Electronic Supporting Information

Improving stability and efficiency of PTAA-based inverted perovskite solar cells through a guest strategy

Jieying Cao,[ab] *Xinxing Yin*[*b], *Lei Lu,*[b] *Jiaxing Song,*[b] *Lin Hu,*[b] *Yingzhi Jin,*[b] *Zhen Su,*[b] *Zaifang Li*[*b] *and Jiefeng Hai*[*a]

Jieying Cao, Associate professor Jiefeng Hai
Guangxi Key Laboratory of Electrochemical and Magneto-chemical Functional Materials, Guilin University of Technology, Guilin, 541004, China
E-mail: haijiefeng@glut.edu.cn

Jieying Cao, Dr. Xinxing Yin, Dr. Lei Lu, Dr. Jiaxing Song, Dr. Lin Hu, Dr. Yingzhi Jin, Dr. Zhen Su, Prof. Zaifang Li
College of Biological, Chemical Science and Chemical Engineering
Jiaxing University, Jiaxing 314001, China.
E-mails: xxyin@zjxu.edu.cn; zaifang.li@zjxu.edu.cn

Contents

1. Experimental section

^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker Avance III 500 (500 MHz) spectrometer at room temperature. Mass spectra were obtained by Bruker ultrafleXtreme MALDITOF/TOF. Thermogravimetric analysis (TGA) was conducted under N_2 atmosphere at a heating rate of 20 ℃ min $^{-1}$ from 50 ℃ to 800 ℃. The instrument type was SAT-409PC (NETZSH). The electrochemical cyclic voltammetry (CV) was conducted on an electrochemical workstation (CHI660D Chenhua, Shanghai) with Pt plate as working electrode, Pt slice as counter electrode, and Ag/AgCl electrode as reference electrode in tetrabutylammonium hexafluorophosphate (n-Bu4NPF6, 0.1 M) acetonitrile solutions at a scan rate of 50 mV s $^{-1}$. The UV-Vis spectrum was registered with a Varian Cary 100 spectrophotometer. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) results were acquired on Zeiss Sigma500 and Rigaku Ultima IV instruments respectively. AFM images were measured on an atomic force microscope (Bruker Dimension Icon).X-ray photoemission spectroscopy (XPS) was measured by Thermo Scientific ESCALAB Xi+. UPS was conducted at the same equipment as XPS while using monochromatized He I radiation at 21.22 eV. TEM images were obtained using Tecnai G2 20 (FEI Tecnai G2). Steady-state photoluminescence (PL) and time-resolved PL (TRPL) results were conducted respectively with FLS980 and Lifespec II (Edinburgh Instrument, U.K.). Raman measurements were collected by a Thermo Scientific DXR 2xi Raman spectrometer.

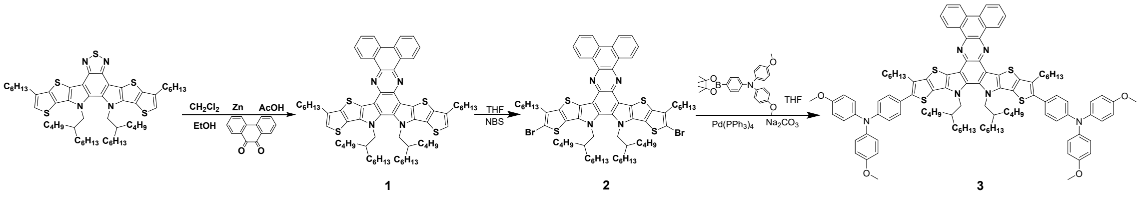
J-V curves testing of the devices was obtained using a Keithley 2400 signal source instrument and an AM1.5G light source provided by Enli. Technology Co.The EQE was obtained using a solar cell spectral response measurement system (Enli Technology Co., Ltd., QE-R3011). The light intensity at each wavelength was also calibrated with a standard Si solar cell. To evaluate the working reliability of the devices, they were aged in LED bulb light-soaking (AM 1.5 G, 100 m W/cm^2) using a multi-channels solar cells stability test system (Wuhan 91PVKSolar Technology Co. Ltd, China). Electrochemical impedance spectroscopy (EIS) results was obtained by electrochemical workstation (Chenhua CHI660E) under dark conditions.

Transmission Electron Microscopy (TEM): Figure 4d-e:PTAA and PTAA:BQ-

BO solutions were applied to copper meshes adhered to clean glass substrates via static spin-coating, followed by a 10min thermal annealing process, after which the samples were characterized using transmission TEM. Figure 4f-g: using the same preparation procedure, the samples were placed on a heating stage at 85°C for continuous heating for four days before being subjected to TEM testing again.

2. Synthesis

Commercially available reagents and solvents were purchased from Energy or Admas and used without further purification.



Scheme S1. Synthesis route for BQ-BO.

Synthesis of BTP$_6$QX-BO ***(1)***

In a 250 mL round-bottom flask, add compound 3 (150 mg, 142.08 umol) and zinc powder (232 mg, 3.5 mmol), vacuum and purged with argon gas three times, then add 30 mL of anhydrous acetic acid and 5 mL of dichloromethane, vacuum and purged with argon gas three times. Stir at 120°C for 10-30 min, track the reaction on a spot plate (petroleum ether/dichloromethane = 5/1). Cool the solution to room temperature, filter off the zinc powder, and obtain a clear solution without further purification. Then in a 250 mL round-bottom flask, add phenanthrenequinone (60 mg, 284.12 umol), vacuum and purged with nitrogen gas three times, add the obtained acetic acid filtrate, and add 40 mL of anhydrous ethanol. Vacuum and purged with argon gas three times, stir at 110°C (adjust the temperature according to the degree of backflow) for 1-3h. Cool the reaction solution to room temperature, pour it into 100 mL of cold water, extract with dichloromethane, combine the organic phase, dry with anhydrous sodium sulfate, and remove the organic solvent using a rotary evaporator to obtain the crude product. Further purify it using silica gel column chromatography, eluting with petroleum ether/dichloromethane = 25/4 to obtain compound 1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.77 (d, *J* = 8.0 Hz, 1H), 8.72 (d, *J* = 8.2 Hz, 1H), 7.95 (t, *J* = 7.6 Hz, 1H), 7.86 (t, *J* = 7.6 Hz, 1H), 7.07 (s, 1H), 4.73 (d, *J* = 7.8 Hz, 2H), 2.98 (d, *J* = 8.2 Hz, 2H), 2.26 – 2.17 (m, 1H), 1.98 (q, *J* = 7.8 Hz, 2H), 1.49 – 1.40 (m, 3H), 1.28 (s, 15H), 0.94 (dt, *J* = 37.2, 7.6 Hz, 12H), 0.64 (dt, *J* = 13.9, 7.3 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.23, 139.01, 137.40, 136.97, 135.83, 131.27, 131.24, 131.08, 128.99, 127.76, 125.95, 123.71, 122.81, 122.72, 122.69, 118.85, 117.78, 77.29, 77.09, 77.03, 76.78, 55.13, 38.72, 31.72, 31.61, 30.39, 30.31, 30.27, 29.72, 29.63, 29.39, 29.16, 28.87, 28.01, 27.89, 25.42, 25.29, 22.79, 22.76, 22.72, 22.67, 22.44, 14.17, 14.14, 13.93, 13.77, 13.74. Melting point: 200 °C.

