

## Supporting Information

# Zinc Complex-Based Hole Transporting Material for Perovskite Solar Cell Applications

*Yogesh S. Tingare<sup>a,\*</sup>, Ya-Chun Hsu<sup>a</sup>, Jyun-Dai Lin<sup>b</sup>, Chaochin Su<sup>a,\*</sup>, Wan-Chun Wang<sup>b</sup>, Sheng-Han Wang<sup>b</sup>, Shi-Yun Lai<sup>a</sup>, Zhi-Ting Wu<sup>a</sup>, Ja-Hon Lin<sup>c</sup>, Hsiou-Hsuan Wang<sup>d</sup>, and Wen-Ren Li<sup>b,\*</sup>*

<sup>a</sup>Institute of Organic and Polymeric Materials/Research and Development Center for Smart Textile Technology, National Taipei University of Technology, Taipei 106344, Taiwan.

<sup>b</sup>Department of Chemistry, National Central University, Zhongli 32001, Taiwan.

<sup>c</sup>Department of Electro-Optical Engineering, National Taipei University of Technology, Taipei 106344, Taiwan.

<sup>d</sup>Department of Chemical and Materials Engineering, National Ilan University, I-Lan 260007, Taiwan.

\*Corresponding Author.

*E-mail Address:* [f12098@ntut.edu.tw](mailto:f12098@ntut.edu.tw) (Y.S.Tingare), [f10913@mail.ntut.edu.tw](mailto:f10913@mail.ntut.edu.tw) (C. Su), [ch01@ncu.edu.tw](mailto:ch01@ncu.edu.tw) (W.R. Li)

