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Electronic Supplementary Information

Heterocyclic D-A-D Hole-transporting Material for High-performance Inverted Perovskite Solar Cells

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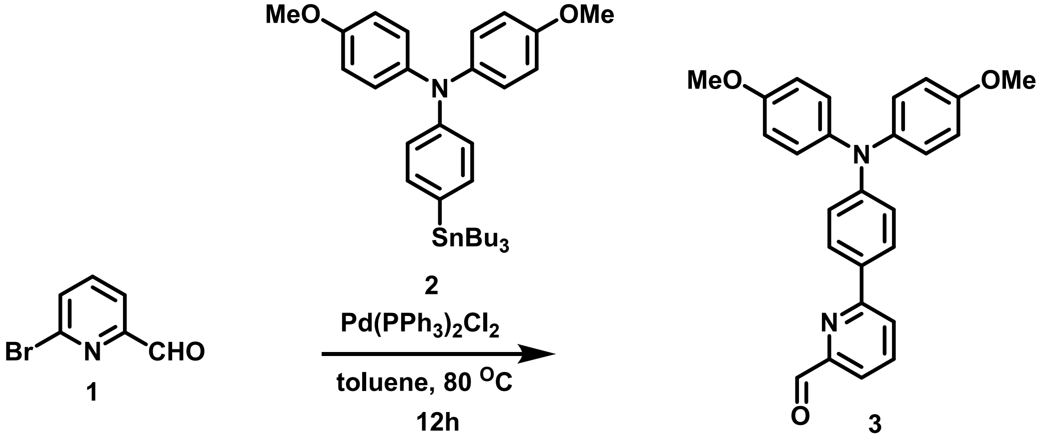
Experimental section

Materials:

Unless otherwise specified, all chemical reagents were obtained from Aldrich, Alfa, and TCI Chemical Co. and used in their original form. The reaction solvents (THF, CH_2Cl_2, and DMF) were dried (VAC 103991, Vacuum Atmospheres). All air-sensitive reactions were carried out in an Argon atmosphere. A silica gel (Scharlau 60, 230-240 mesh) was used for flash chromatography. Thin-layer chromatography (TLC) was used to monitor reaction progress using aluminum-coated Merck Kieselgel 60 F254 plates developed with I_2 or UV light. All intermediates and final products were analyzed using ^{1}H and ^{13}C NMR spectra obtained by Bruker Avance 300 or 500 MHz spectrometer. Chemical shifts (δ) and coupling constants (J) are expressed in Hz and ppm, respectively. Multiplicities were reported as: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, b = broad. Bruker Daltonics flex Analysis spectrometer was used to record mass spectra matrix-assisted Laser desorption ionization (coupled to a Time-of-Flight analyzer) experiments (MALDI-TOF). CV experiments were conducted using a CHI 627C electrochemical setup that included a glassy carbon electrode as the working electrode, a silver wire (Ag/$AgNO_3$ in acetonitrile) as the reference electrode, a Pt wire as the counter-electrode, and 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The cyclic voltammogram of **WWC106** was typically recorded at a scan rate of 50 mVs^{-1}. Following the measurement, ferrocene was used as an internal reference for calibration. Thermogravimetric analysis (TGA) was performed using a TA Instruments TGAQ500 with a ramp rate of 10 °C/min under N_2 from 100 to 600 °C. DSC was completed using a Discovery DSC from TA instruments. Two cycles were recorded under nitrogen, heating (up to 400 °C) and cooling (50 °C) at a scanning rate of 10 °C/min. A Shimadzu UV3600 UV-vis-NIR spectrophotometer was used to examine the films' optical characteristics. Scanning electron microscopy (SEM, Hitachi SU4800) and X-ray diffraction (XRD, BRUKER ECO D8 series) were used to examine the morphology of the perovskite films. A Spectrofluorometer (FS5, Edinburgh instruments) was used to measure time-resolved PL spectra with the PL excitation set to 405 nm. The contact angle was measured using a Phoenix

300 from Surface Electro-Optics (SEO) Co., Ltd and de-ionized water as the solvent. XPS measurements were done on an JEOL (JPS-9030) instrument.