*Synthesis of BTP$_6$QX-BO-Br **(2)***

In a 100 ml three-neck flask, add compound 1 (100 mg, 373.36 umol), vacuum, and then fill with nitrogen gas. Add 20 mL of anhydrous tetrahydrofuran, cover the entire reaction flask with aluminum foil, and cool it in an ice bath to 0°C. Under nitrogen protection, add 62 mg of N-Bromosuccinimide(NBS). Stir in the dark for 8-10 hours. Stop the reaction, quench it with water, extract with dichloromethane, wash the organic phase with a large amount of water, dry it with anhydrous sodium sulfate, and then remove the organic solvent using a rotary evaporator to obtain the crude product. Purify it further using silica gel column chromatography, with the eluent being petroleum ether. Obtain compound 2.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.74 (d, *J* = 7.9 Hz, 2H), 8.72 (d, *J* = 8.1 Hz, 2H), 7.95 (t, *J* = 7.5 Hz, 2H), 7.86 (t, *J* = 7.6 Hz, 2H), 4.65 (d, *J* = 7.8 Hz, 4H), 2.97 (t, *J* = 7.6 Hz, 4H), 2.17 (s, 2H), 1.94 (p, *J* = 7.7 Hz, 4H), 1.67 – 1.53 (m, 6H), 1.45 (h, *J* = 7.1, 6.6 Hz, 8H), 1.28 (s, 12H), 0.96 (tdt, *J* = 22.1, 15.1, 6.7 Hz, 40H), 0.66 (dt, *J* = 13.0, 6.9 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.19, 131.34, 130.92, 129.16, 127.81, 125.91, 122.86, 121.93, 77.29, 77.22, 77.03, 76.96, 76.89, 76.78, 76.71, 55.24, 38.76, 31.66, 31.61, 30.37, 30.32, 30.29, 30.22, 29.72, 29.68, 29.38, 29.06, 28.98, 28.34, 27.98, 27.87, 25.37, 25.25, 22.78, 22.75, 22.71, 22.63, 22.55, 22.45, 14.19, 14.14, 13.95, 13.77. Melting point: 120 °C.

*Synthesis of BQ-BO **(3)***

500 ml three-neck flask, add compound 6 (520 mg, 383umol), triphenylamine

borate (496 mg, 1.15mmol), Pd(PPh_3)$_4$ (31 mg, 26.81umol), vacuum and nitrogen gas three times, then add 60 mL of Na_2CO_3 (1 mol/L), 120 mL of tetrahydrofuran (no need for anhydrous), vacuum and argon gas three times. Add at 85℃ for 12~24 h. Stop the reaction and cool to room temperature, quench with water, extract with dichloromethane, combine the organic phase, add anhydrous sodium sulfate to remove water, evaporate the organic solvent using a rotary evaporator to obtain the crude product. Purify further by silica gel column chromatography, eluting with a mixture of petroleum ether/ethyl acetate = 100/1), to obtain the final product.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.79 (d, J = 8.2 Hz, 2H), 8.73 (d, J = 8.4 Hz, 2H), 7.95 (t, J = 7.6 Hz, 2H), 7.86 (t, J = 7.8 Hz, 2H), 7.56 – 7.31 (m, 3H), 7.18 (d, J = 8.4 Hz, 8H), 7.05 (d, J = 8.1 Hz, 4H), 6.92 (d, J = 8.4 Hz, 8H), 4.75 (d, J = 22.4 Hz, 4H), 3.85 (s, 12H), 3.03 (d, J = 8.2 Hz, 4H), 2.38 – 2.17 (m, 2H), 2.00 (p, J = 8.0 Hz, 4H), 1.73 – 1.25 (m, 20H), 0.98 (h, J = 23.3, 18.0 Hz, 42H), 0.78 – 0.32 (m, 16H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.22, 138.95, 131.26, 131.11, 128.98, 127.76, 127.05, 125.96, 122.82, 119.77, 114.82, 77.30, 77.04, 76.79, 55.54, 55.12, 38.65, 31.66, 31.58, 30.37, 30.29, 30.20, 29.73, 29.45, 29.40, 29.33, 28.24, 27.98, 27.87, 25.38, 25.24, 22.82, 22.65, 22.48, 14.23, 14.00, 13.82, 0.02. Melting point: 123 °C.MS (MALDI-TOF): calculated for $C_{108}H_{120}N_6O_4S_4$ (M^+): 1693.82, found: 1694.71.

3. Device fabrication:

We constructed an inverted perovskite solar cell ITO/HTL/$FA_{0.9}MA_{0.05}Cs_{0.05}Pb(I_{0.95}Br_{0.05})_3$/PEABr/$PC_{61}BM$/BCP/Ag. The ITO glass substrate was washed deionized water, acetone, and ethanol solvents to ultrasonically clean indium tin oxide for 15 minutes. After N_2 drying, treat with O_2 plasma for 6 minutes. Dissolve the hole transport layer PTAA in toluene, rotate and coat at 4000 rpm for 30 s, and anneal at 100°C for 10 min. When preparing the PTAA:BTP_6QX-BO-TPA solution, first mix PTAA and BTP_6QX-BO-TPA at a mass ratio of 3:1, and then dissolve it in 1 mL of chloroform. Spin coating at 6000 rpm for 30 s, then anneal at 100°C for 10 min. Then, 45 μL of PFN-Br:PEABr (mass ratio 1:10) was spin-coated on the prepared substrate at a speed of 6000 rpm for 30 s to improve the wetting properties of the perovskite precursor solution. Mix FAI (196.1 mg), CsI (18.2 mg), PbI_2 (572 mg), $PbBr_2$ (22 mg), MABr (6.7mg), MACl (8.8mg) in 865ml DMF/DMSO solution at a volume ratio of 4:1 , heated and stirred at 60°C for 2 hours to obtain a clear perovskite precursor solution. The prepared perovskite precursor solution was spin-coated on the modified ITO substrate at a rotation speed of 1000 rpm for 5 s and 4000 rpm for 30 s. In the last 15 s of the spin coating process, 150 μl of chlorobenzene solvent was added dropwise, and placed on the heating stage for annealing at 100°C for 50 min; After cooling to room temperature, dynamically spin-coat PEABr with a concentration of 1 mg/ml (volume ratio IPA: DMSO = 200:1, 4000rpm, 30 s), and anneal at 100°C for 5 min. Then apply a layer of $PC_{61}BM$ (20 mg/ml, chlorobenzene, 1500 rpm, 35 s) and anneal at 100°C for 10 min. BCP with a concentration of 0.5 mg/ml dissolved in IPA was spin-coated onto the surface at 4000rpm for 30s. Finally, 100 nm of Ag was deposited by thermal evaporation.