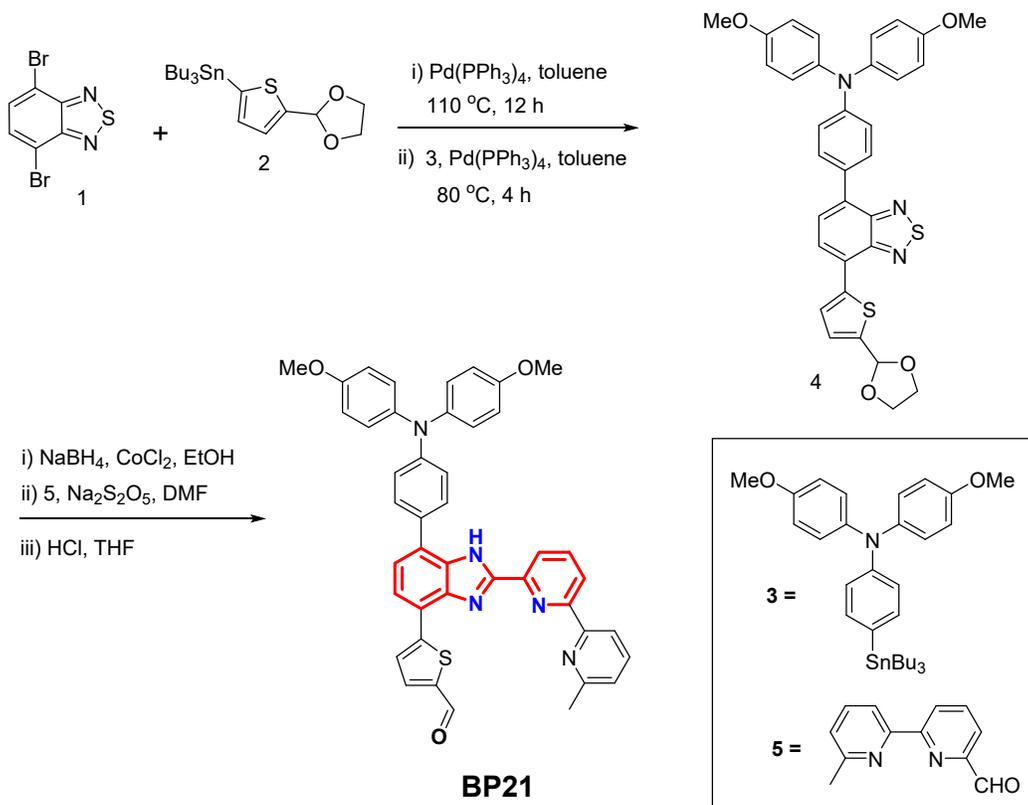
## Experimental section

### Materials:

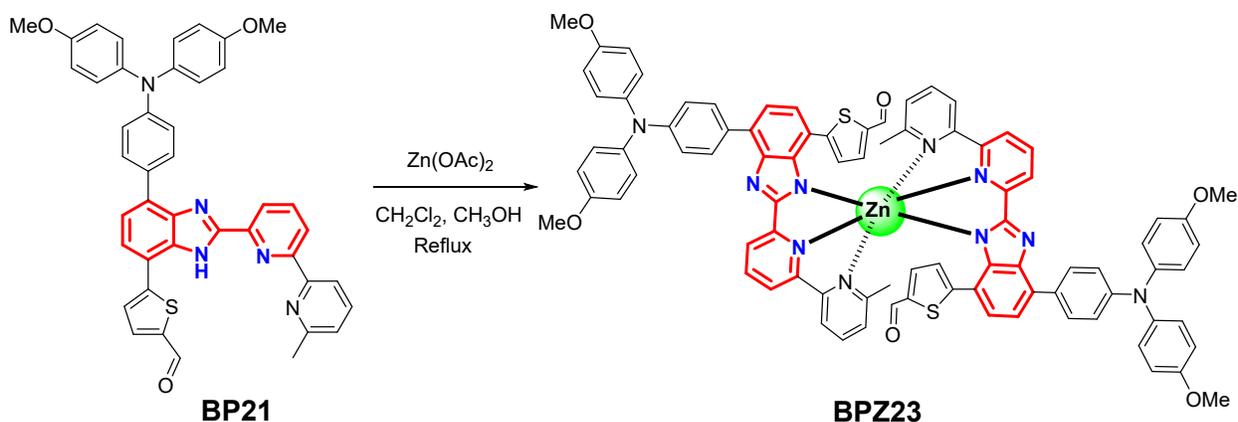
Unless otherwise specified, all chemical reagents were obtained commercially from Aldrich, Alfa, and TCI Chemical Co. The solvents (THF, CH<sub>2</sub>Cl<sub>2</sub>, and DMF) were dried using a VAC purifier (VAC 103991, Vacuum Atmospheres) before being used in air-sensitive reactions in an argon atmosphere. All reactions' progress was monitored using thin-layer chromatography using aluminum-coated Merck Kieselgel 60 F254 plates developed with I<sub>2</sub> or UV light. Purification of crude compounds are carried out using flash chromatography with Silica gel (Scharlau 60, 230-240 mesh). The compounds were characterized using <sup>1</sup>H, <sup>13</sup>C NMR, and mass spectra obtained with a Bruker Avance 500 MHz spectrometer and a Bruker Daltonics Flex Analysis spectrometer with matrix-assisted laser desorption ionization (MALDI-TOF) experiments. Thermogravimetric analysis (TGA) was performed using a TA Instruments TGAQ500 with a ramp rate of 10 °C/min under N<sub>2</sub> from 100 to 600 °C. DSC was run on a Discovery DSC from TA instruments, and two cycles were recorded under nitrogen, heating (up to 400 °C), and cooling (50 °C) at a scanning rate of 10 °C/min. Shimadzu UV3600 UV-vis-NIR spectrophotometer was used to examine the optical properties of the solutions. Cyclic voltammograms of **BP21** and **BPZ23** were recorded using cyclic voltammetry (CV) experiments with a CHI 627C electrochemical setup, which included a glassy carbon electrode as the working electrode, a silver wire (Ag/AgNO<sub>3</sub> in acetonitrile) as the reference electrode, a Pt wire as the counter-electrode, and 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte and at 50 mVs<sup>-1</sup> scan rates. Ferrocene was added for internal reference for calibration after measurement. A Spectrofluorometer (FS5, Edinburgh instruments) was used to measure time-resolved PL spectra, with the PL excitation at = 405 nm. The morphologies of the perovskite films

were checked using scanning electron microscopy (SEM, Hitachi SU4800) and X-ray diffraction (XRD, BRUKER ECO D8 series). The contact angle was measured using the Phoenix 300, Surface Electro Optics (SEO) Co., Ltd, and de-ionized water as the solvent.