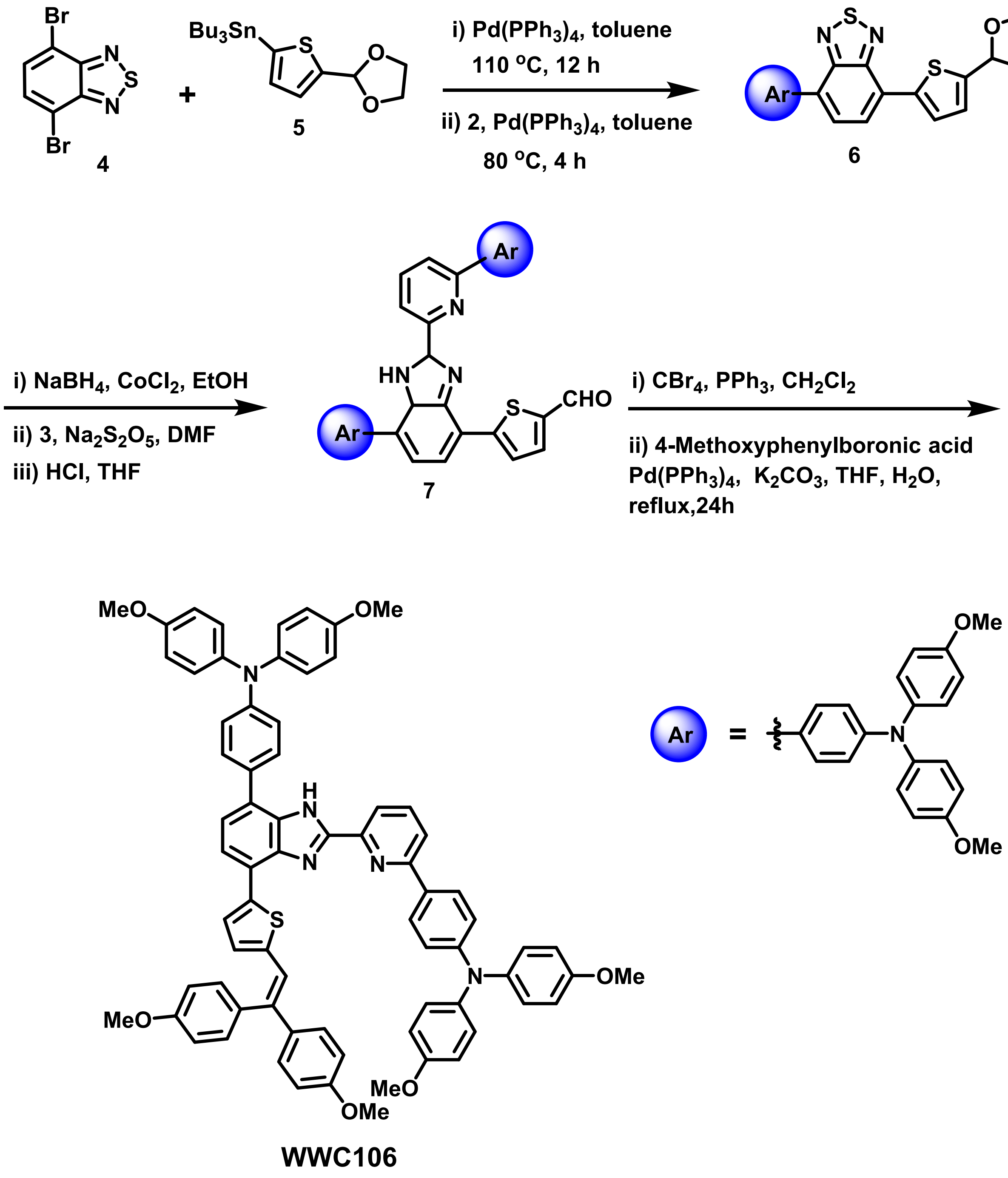
Synthetic Procedures:



Scheme 1. Synthesis of intermediate **3**.

Synthesis of 6-(4-(bis(4-methoxyphenyl)amino)phenyl)picolinaldehyde (3)

A toluene mixture of pyridyl aldehyde **1** (1.5 g, 8.06 mmol), 4-methoxy-N-(4-methoxyphenyl)-N-(4-(tributylstannyl)phenyl)aniline **2** (5.75 g, 9.67 mmol), and $Pd(PPh_3)_4$ (233 mg, 0.201 mmol) was stirred overnight at 80 ^oC under argon. After the reaction, the mixture was filtered through celite, and the solvent was removed under pressure. The residue was purified by flash column chromatography on SiO_2 using (ethyl acetate/Hexane = 10%) as eluant to get compound **3** as bright yellow solid (2.2 g, yield: 66.2%). ^1H NMR (300 MHz, DMSO-d_6, ppm): δ 10.01(s, 1H), 8.11 (d, 2H, J = 7.7 Hz), 8.03 (t, 1H, J = 7.7 Hz), 7.99 (d, 2H, J = 8.8 Hz), 7.77 (d, 1H, J = 7.35 Hz), 7.10 (d, 4H, J = 8.85 Hz), 6.95 (d, 4H, J = 8.9 Hz), 6.84 (d, 2H, J = 8.85 Hz), 3.76 (s, 6H). ^{13}C NMR (125 MHz, DMSO-d_6, ppm): δ 193.9, 156.6, 156.2, 152.1, 149.8, 139.4, 138.4, 128.4, 127.7, 127.3, 123.5, 119.0, 118.1, 115.0, 55.2. (HRMS (EIS) m/z calculated for $C_{26}H_{23}N_2O_3$ $[M+H]^+$: 411.170319, found: 411.128256.