4. Material characteriz

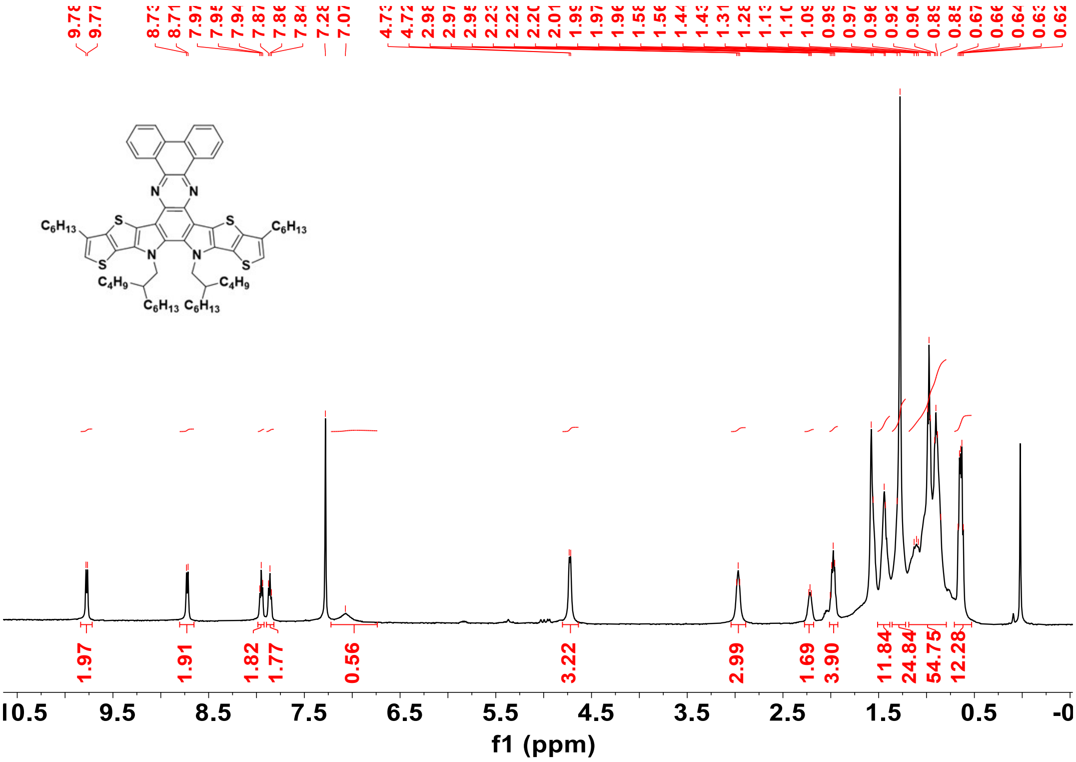


Figure S1. ^{1}H NMR spectrum of BTP6QX-BO (1).

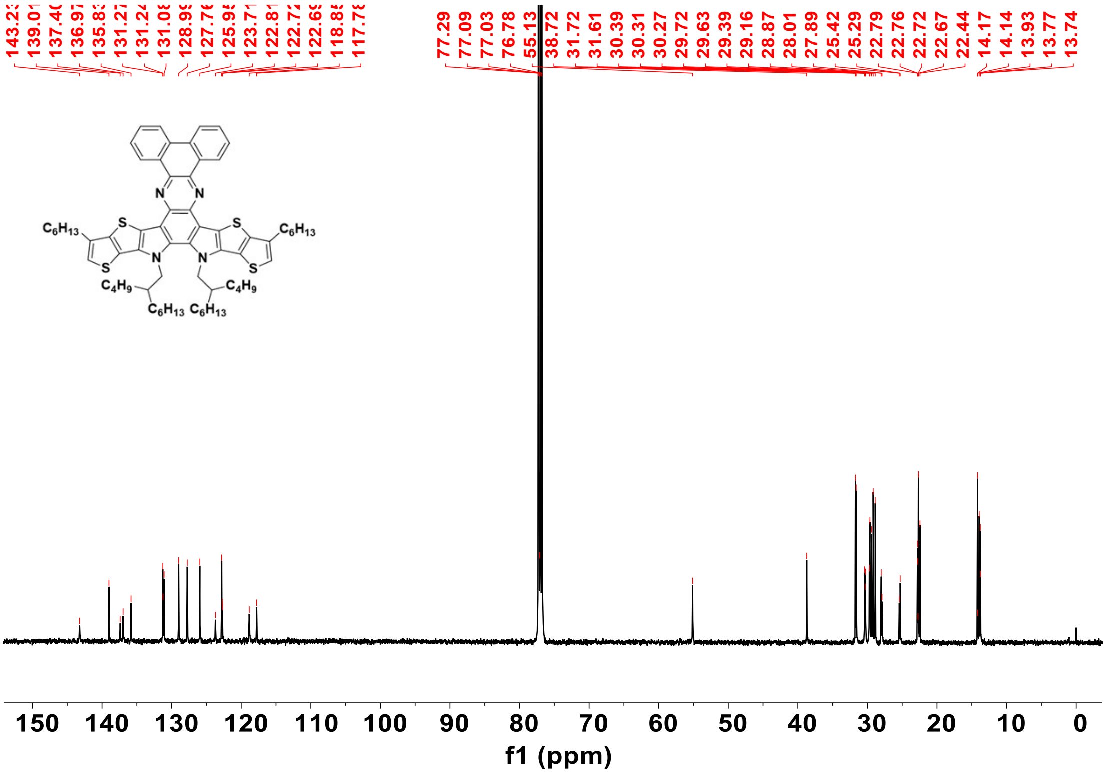


Figure S2. ^{13}C NMR spectrum of BTP6QX-BO (1).