### Synthetic Procedures:



**Scheme 1.** Synthesis of final HTM **BP21**.



**Scheme 2.** Synthesis of final HTM **BPZ23**.

## Experimental Section

### Synthesis of 4-(7-(5-(1,3-dioxolan-2-yl)thiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)-N,N-bis(4-methoxyphenyl)aniline (**4**):

In a 250 mL round-bottomed flask, 4,7-dibromobenzo[c][1,2,5]thiadiazole **1** (2.0 g, 6.8 mmol), (5-(1,3-dioxolan-2-yl)thiophen-2-yl)tributylstannane<sup>66</sup> **2** (4.54 g, 10.2 mmol), and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.24 g, 0.34 mmol) were dissolved in THF (13 mL). The reaction mixture was stirred at 60 °C in an argon atmosphere for 2 h. After the reaction was completed, the mixture was filtered through celite, and the solvent was removed under reduced pressure. To the resulting residue, 4-methoxy-N-(4-methoxyphenyl)-N-(4-(tributylstannyl)phenyl)aniline<sup>67</sup> **3** (2.5 g, 4.47 mmol) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> was added in toluene (10 mL) and heated at 80 °C for 4 h in an argon atmosphere. The reaction was monitored using basic TLC (CH<sub>2</sub>Cl<sub>2</sub>/Hexane = 40%). The obtained mixture was filtered through celite, and the solvent was reduced under pressure. Finally, the crude residue was purified using gradient column chromatography on SiO<sub>2</sub> with (CH<sub>2</sub>Cl<sub>2</sub>/Hexane) as the eluant, yielding compound **4** as a red solid (2.1 g, yield: 76%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): δ 7.97 (d, 1H, *J* = 4 Hz), 7.86 (d, 1H, 7.5 Hz), 7.84 (d, 2H, *J* = 8.75 Hz), 7.64 (d, 1H, *J* = 7 Hz), 7.24 (d, 1H, *J* = 4 Hz), 7.14 (d, 4H, *J* = 8.5 Hz), 7.04 (d, 2H, *J* = 8.5 Hz), 6.86 (d, 4H, *J* = 9 Hz), 6.18 (s, 1H), 4.20-4.18 (m, 2H), 4.07-4.04 (m, 2H), 3.81 (s, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm): δ 156.2, 153.9, 152.8, 149.0, 142.5, 140.5, 132.8, 129.7, 128.6, 127.0, 126.9, 126.7, 126.6, 126.0, 125.1, 119.6, 114.8, 100.4, 65.2, 55.4. (HRMS (MOLDI) *m/z* calculated for C<sub>33</sub>H<sub>27</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub> [M]<sup>+</sup>: 593.1443, found: 593.1437

### Synthesis of HTM BP21:

In a 250 mL round-bottom flask, compound **4** (1.0 g, 1.7 mmol) was dissolved in a mixture of ethanol (50 mL) and dichloromethane (56 mL) solvents, and the reaction was degassed with argon.

Next, sodium borohydride (2.26 g, 67.3 mmol) and cobalt dichloride (0.22 g, 1.7 mmol) were added to the above mixture (the bubbles produced were flushed out with argon gas) and stirred for 2 h at 40 °C. The reaction was monitored using an alkalized TLC sheet (ethyl acetate/Hexane = 40%). After the reaction was completed, it was filtered through celite, extracted with dichloromethane, washed with water, and the solvent was removed under reduced pressure to produce a white-blue foamy solid. The solid was then dissolved in DMF (0.2 M), 6'-methyl-[2,2'-bipyridine]-6-carbaldehyde<sup>68</sup> **5** (0.11 g, 0.53 mmol), and Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (0.10 g, 0.53 mmol) was added, and the reaction was stirred at 50 °C for 2 h. The reaction was monitored by TLC (CH<sub>2</sub>Cl<sub>2</sub>/Hexane = 50%). Upon completion, the reaction mixture was concentrated under reduced pressure, and the residue was extracted with dichloromethane, washed with water, and dried over MgSO<sub>4</sub>. Concentrating the solvent gave a yellow solid, which was mixed with THF and treated with a 3 M aqueous hydrochloric acid solution at room temperature. After the solid precipitate disappeared completely, the solution was concentrated under reduced pressure, and the residue was extracted with dichloromethane, washed with water, and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure, and the crude product was subjected to column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/Hexane = 30%) to get HTM **BP21** as an orange solid. (0.21 g, yield: 58%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 12.99 (s, 1H), 8.50 (d, 1H, *J* = 7.5 Hz), 8.34 (d, 2H, *J* = 4 Hz), 8.17 (d, 1H, *J* = 8 Hz), 8.10 (d, 1H, *J* = 4 Hz), 7.92-7.88 (m, 2H), 7.62 (d, 2H, *J* = 8.5 Hz), 7.36 (t, 2H, *J* = 14.4 Hz), 7.14 (d, 4H, *J* = 9 Hz), 6.97 (d, 4H, *J* = 8.5 Hz), 6.93 (d, 2H, *J* = 8.5 Hz), 3.77 (s, 1H), 2.60 (s, 3H). ; <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 184.6, 157.9, 156.53, 156.0, 154.5, 152.8, 150.1, 148.8, 148.4, 142.7, 141.8, 140.3, 138.9, 138.7, 137.8, 133.4, 129.7, 129.1, 128.0, 127.5, 127.0, 124.3, 123.9, 123.0, 121.8, 121.2, 119.4, 115.5, 55.7, 24.7. (HRMS (MOLDI) *m/z* calculated for C<sub>43</sub>H<sub>33</sub>N<sub>5</sub>O<sub>3</sub>S [M]<sup>+</sup>: 699.2304, found: 699.2299.

