

## **Carbazolyl phenylacetone-based asymmetric hole transport material enables high-performance perovskite solar cells**

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### **Materials and instruments**

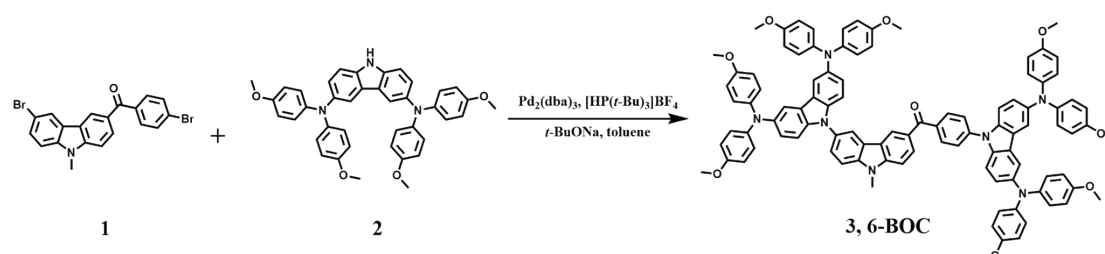
Unless otherwise stated, all starting materials were purchased from commercial suppliers (Sigma Aldrich, and the Energy Chemical) and used without further purification. All solvents used were purified by standard procedures and purged with

nitrogen before use. The nuclear magnetic resonance (NMR) spectra were obtained from a BRUKER AVANCE III 600 MHz NMR Instrument (in DMSO- $d_6$  and  $CDCl_3$ ). The HRMS was measured on Thermo Scientific Q Exactive instrument. UV-vis absorption spectra were measured on a Shimadzu UV-2450 absorption spectrophotometer. Cyclic voltammetry (CV) test was performed on a CHI instrument electrochemical work-station (CS 310s) in  $CH_2Cl_2$  under a nitrogen atmosphere, using saturated calomel electrode (SCE) as reference electrode and ferrocene as internal standard. Thermal gravimetric analysis (TGA) was performed on a TGA Q50 at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  under a nitrogen atmosphere. Differential scanning calorimetry (DSC) measurement was performed on a DSC Q20 instrument under a nitrogen atmosphere at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ . Field emission scanning electron microscope (FE-SEM) images were taken on JSM-7800F. Atomic force microscopy (AFM) were collected in air on a scanning probe microscope (Being Nano-Instruments, Ltd, CSPM5500) using a tapping mode. Fluorescence spectra were measured on a Hitachi F-4600 FL Spectrophotometer. The photoluminescence (PL) lifetimes were measured by a single photon counting spectrometer from Edinburgh Instruments (FLS920) with a Picosecond Pulsed UV-LASTER (LASTER377) as the excitation source. Current-voltage ( $J-V$ ) characteristics were measured under  $100\text{ mW cm}^{-2}$  (AM 1.5G illumination) using a Newport solar simulator (model 91160) and a Keithley 2400 source/meter. A certified reference solar cell (Fraunhofer ISE) was used to calibrate the light source for an intensity of  $100\text{ mW cm}^{-2}$ . The external quantum efficiency (EQE) spectra were recorded using a computer-controlled setup consisting of a Xenon light

source (Spectral Products ASB-XE-175), a monochromator (Spectra Products CM110), and a potentiostat (LabJack U6 DAQ board), calibrated by a certified reference solar cell (Fraunhofer ISE). Transient photocurrent (TPC) and transient photovoltage (TPV) were recorded using a ZAHNER<sup>®</sup>MESSSYSTEME (Instrument model: PP211). For transient photovoltage/photocurrent decay measurements were performed using a light source (LS530). Electron lifetime measurements were performed using a white LED (Luxeon Star 1W) as the light source. The photocurrent decay was determined by monitoring photocurrent transients by applying a small square-wave modulation to the base light intensity.

## Synthesis and characterization

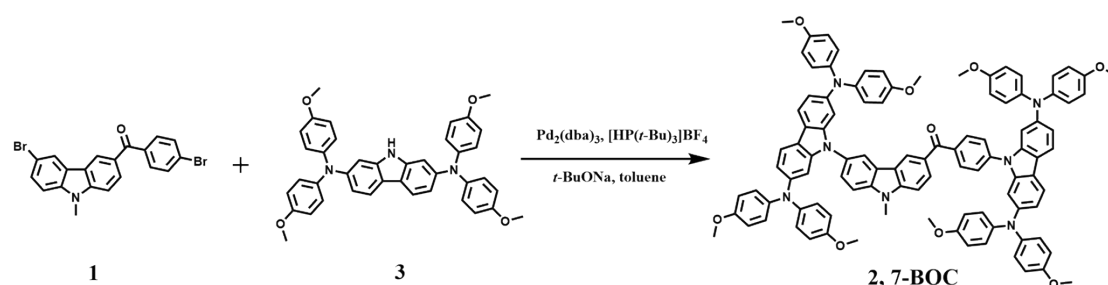
Compound **1-3** were synthesized according to method reported in literature.<sup>1, 2</sup>