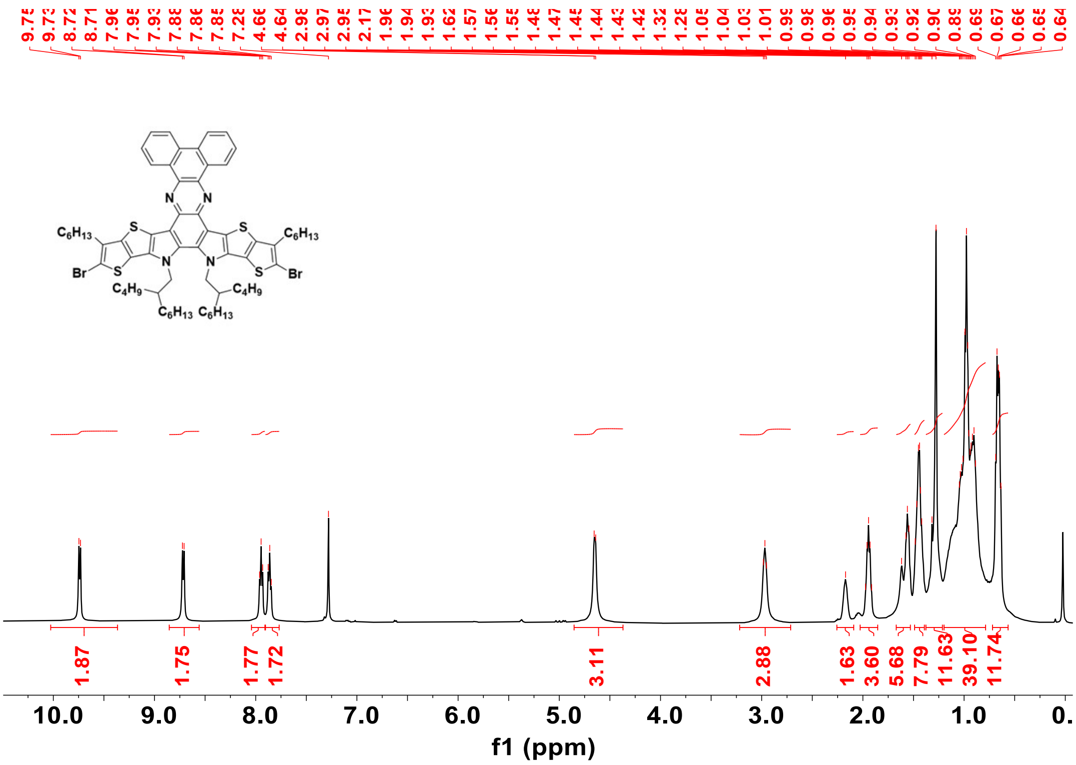


Figure S3. ^{1}H NMR spectrum of BTP6QX-BO-Br (2).

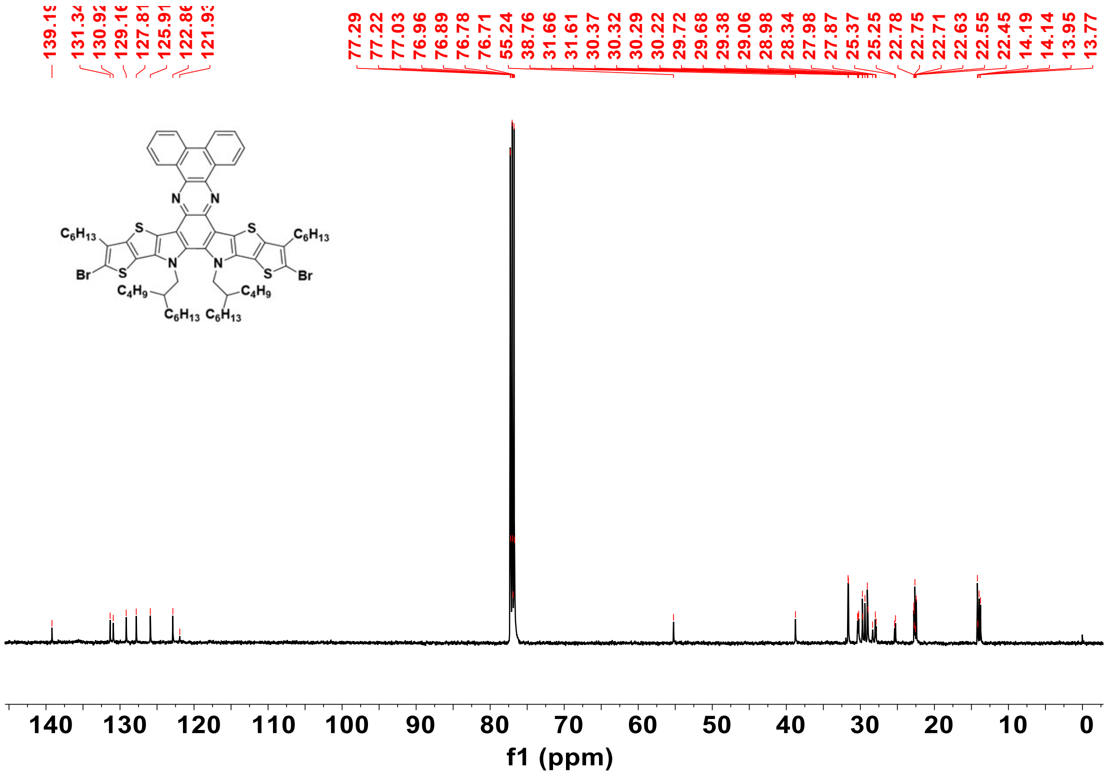


Figure S4. ^{13}C NMR spectrum of BTP6QX-BO-Br (2).