**Synthesis of HTM BPZ23:** HTM **BP21** (0.7 g, 0.7 mmol) was dissolved in anhydrous dichloromethane (47 mL), and the above mixture was supplemented with Zn(OAc)<sub>2</sub> (0.2 g, 167 mmol) dissolved in MeOH (41 mL). The reaction was degassed with argon and stirred at room temperature for 2-3 days. After the reaction was completed, an additional amount of MeOH/CH<sub>2</sub>Cl<sub>2</sub> (1:1; 100 mL) was added, and the precipitated formed was filtered and dried. Finally, the obtained solid was recrystallized in a MeOH/CH<sub>2</sub>Cl<sub>2</sub> mixed solvent to obtain pure HTM **BPZ23** (64 mg, 49%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 9.97 (s, 2H), 8.54 (d, 2H, *J* = 7.5 Hz), 8.39 (d, 2H, *J* = 4 Hz), 8.25 (t, 2H, *J* = 15.5 Hz), 8.10 (d, 2H, *J* = 3.5 Hz), 7.82 (d, 2H, *J* = 7.5 Hz), 7.57 (d, 2H, *J* = 7.5 Hz), 7.37 (d, 2H, *J* = 7.5 Hz), 7.33 (d, 2H, *J* = 7.5 Hz), 7.11 (d, 4H, *J* = 8.5 Hz), 7.05 (d, 8H, *J* = 8 Hz), 6.74 (d, 12H, *J* = 8 Hz), 5.85 (d, 4H, *J* = 8 Hz), 3.77 (s, 2H), 3.61 (s, 12H), 1.46 (s, 6H). ; <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 184.36, 158.50, 157.63, 154.06, 152.86, 151.80, 151.34, 147.69, 146.42, 142.01, 141.65, 140.87, 139.44, 139.00, 137.07, 131.13, 128.92, 128.48, 128.23, 127.56, 127.12, 125.83, 124.34, 123.31, 121.51, 121.17, 120.65, 119.62, 119.45, 119.29, 116.13, 115.57, 115.45, 115.20, 55.77, 55.49. (HRMS (MOLDI) *m/z* calculated for C<sub>86</sub>H<sub>66</sub>N<sub>10</sub>O<sub>6</sub>S<sub>2</sub>Zn [M+1]<sup>+</sup>: 1462.3900, found: 1463.3738.

### Crystal data and structure refinement for **BPZ23**.

Bond precision: C-C = 0.0051 Å Wavelength=0.71073  
Cell: a = 64.830(3) b = 14.2809(7) c = 17.4314(7)  
alpha = 90 beta = 94.233(2) gamma = 90

Temperature: 200 K

	Calculated	Reported
Volume	16094.5(13)	16094.6(12)
Space group	C 2/c	C 2/c
Hall group	-C 2yc	?
Moiety formula	C <sub>86</sub> H <sub>64</sub> N <sub>10</sub> O <sub>6</sub> S <sub>2</sub> Zn [+ solvent]	C <sub>86</sub> H <sub>64</sub> N <sub>10</sub> O <sub>6</sub> S <sub>2</sub> Zn
Sum formula	C <sub>86</sub> H <sub>64</sub> N <sub>10</sub> O <sub>6</sub> S <sub>2</sub> Zn [+solvent]	C <sub>86</sub> H <sub>64</sub> N <sub>10</sub> O <sub>6</sub> S <sub>2</sub> Zn
Mr	1462.99	1462.96
Dx,g cm <sup>-3</sup>	1.208	1.208
Z	8	8
Mu (mm <sup>-1</sup> )	0.415	0.415
F000	6080.0	6080.0
F000'	6086.39	
h,k,lmax	78,17,21	78,17,20
Nref	14782	14611
Tmin,Tmax	0.840,0.883	0.826,0.886
Tmin'	0.819	