Synthesis of **3, 6-BOC** ((3',6'-bis(bis(4-methoxyphenyl)amino)-9-methyl-9H-[3,9'-bicarbazol]-6-yl)(4-(3, 6-bis(bis(4-methoxyphenyl)amino)-9H-carbazol-9-yl)phenyl)methanone):

A mixture of Compound **1** (100 mg, 0.23mmol), Compound **2** (353 mg, 0.57 mmol),  $\text{Pd}_2(\text{dba})_3$  (11 mg, 0.0115 mmol),  $[\text{HP}(t\text{-Bu})_3]\text{BF}_4$  (4 mg, 0.0115 mmol) and  $t\text{-BuONa}$  (66 mg, 0.68 mmol) in anhydrous toluene (15 mL) were placed in a Schlenk tube under an Argon atmosphere and stirred at 110 °C for 24 h. After cooling, the reaction was

quenched by adding water, and then was extracted with dichloromethane. The organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After solvents were evaporated, the residue was purified by column chromatography over silica gel using dichloromethane as the eluent to give the product as an orange solid (231 mg, 66%). <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ 8.69 (s, 1H), 8.25 (s, 1H), 8.08 (d, *J* = 8.6 Hz, 1H), 7.92 (dd, *J* = 22.9, 6.0 Hz, 3H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 16.3 Hz, 5H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 7.7 Hz, 2H), 6.99 (d, *J* = 7.9 Hz, 4H), 6.71 (d, *J* = 10.2 Hz, 32H), 4.05 (s, 3H), 3.62 (s, 12H), 3.59 (s, 12H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 195.28, 154.85, 144.23, 136.89, 131.73, 129.14, 124.59, 124.45, 124.30, 114.61, 110.66, 108.60, 55.52, 29.72. HRMS [M+H]<sup>+</sup> for C<sub>100</sub>H<sub>81</sub>N<sub>7</sub>O<sub>9</sub> m/z: calcd 1524.6169; found 1524.6120.



Synthesis of **2, 7-BOC** ((2',7'-bis(bis(4-methoxyphenyl)amino)-9-methyl-9H-[3,9'-bicarbazol]-6-yl)(4-(2,7-bis(bis(4-methoxyphenyl)amino)-9H-carbazol-9-yl)phenyl)methanone):

A mixture of Compound **1** (100 mg, 0.23mmol), Compound **3** (353 mg, 0.57 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (11 mg, 0.0115 mmol), [HP(*t*-Bu)<sub>3</sub>]BF<sub>4</sub> (4 mg, 0.0115mmol) and *t*-BuONa (66 mg, 0.69 mmol) in anhydrous toluene (15 mL) was placed in a Schlenk tube under an Argon atmosphere and was stirred at 110 °C for 24 h. After cooling, the reaction was

quenched by adding water, and then was extracted with dichloromethane. The organic layer was washed with brine and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After solvents were evaporated, the residue was purified by column chromatography over silica gel using dichloromethane as the eluent to give the product (207 mg, 59%) as an orange solid.  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO}-d_6$ )  $\delta$  8.31 (d,  $J = 7.6$  Hz, 1H), 8.21 (s, 1H), 8.09 (t,  $J = 7.6$  Hz, 1H), 7.99 (d,  $J = 8.3$  Hz, 1H), 7.90 (d,  $J = 8.4$  Hz, 3H), 7.81 (d,  $J = 4.1$  Hz, 2H), 7.74 (s, 1H), 7.60 (d,  $J = 7.6$  Hz, 2H), 6.96 (s, 4H), 6.92 (s, 6H), 6.90 (d,  $J = 6.9$  Hz, 10H), 6.76 (d,  $J = 7.5$  Hz, 14H), 6.73 (s, 6H), 6.63 (d,  $J = 7.2$  Hz, 2H), 3.95 (s, 3H), 3.62 (s, 12H), 3.58 (s, 12H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{DMSO}-d_6$ )  $\delta$  155.66, 147.05, 141.38, 141.18, 140.25, 131.74, 126.31, 123.35, 120.75, 120.42, 115.11, 55.53. HRMS  $[\text{M}+\text{H}]^+$  for  $\text{C}_{100}\text{H}_{81}\text{N}_7\text{O}_9$   $m/z$ : calcd 1524.6169; found 1524.6141.