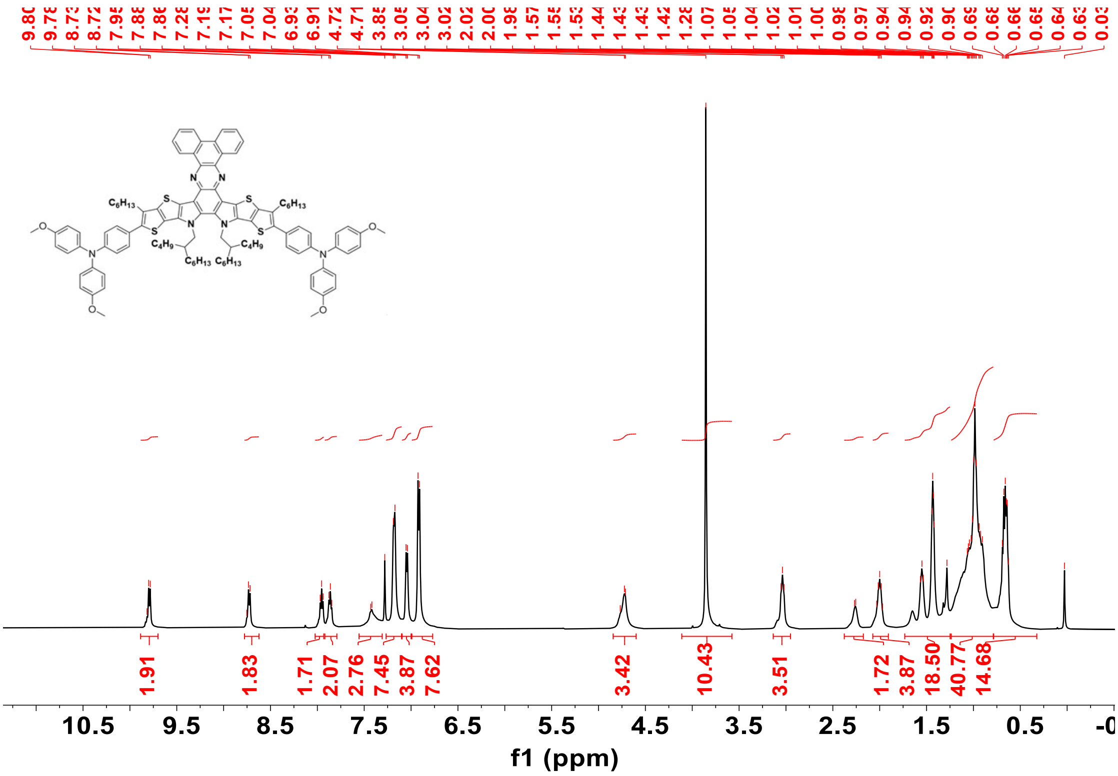


Figure S5. ^{1}H NMR spectrum of BQ-BO.

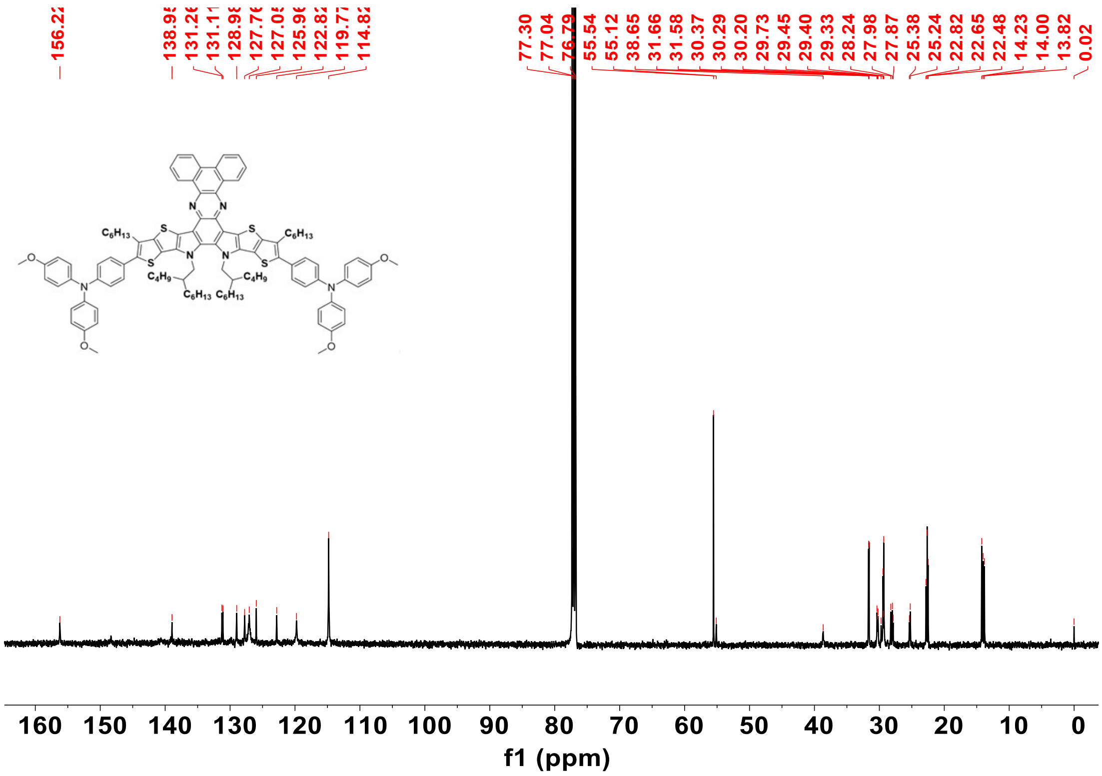


Figure S6. ^{13}C NMR spectrum of BQ-BO.

