOT:PSS/HTM/MoO₃/Ag.

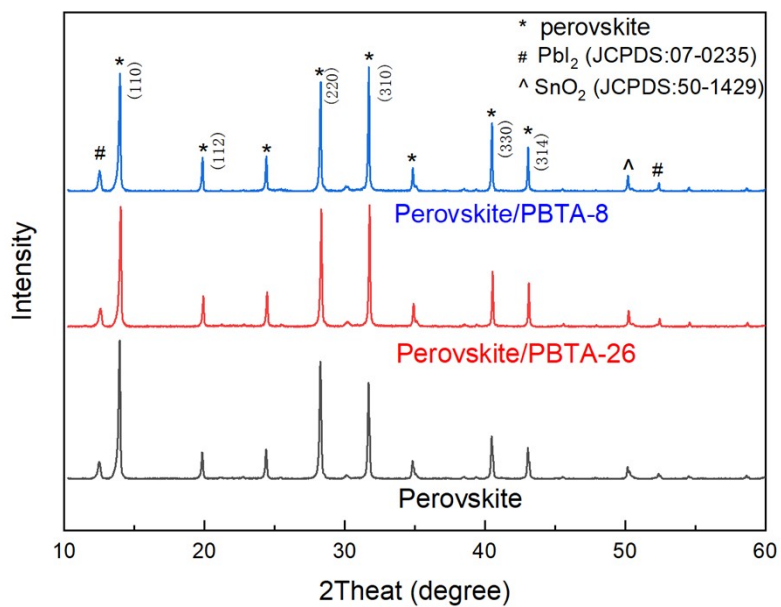


Fig. S3 XRD patterns of the pristine perovskite as well as the perovskite covered with PBTA-8 and PBTA-26.

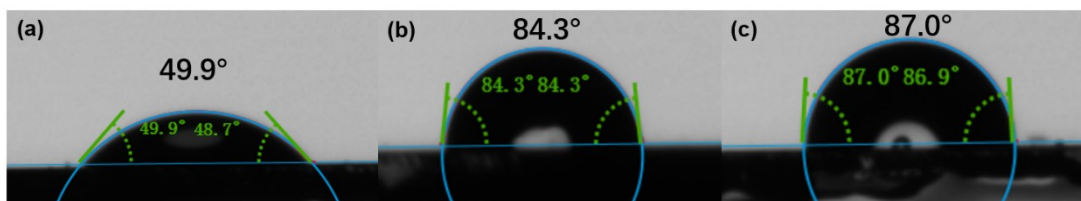


Fig. S4 Water contact angles of a) the pristine perovskite film as well as b) PBTA-8 and c) PBTA-26 deposited on perovskite.

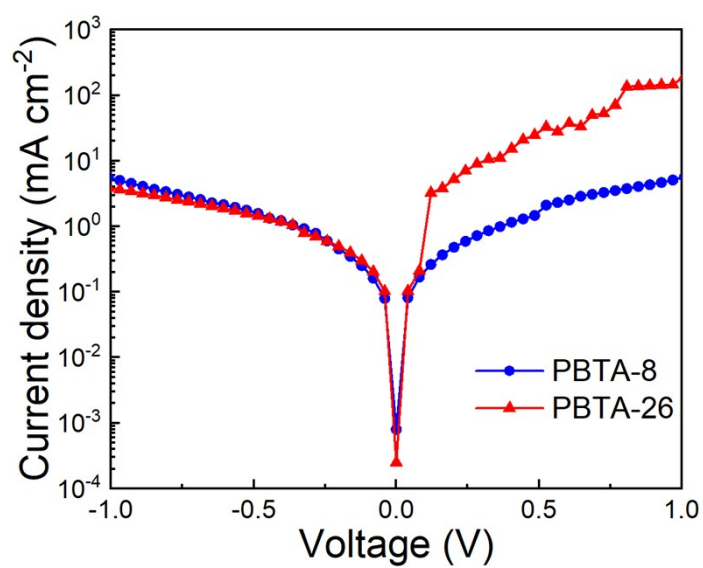


Fig. S5 Dark J - V curves of the PVSCs with different HTM.

Table S1 Photovoltaic parameters of the PVSCs employing BTA based HTM

HTM	Device structure	PCE	Dopant	Ref.
2FBTA-1	FTO/cm-TiO ₂ /mp-TiO ₂ /perovskite/HTM/Au	7.55%	dopant	[1]
BTA-2	ITO/SnO ₂ /perovskite/HTM/Au	8.28%	dopant	[2]
DT-2	ITO/SnO ₂ /perovskite/HTM/Au	13.22%	dopant	[2]
2FBTA-2	FTO/cm-TiO ₂ /mp-TiO ₂ /perovskite/HTM/Au	17.94%	dopant	[1]
BTA-1	ITO/SnO ₂ /perovskite/HTM/Au	5.83%	Dopant -free	[2]
pBBTa -BDT1	FTO/cm-TiO ₂ /perovskite/HTM/Au	7.00%	Dopant -free	[3]
SGT-513	FTO/cm-TiO ₂ /mp-TiO ₂ /perovskite/HTM/Au	8.86%	Dopant -free	[4]
DT-1	ITO/SnO ₂ /perovskite/HTM/Au	10.37%	Dopant -free	[2]
J71	FTO/cm-TiO ₂ /mp-TiO ₂ /perovskite/HTM/Au	12.12%	Dopant -free	[5]
pBBTa -BDT2	FTO/cm-TiO ₂ /perovskite/HTM/Au	14.50%	Dopant -free	[3]
SGT-512	FTO/cm-TiO ₂ /mp-TiO ₂ /perovskite/HTM/Au	15.20%	Dopant -free	[4]
BT-TT	ITO/SnO ₂ /perovskite/HTM/MoO ₃ /Ag	15.80%	Dopant -free	[6]
BT-T	ITO/SnO ₂ /perovskite/HTM/MoO ₃ /Ag	17.10%	Dopant -free	[6]
PTBz-8	ITO/SnO ₂ /perovskite/HTM/MoO ₃ /Ag	17.83%	Dopant -free	this work
PTBz-26	ITO/SnO ₂ /perovskite/HTM/MoO ₃ /Ag	19.83%	Dopant -free	this work

Table S2 Fitting parameters for TRPL of perovskite films covered with different HTM

sample	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_{ave} (ns)
Perovskite	8.38	29.21	196.81	70.79	194
Perovskite/PBTA-8	1.01	56.31	167.01	43.69	166
Perovskite/PBTA-26	0.99	70.97	132.34	29.03	130

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