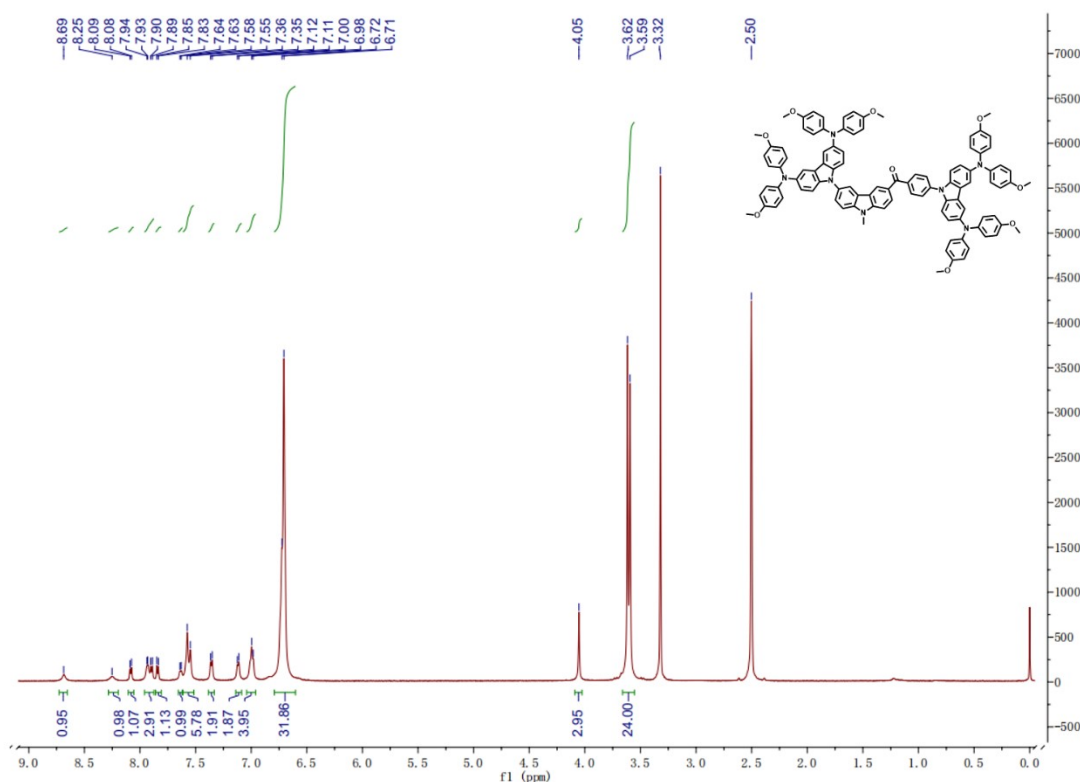


Fig. S1.  $^1\text{H}$  NMR spectrum of 3, 6-BOC in  $\text{DMSO}-d_6$ .

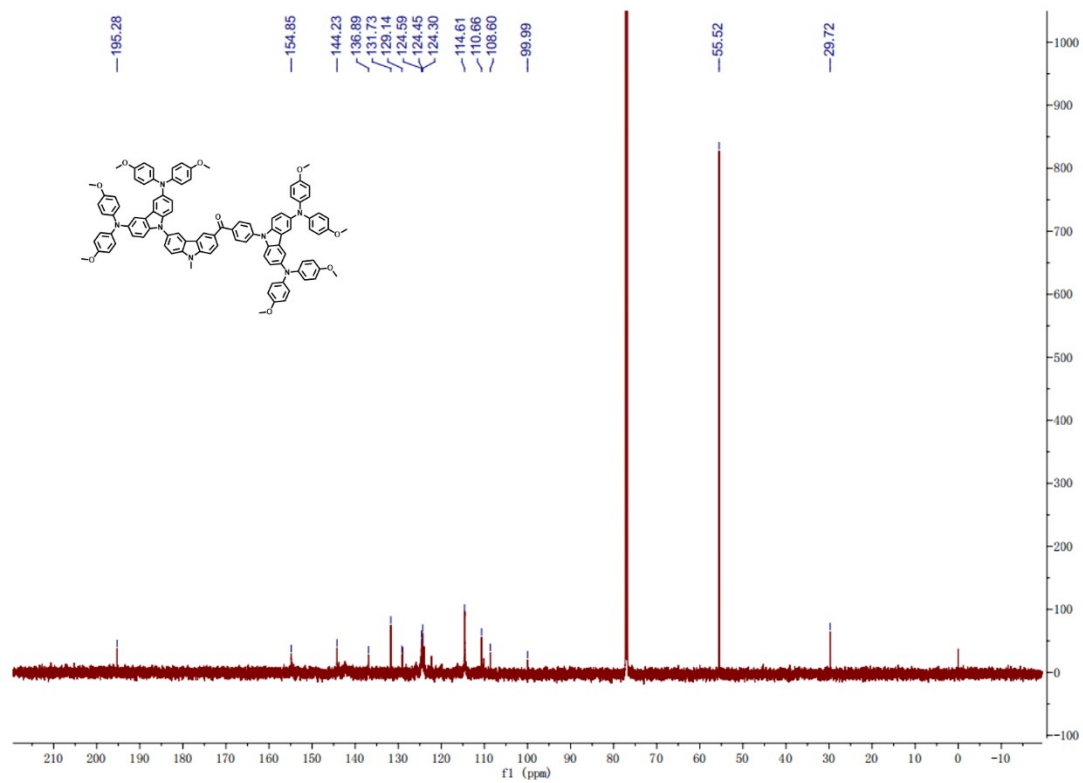


Fig. S2. <sup>13</sup>C NMR spectrum of 3, 6-BOC in CDCl<sub>3</sub>.