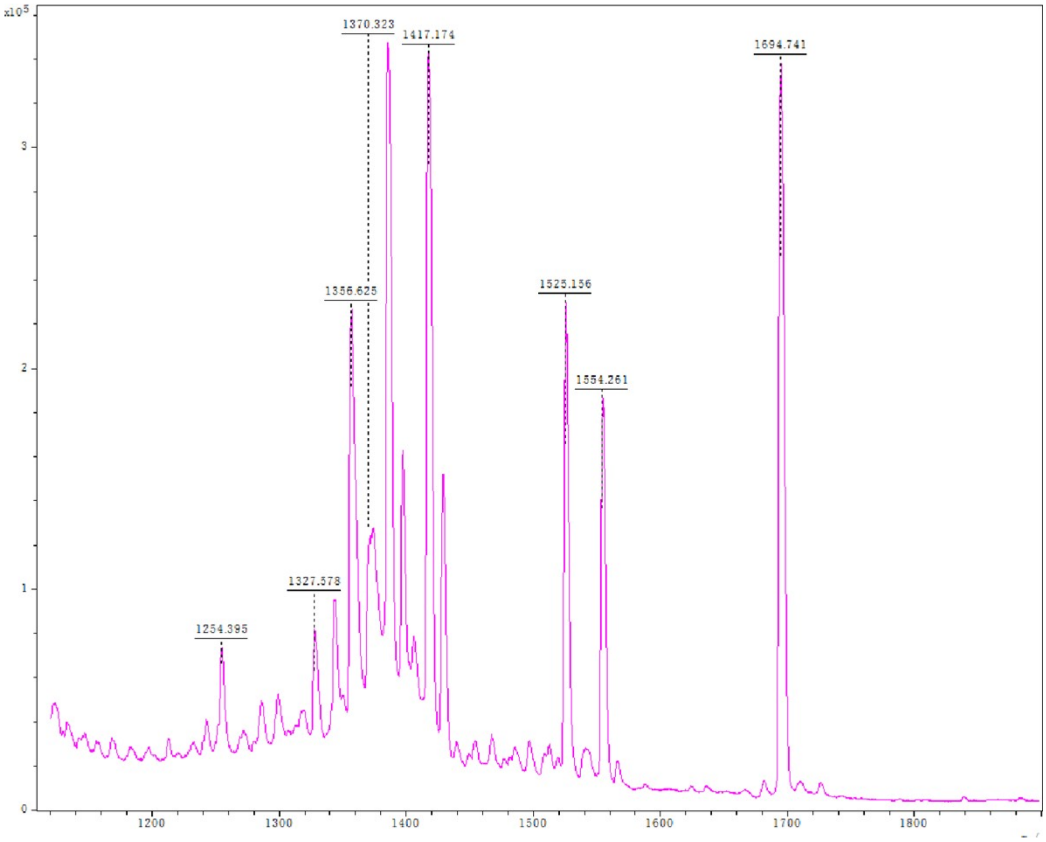


Figure S7. HRMS spectrum of BQ-BO.

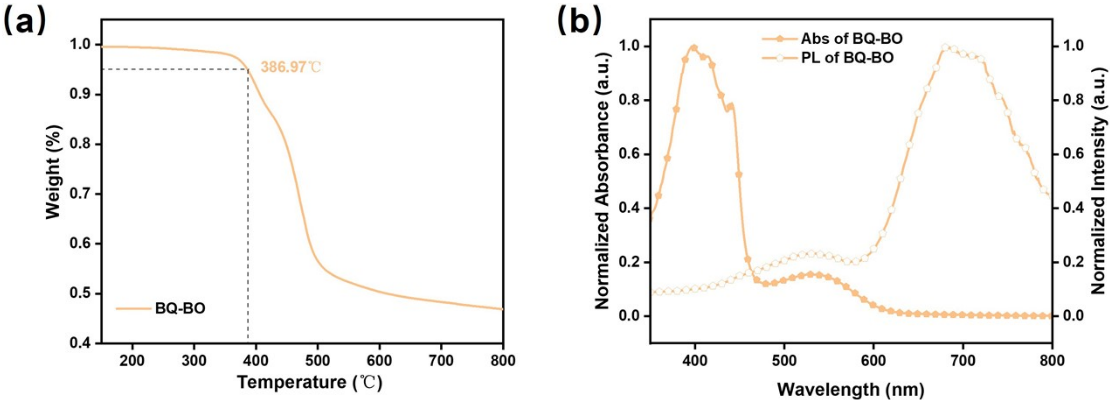


Figure S8. a) TGA thermogram of BQ-BO, b) UV–Vis absorption and PL spectra of BQ-BO.

5. Device Test

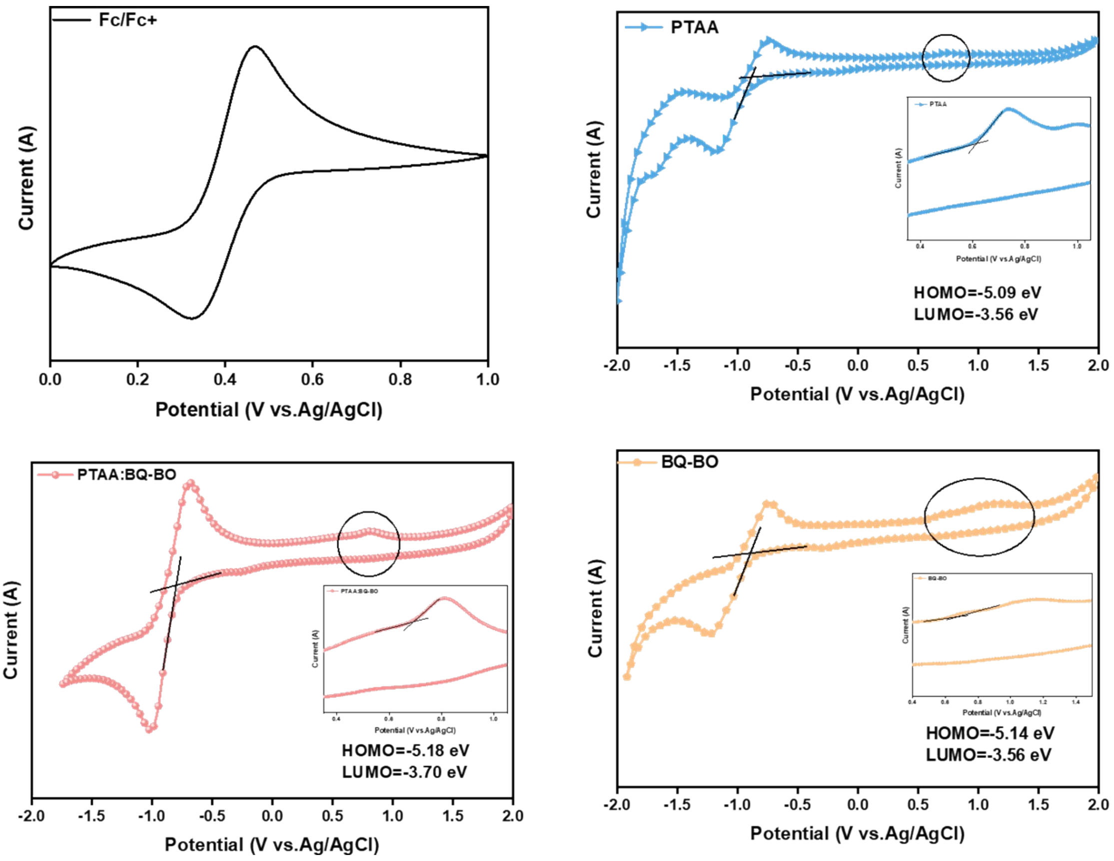


Figure S9. Cyclic voltammograms of PTAA:BQ-BO and PTAA in 0.1 mol/L Bu_4NPF_6 acetonitrile solution at a scan rate of 20 mV/s, the ferrocene/ferrocenium (Fc/Fc+) couple was also provided for an internal reference.