Correction method = # Reported T Limits: Tmin = 0.826 Tmax = 0.886 AbsCorr = MULTI-SCAN

Data completeness = 0.988 Theta (max) = 25.380

R(reflections) = 0.0585 (10266), wR2(reflections) = 0.1916 (14611), S = 1.069 Npar = 996

Crystallographic data for **BPZ23** have been deposited with the Cambridge Crystallographic Data Centre as deposition No **CCDC-2267695**. Copies of the data can be obtained, free of charge, on

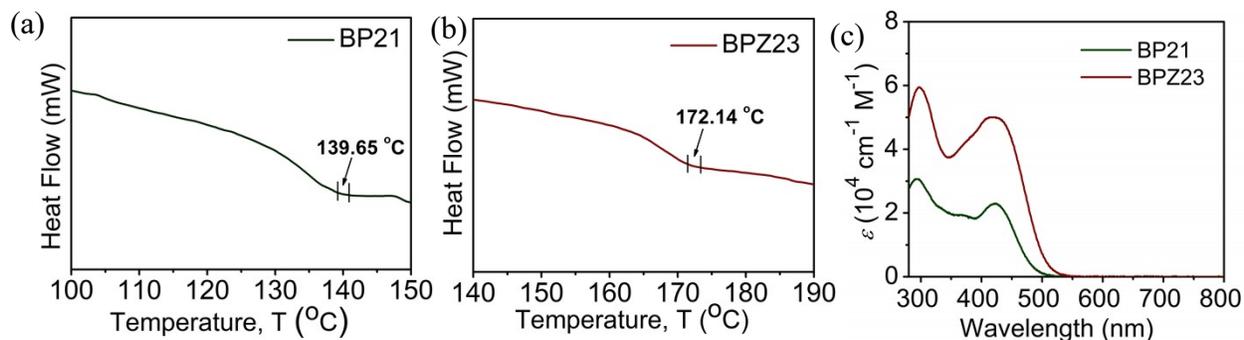
application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

### **Device fabrication:**

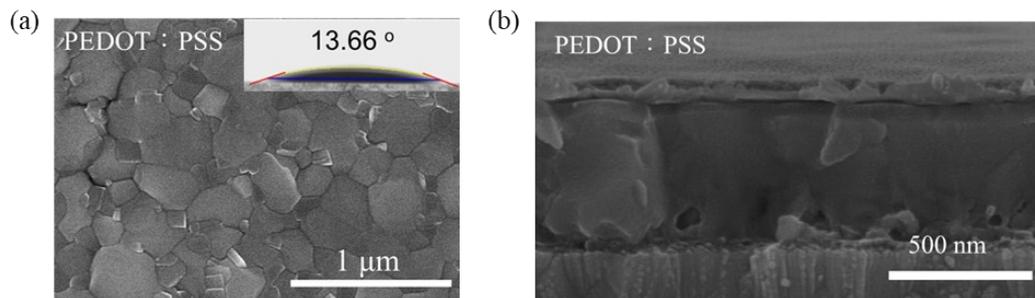
Conducting glass substrate, Indium tin oxide (ITO), the surface was cleaned in an ultrasonic cleaner using detergent, deionized water, acetone, and isopropanol sequentially every 20 min and at 110 °C for 1 hr. Then, the substrates were dried, treated with ultraviolet ozone (UV-ozone) for 15 min, and transferred to a glovebox. Inside the N<sub>2</sub>-filled glovebox, the chlorobenzene solutions of HTM **BP21** (conc. 1 mg/mL) and **BPZ23** (conc. 1 mg/mL) were prepared, and 50 µL/cell solution were spin-coated on the ITO substrates at a rate of 3000 rpm for 30 s and then were annealed at 110 °C for 30 min. For HTM **PEDOT:PSS**, its stock solution was first filtered through a 0.2 µm PVDF and then spin-coated on the ITO at 3500 rpm for 40 s and heated at 110 °C for 30 min before transferring to the glove box. The MAPb(I<sub>0.9</sub>Cl<sub>0.1</sub>)<sub>3</sub> solution used was prepared by mixing MAI (206.65 mg), PbI<sub>2</sub> (509.52 mg), and PbCl<sub>2</sub> (54.23 mg) in 1000 µL of DMF: DMSO (885:115) mixed solvent and stirred at 70 °C inside the N<sub>2</sub>-filled glove box. The above-prepared perovskite solution (50 µL) was then spin-coated on the HTM layers at the rate of 2700 rpm for 50 s, and 200 µL of toluene was dropped on the perovskite layer at 35 s before the end. While for the gas-assisted method, a 5 psi N<sub>2</sub> gas stream was blown through the film after dropping antisolvent and kept for 30 s. The films were annealed at 60 °C for 5 min and 100 °C for 3 min. After cooling, 50 µL of [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM, 20 mg mL<sup>-1</sup> in chlorobenzene) filtered through a 0.45 µm PTFE, was spin-coated at 2000 rpm for 40 s and annealed at 90 °C for 5 min. Later, the film was cooled, and 60 µL of BCP (0.5 mg mL<sup>-1</sup> in IPA) was spin-coated at 4000 rpm for 50 s. Finally, an Ag electrode (100 nm thick) was deposited by thermal evaporation in a vacuum deposition chamber with a 10<sup>-7</sup> torr pressure.