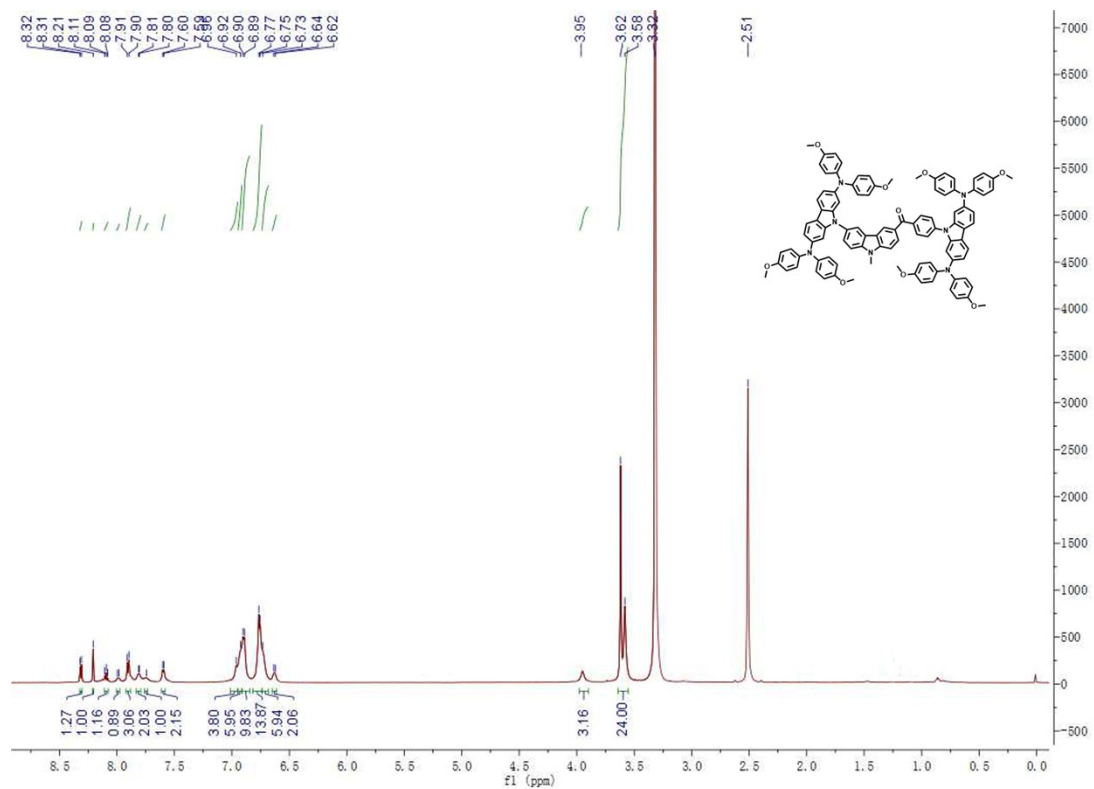


Fig. S3. <sup>1</sup>H NMR spectrum of 2, 7-BOC in DMSO-*d*<sub>6</sub>.

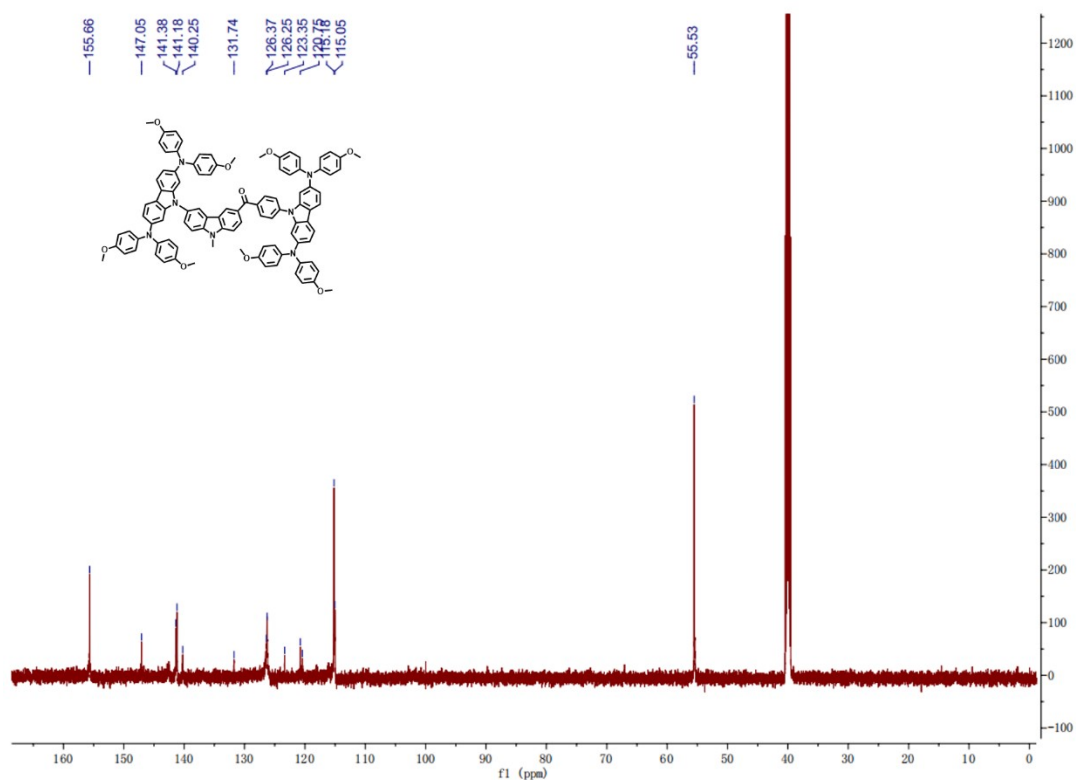


Fig. S4.  $^{13}\text{C}$  NMR spectrum of 2, 7-BOC in  $\text{DMSO-}d_6$ .