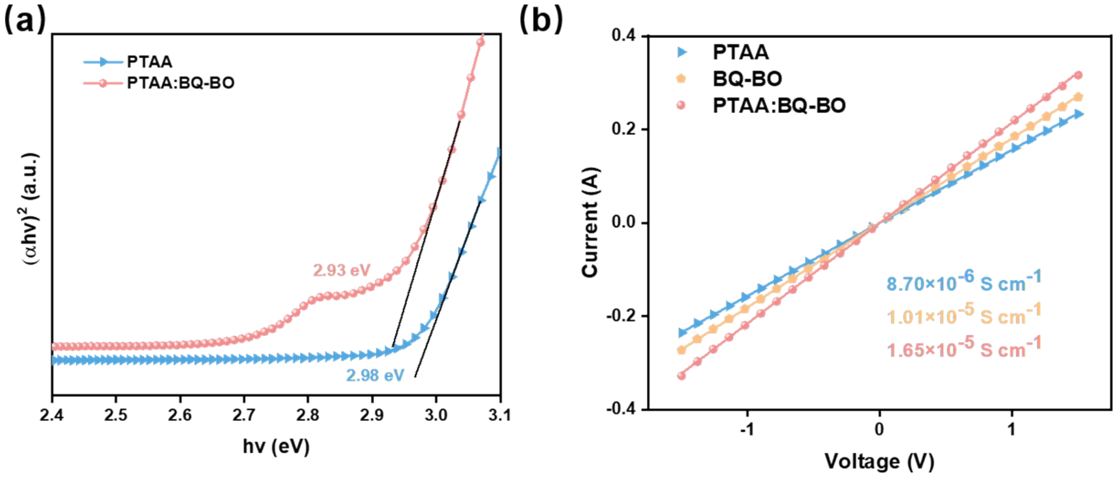


Figure S10. (a) The E_g of PTAA and PTAA:BQ-BO films. (b) *J-V* characteristics of the hole-only devices with a structure of ITO/PEDOT:PSS/PTAA, BQ-BO or PTAA:BQ-BO/Au.

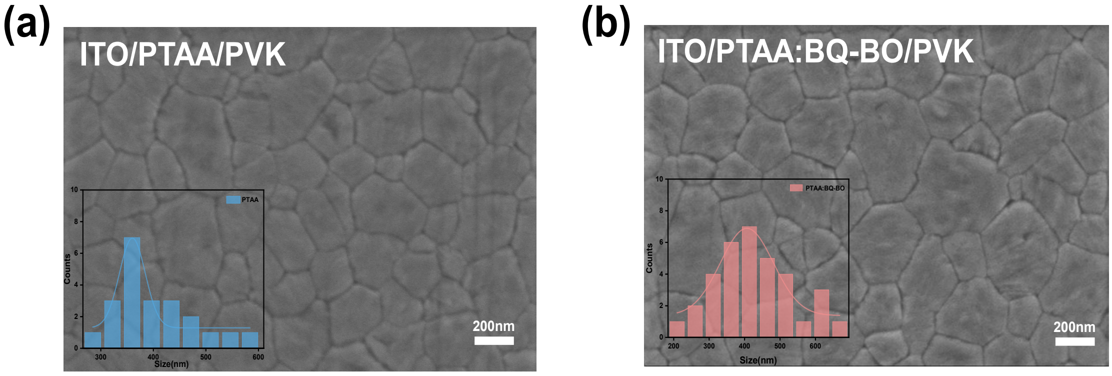


Figure S11. SEM images of bottom surface and the corresponding grain size distributions (inset) of perovskite film.

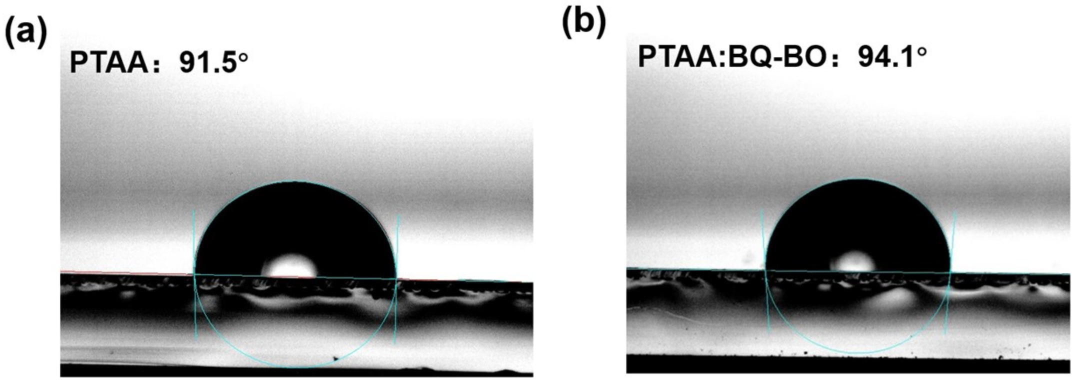


Figure S12. Water contact angles of (a) PTAA and (b) PTAA:BQ-BO.

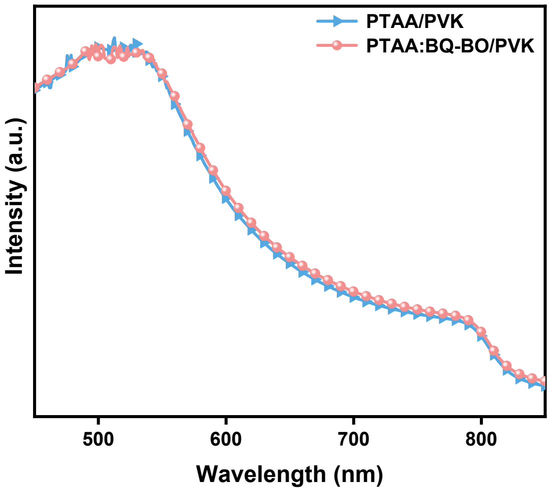


Figure S13. Absorption spectra of the perovskite films based on PTAA and PTAA:BQ-BO.