## Device characterizations:

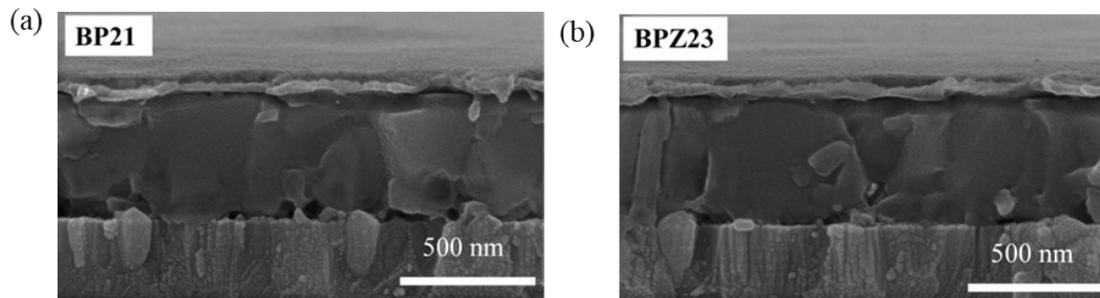
Keithley 2400 measurement source units were used in a glovebox with devices kept at room temperature to measure J-V characteristics. A calibrated solar simulator (Class 3A, SS-F5-ABA, Enli Technology) was used for photovoltaic testing at  $100 \text{ mW cm}^{-2}$ . To calibrate the light intensity, a standard photovoltaic reference cell was used (SRC-2020 series, Enli Technology). In addition, Enli Technology's software was used to modify the light intensity test (IVS-KA6000). The EQE spectrum was measured using Enli Technology's QE-R Model.



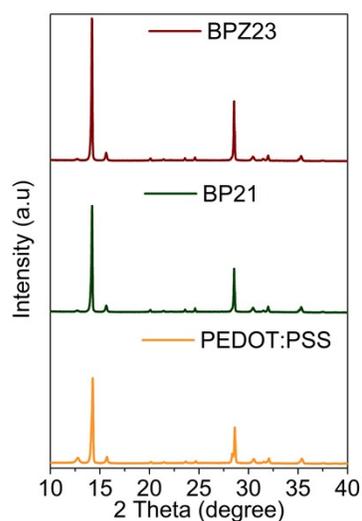
**Figure S1.** DSC curves of (a) **BP21** and (b) **BPZ23**. (c) UV-vis absorption spectra of HTM **BP21** and **BPZ23** in CH<sub>2</sub>Cl<sub>2</sub> solutions.