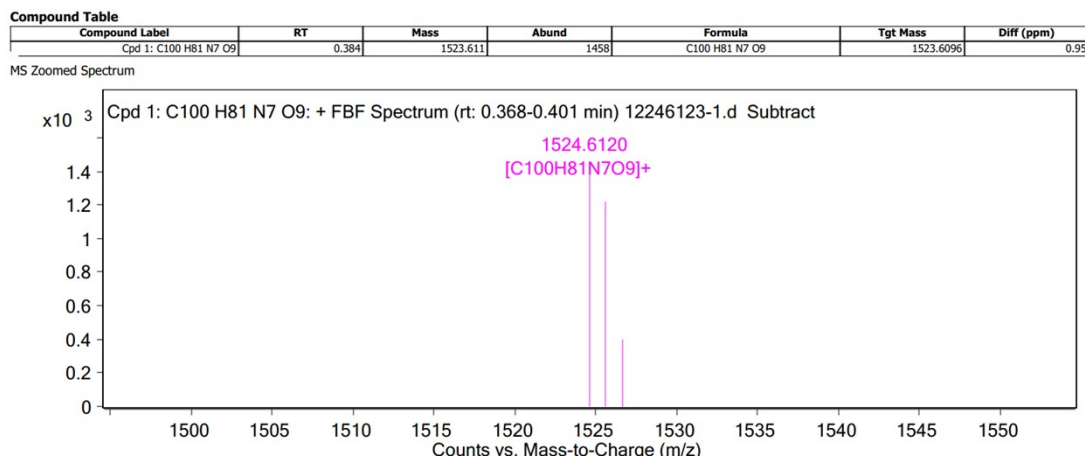


Fig. S5. High resolution mass spectrometry of 3, 6-BOC.

Compound Table						
Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: C100 H81 N7 O9	0.404	1523.6118	49590	C100 H81 N7 O9	1523.6096	1.45

MS Zoomed Spectrum

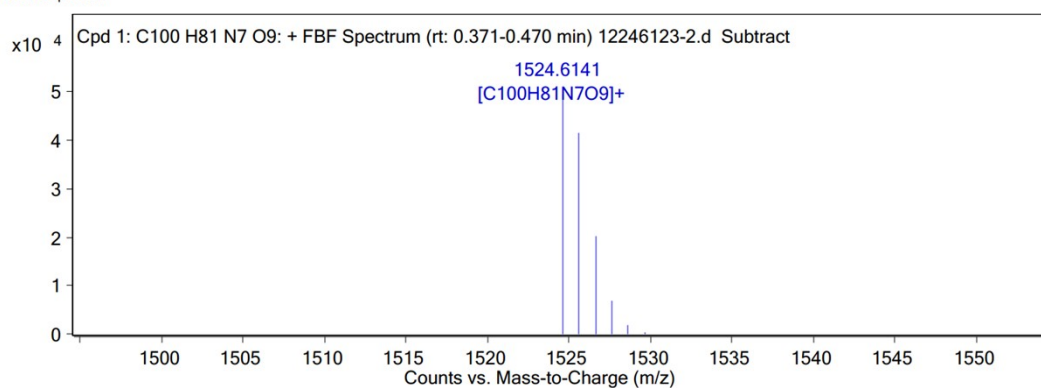


Fig. S6. High resolution mass spectrometry of 2, 7-BOC.

Table S1. The calculated HOMO, LUMO energy levels and reorganization energy of 3, 6-BOC and 2, 7-BOC.

Materials	$E_{\text{HOMO}}/\text{eV}$	$E_{\text{LUMO}}/\text{eV}$	Reorganization energy/eV
3, 6-BOC	-4.807709	-1.712685	0.162
2, 7-BOC	-4.783763	-1.848470	0.174

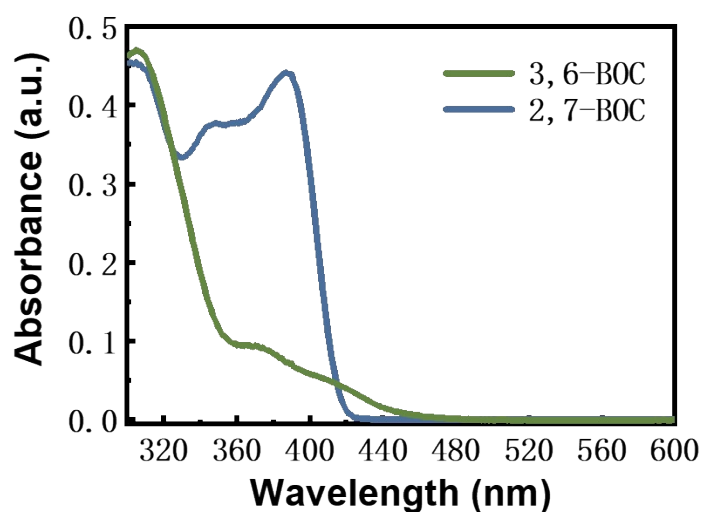


Fig. S7. UV-vis absorption spectra of 3, 6-BOC and 2, 7-BOC in  $\text{CH}_2\text{Cl}_2$ .