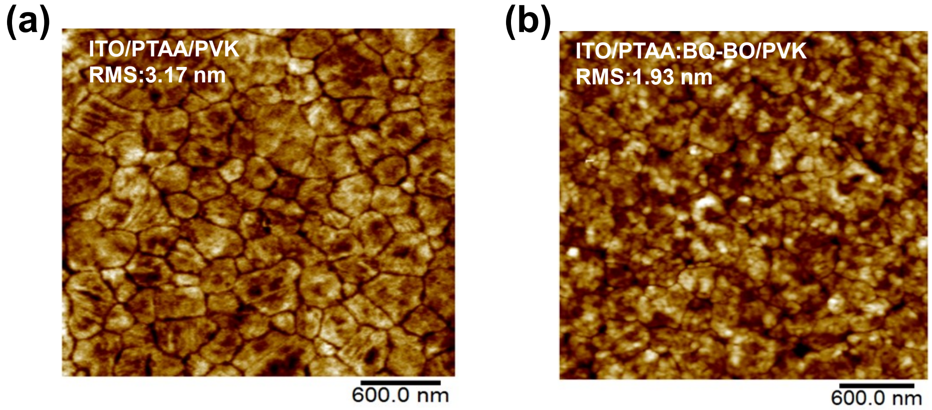
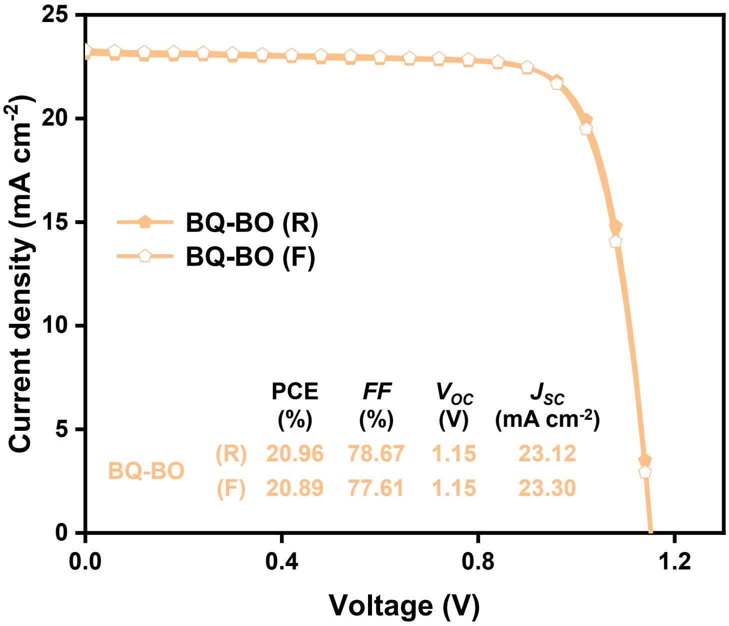


Figure S14. AFM topography images of the perovskite films deposited on (a) PTAA and (b) PTAA:BQ-BO.



		PCE (%)	*FF* (%)	V_{OC} (V)	J_{SC} (mA cm^{-2})
BQ-BO	(R)	20.96	78.67	1.15	23.12
	(F)	20.89	77.61	1.15	23.30

Figure S15. *J*-*V* curves of the BQ-BO-devices measured in both reverse and forward scanning directions.

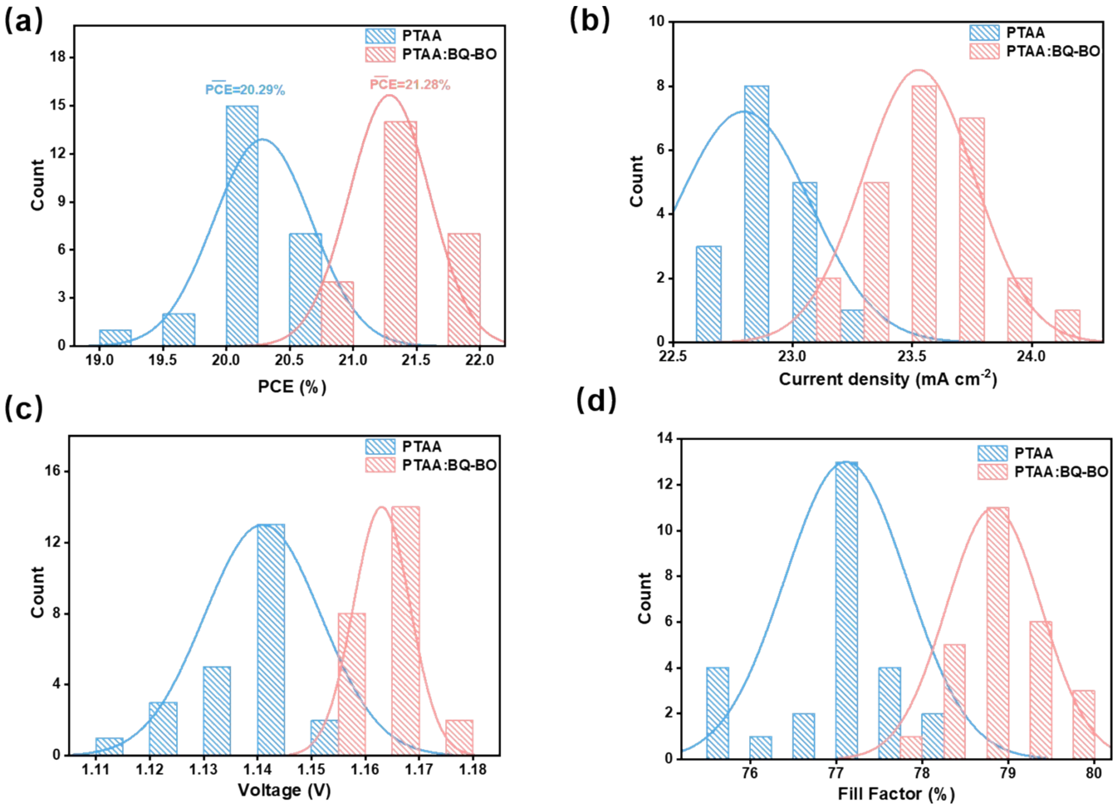


Figure S16. statistics of (a) PCE, (b) J_{SC}, (c) V_{OC} and (d) FF distribution of perovskite solar cells with PTAA or PTAA:BQ-BO HTL.

Table S1. Energy levels calculated from UPS data

Sample	$E_{cut-off}$ (eV)	WF (eV)	E_{onset} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	Eg (eV)
PTAA	16.83	4.39	0.60	-4.99	-2.01	2.98
PTAA:BQ-BO	16.71	4.51	0.64	-5.15	-2.22	2.93

Table S2. Holy mobility and conductivity of PTAA and PTAA:BQ-BO films

Sample	Mobility ($cm^2 S^{-1} V^{-1}$)	Conductivity ($S cm^{-1}$)
PTAA	1.10×10^{-4}	8.7×10^{-6}
BQ-BO	2.68×10^{-4}	1.01×10^{-5}
PTAA:BQ-BO	6.35×10^{-4}	1.65×10^{-5}

Table S3. TRPL spectral parameters based on perovskite, PTAA/perovskite and PTAA:BQ-BO /perovskite.

Sample	**A_1**	**τ_1**	**A_2**	**τ_2**	**τ_{avg}**
PVK	2726.14	32.69	2390.14	32.70	1041.92
PTAA/PVK	12704.30	11.32	230.34	62.74	709.28
PTAA:BQ-BO/PVK	231.58	37.16	30161.18	6.42	57.95