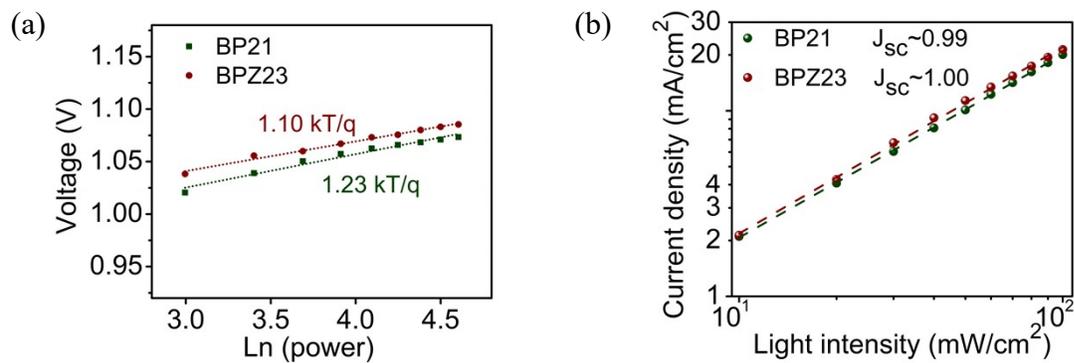
**Figure S2.** (a) Scanning electron microscopy (SEM) top-view image, with inset water contact angle, of **PEDOT:PSS** film (b) Cross-section SEM image of the PSC device based on HTM **PEDOT:PSS**.



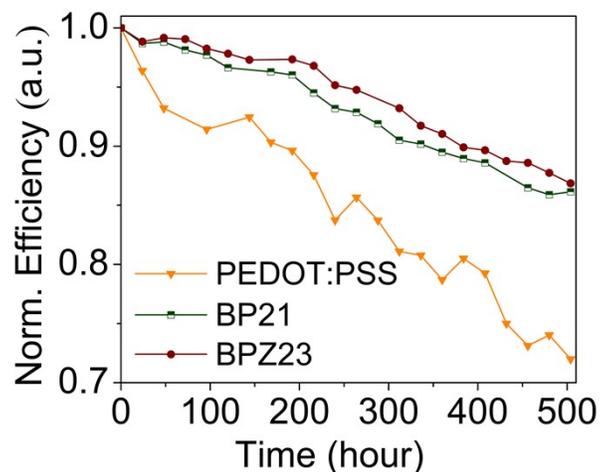
**Figure S3.** Cross-section SEM image of the PSC device based on (a) **BP21** and (b) **BPZ23**.



**Figure S4.** XRD of perovskite layers on different HTMs.



**Figure S5.** (a)  $V_{OC}$  and (b)  $J_{SC}$  as function of light intensity of the perovskite layer growth on top of **BP21** and **BPZ23**.



**Figure S6.** The stability testings of the PSCs incorporated with **PEDOT:PSS**, **BP21** and **BPZ23** measured under ambient conditions.

**Table S1.** The detailed parameters of PL obtained by fitting the TRPL of **PEDOT:PSS**, **BP21**, and **BPZ23**.

HTMs	$\tau_1$	$A_1$	$\tau_2$	$A_2$	$\tau_{Average}$
ITO	2.0363	4665.19	11.1796	4806.94	6.676365
<b>PEDOT:PSS</b>	1.33	3311.57	8.9557	5640.98	6.134935
<b>BP21</b>	1.2836	3501.31	7.3153	5503.34	4.969973
<b>BPZ23</b>	1.1372	3858.58	6.4639	5462.72	4.258897

**Table S2.** The average efficiency performance of the PSCs with forward scan and based on **PEDOT:PSS**, **BP21**, and **BPZ23**.

<b>HTM</b>	<b>Scan</b>	<b>VOC</b> [V]	<b>JSC</b> [mA cm <sup>2</sup> ]	<b>FF</b>	<b>η</b> [%]
<b>PEDOT:PSS</b>	Forward	0.95 ± 0.02	18.89 ± 0.65	75.57 ± 1.9 0	13.62 ± 0.4 7
	Reverse	0.95 ± 0.02	18.77 ± 0.63	75.39 ± 2.5 2	13.50 ± 0.5 0
<b>BP21</b>	Forward	1.06 ± 0.01	20.51 ± 0.99	75.71 ± 1.9 5	16.42 ± 0.6 3
	Reverse	1.07 ± 0.01	20.27 ± 0.90	76.51 ± 4.4 7	16.62 ± 1.0 3
<b>BPZ23</b>	Forward	1.08 ± 0.02	22.14 ± 0.69	78.51 ± 1.8 9	18.86 ± 0.5 0
	Reverse	1.08 ± 0.01	22.06 ± 0.70	77.19 ± 3.7 7	18.51 ± 0.9 4