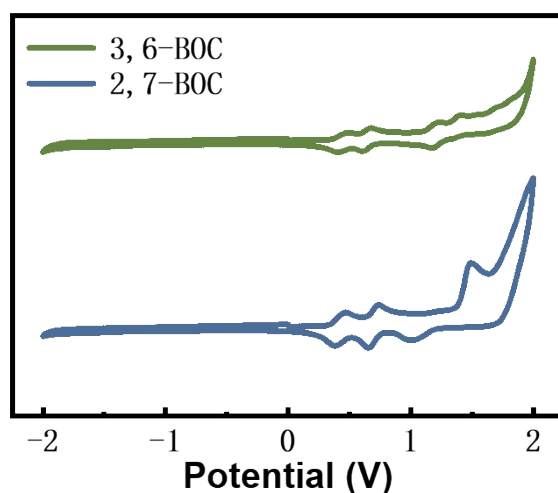


Fig. S8. Cyclic voltammetry curves of 3, 6-BOC and 2, 7-BOC.

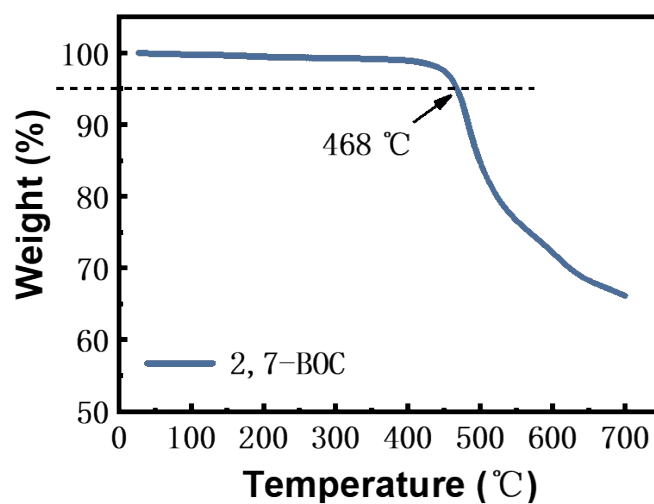


Fig. S9. TGA of 2, 7-BOC.

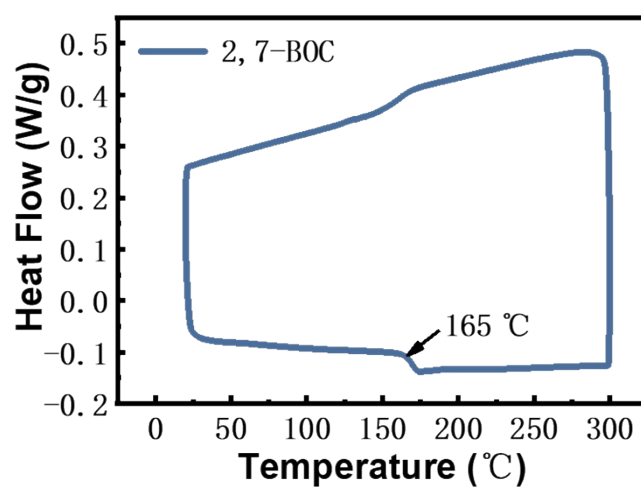


Fig. S10. DSC of 2, 7-BOC.

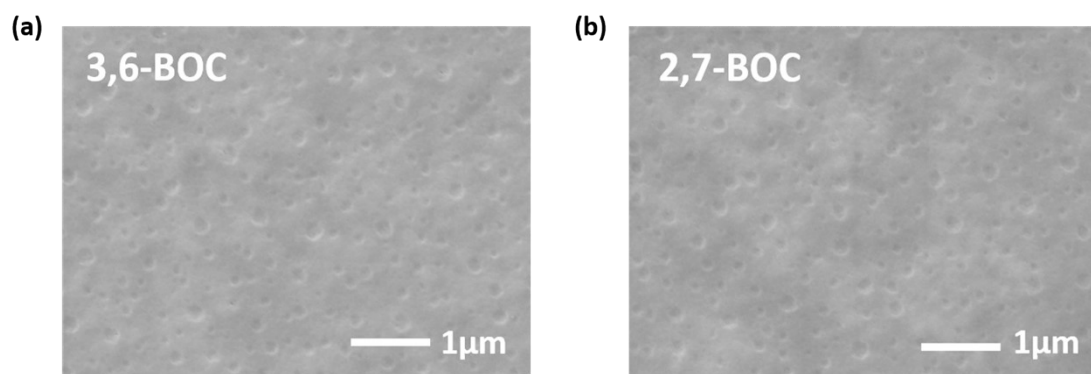


Fig. S11. Top-view FE-SEM images of (a) 3, 6-BOC and (b) 2, 7-BOC deposited on the perovskite films.

## The Space-charge-limited current (SCLC) hole mobility measurements

The hole mobilities were extracted using the Mott–Gurney Law:

$$\mu = \frac{8J_D L^3}{9\epsilon_0 \epsilon_r V^2}$$

where  $\epsilon_0$  is the vacuum permittivity,  $\epsilon_r$  is the relative dielectric constant,  $L$  is the thickness of the hole transporting layer,  $J_D$  is the dark current density, and  $V$  is the applied voltage.

## Device fabrication

### Preparation of HTM solutions

The HTMs solution were prepared according to previously reported methods.<sup>3</sup> Spiro-OMeTAD solution (80 mg Spiro-OMeTAD, 31.6  $\mu\text{L}$  4-tert butylpyridine and 18.1  $\mu\text{L}$  lithium-bis(trifluoromethanesulfonyl)imide (Li-TSFI) stock solution (520 mg  $\text{mL}^{-1}$  in acetonitrile)) in 1 mL chlorobenzene was prepared. 3, 6-BOC and 2, 7-BOC were

dissolved in chlorobenzene in a concentration of 50 mg mL<sup>-1</sup>. In order to improve the conductivity of the HTMs, 19.7 μL of *t*BP and 11.3 μL of Li-TSFI stock solution were added in 1 mL of the HTMs solution.

### **Device fabrication**

FTO-coated glass with a sheet resistance of 14 Ω sq<sup>-1</sup> was washed by sonication with deionized water, ethanol and acetone and then treated with oxygen plasma for two minutes. All devices were fabricated based on the conventional structures (FTO/compact-TiO<sub>2</sub>/meso-TiO<sub>2</sub>/perovskite/HTM/Au). The compact TiO<sub>2</sub> layer was prepared on FTO substrates by spray pyrolysis of the solution (0.2M titanium isopropoxide and 2M acetylacetonate in isopropanol). After that, the mesoporous TiO<sub>2</sub> was coated on the substrate by spin-coating for 30 s at 5000 rpm and annealed at 500 °C for 40 min, using the commercial TiO<sub>2</sub> paste (provided by Xi'an 10 Polymer Light Technology Corp, 30NR-D) diluted with anhydrous ethanol at a weight ratio of 1/6. The perovskite precursor solutions were prepared by dissolving 1.30M PbI<sub>2</sub>, 1.19 M FAI, 0.14M PbBr<sub>2</sub>, 0.14M MABr and 0.07M CsI into a DMSO/DMF (1:4, v:v) mixture. The perovskite films were deposited on the electron transport layer by a two-step spin-coating process at 2000 rpm for 10 s, followed by 6000 rpm for 30 s. At the time of 15 s prior to the program end, 100 μL of chlorobenzene was dropped on the spinning substrate and the films were annealed at 120 °C for 1 h. The HTM solution was spin-coated onto the perovskite layer at 5000 rpm for 30 s. After oxidizing the HTM layer in air for 15 h, the device was pumped into an evaporation chamber below 10<sup>-5</sup> torr and

an approximately 60 nm thick Au counter electrode was deposited atop. The active area of our device is 0.0625 cm<sup>2</sup>.

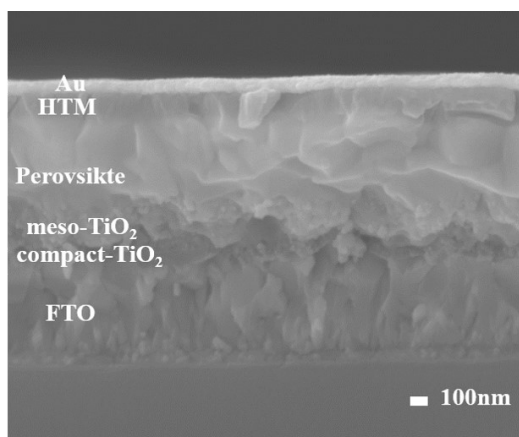


Fig. S12. Cross-sectional SEM image of the 3, 6-BOC-based device.

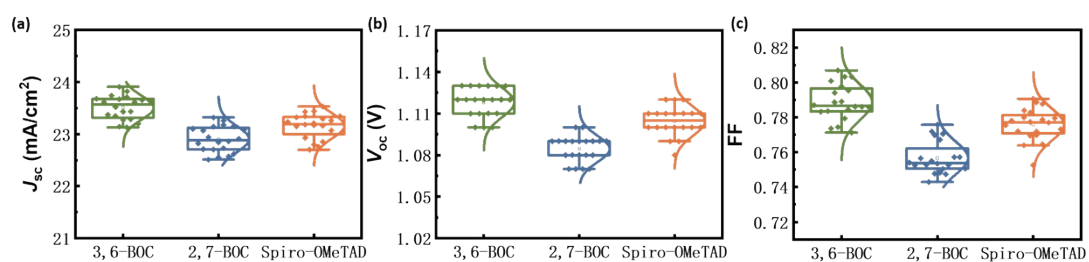


Fig. S13. Statistics of photovoltaic parameters (a)  $J_{sc}$ , (b)  $V_{oc}$  and (c)  $FF$  of PSCs containing different interlayers measured under AM 1.5 G illumination (100 mW cm<sup>-2</sup>). 20 devices were measured for each HTM.

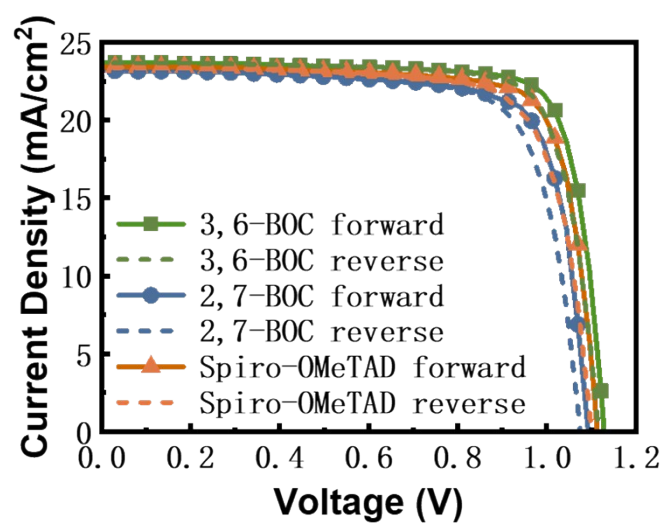


Fig. S14.  $J$ - $V$  curves of PSCs measured in reverse and forward directions.

Table S2. Photovoltaic parameters based on 3, 6-BOC, 2, 7-BOC and Spiro-OMeTAD PSCs with different scanning directions.

HTMs	Scan Direction	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	$FF$	PCE (%)
3, 6-BOC	forward	1.13	23.71	0.80	21.52
	reverse	1.12	23.68	0.79	20.88
2, 7-BOC	forward	1.09	23.18	0.78	19.60
	reverse	1.08	23.14	0.75	18.64
Spiro-OMeTAD	forward	1.11	23.43	0.79	20.57
	reverse	1.10	23.38	0.76	19.47

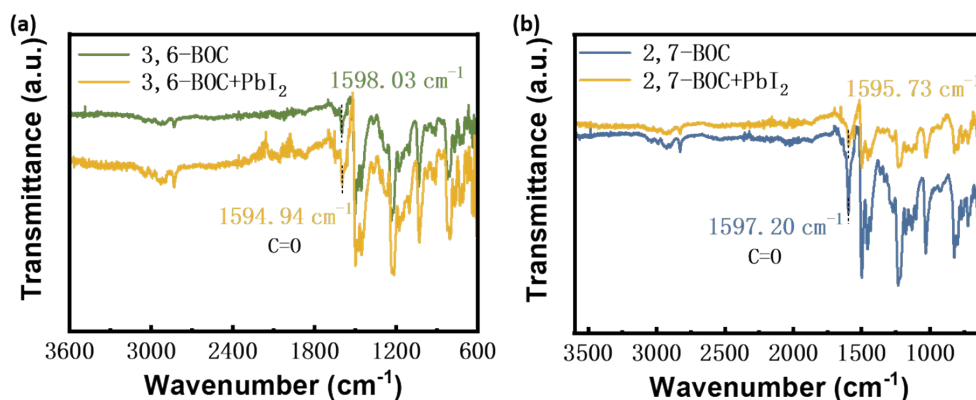


Fig. S15. Full FT-IR spectra of (a) 3, 6-BOC and (b) 2, 7-BOC with or without PbI<sub>2</sub>.

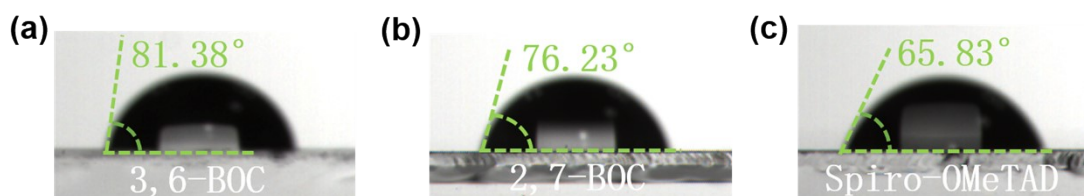


Fig. S16. Water contact angle measurements of (a) 3, 6-BOC, (b) 2, 7-BOC and (c) Spiro-OMeTAD films.

## References

1. Y. Liu, X. Ye, G. Liu, Y. Lv, X. Zhang, S. Chen, J. W. Y. Lam, H. S. Kwok, X. Tao and B. Z. Tang, *Journal of Materials Chemistry C*, 2014, **2**, 1004-1009.
2. F. Wu, Y. Shan, J. Qiao, C. Zhong, R. Wang, Q. Song and L. Zhu, *ChemSusChem*, 2017, **10**, 3833-3838.
3. D. Zhang, P. Xu, T. Wu, Y. Ou, X. Yang, A. Sun, B. Cui, H. Sun and Y. Hua, *Journal of Materials Chemistry A*, 2019, **7**, 5221-5226.