Scheme 2. Synthesis of final HTM **WWC106**.

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 (6): Compound **4** (2.0 g, 6.8 mmol), compound **5** (3.63 g, 8.16 mmol), and $Pd(PPh_3)_2Cl_2$ (0.38 g, 0.54 mmol) were dissolved in THF (68mL) in a 250 mL round-bottomed flask. For 4 hours, the reaction mixture was stirred at 60 ^{o}C in an argon atmosphere. After the reaction was completed, the mixture was filtered through celite, and the solvent was removed under reduced pressure. The resulting residue was mixed in toluene (10 mL) with compound **2** (2.9 g, 4.87 mmol) and $Pd(PPh_3)_2Cl_2$ and heated at 80 ^{o}C for 4 hours in an argon atmosphere. The reaction was monitored using basic TLC (CH_2Cl_2/Hexane = 40%). After completion of the reaction, the mixture was filtered through celite, and the solvent was reduced under pressure. The resulting residue was purified using gradient column chromatography on SiO_2 with (CH_2Cl_2/Hexane) as the eluant to get compound **6** as a red solid (1.68 g, yield: 87%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.01 (d, 1H, J = 3.7 Hz), 7.92 (d, 1H, 7.6 Hz), 7.84 (d, 2H, J = 8.75 Hz), 7.69 (d, 1H, J = 7.4 Hz), 7.28 (d, 1H, J = 3.85 Hz), 7.17 (d, 4H, J = 8.95 Hz), 7.07 (d, 2H, J = 8.8 Hz), 6.89 (d, 4H, J = 8.95 Hz), 6.21 (s, 1H), 4.24-4.21 (m, 2H), 4.11-4.08 (m, 2H), 3.84 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 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 $C_{33}H_{27}N_3O_4S_2$ $[M]^+$: 593.1437, found: 593.1439)

Synthesis of 5-(7-(4-(bis(4-methoxyphenyl)amino)phenyl)-2-(6-(4-(bis(4-methoxyphenyl)amino)phenyl)pyridin-2-yl)-1H-benzo[d]imidazol-4-yl)thiophene-2-carbaldehyde (7): Compound **6** (1.68 g, 1.7 mmol) was dissolved in a mixture of ethanol (83 mL) and dichloromethane (94 mL) solvents in a 250mL round-bottom flask, and the reaction was degassed with argon. Next, sodium borohydride (4.36 g, 67.3 mmol) and cobalt dichloride (0.36

g, 1.7 mmol) were added to the above mixture (the bubbles produced are flushed out with argon gas) and stirred for 2 hours at 40 ^oC. The reaction was being 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. Next, DMF (20 mL, 0.2 M) was used to dissolve the solid, and compound **3** (1.09 g, 2.43 mmol) and $Na_2S_2O_5$ (0.50 g, 2.47 mmol) was added. At 50 ^oC, the reaction mixture was stirred for 2 hours, monitoring the reaction by TLC (CH_2Cl_2/Hexane = 50%). The reaction mixture was concentrated under reduced pressure, and the residue was extracted with dichloromethane, washed with water, and dried over $MgSO_4$. The solvent was removed, and the yellow solid obtained was dissolved in THF and treated with a 3 M aqueous hydrochloric acid solution at room temperature. After the solid precipitate has completely disappeared, the solution was concentrated under reduced pressure, and the residue was extracted with dichloromethane, while the organic layer was washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the obtained crude product was subjected to column chromatography (CH_2Cl_2/Hexane = 30%) to obtain compound **7** as an orange solid. (1.34 g, yield: 52%).^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 12.70 (s, 1H), 9.97 (s, 1H), 8.33 (d, 1H, J = 3.85 Hz), 8.30 (d, 1H, J = 7.85 Hz), 8.16 (d, 2H, J = 8.6 Hz), 8.05 (t, 1H, J = 15.55 Hz), 7.96 (d, 1H, J = 7.85 Hz), 7.89 (d, 1H, J = 7.75 Hz), 7.59 (d, 2H, J = 8.3 Hz), 7.34 (d, 1H, J = 7.85 Hz), 7.13~7.09 (m, 4H), 6.97~6.92(m, 4H), 6.89 (d, 2H, J = 8.86 Hz), 6.85 (d, 2H, J = 8.8 Hz), 3.76 (d, 12H, J = 2.95Hz). ; ^{13}C NMR (125 MHz, DMSO-d_6, ppm): δ 184.62, 157.90, 156.53, 156.01, 154.51, 152.79, 150.13, 148.83, 148.40, 142.72, 141.88, 140.33, 138.89, 138.74, 137.87, 133.40, 129.71, 129.13, 128.05, 127.55, 127.06, 124.36, 123.93, 123.07, 121.86, 121.28, 119.46, 115.56, 55.78, 24.73. (HRMS (MOLDI) m/z calculated for $C_{57}H_{45}N_5O_5S$ $[M]^+$: 911.3141, found: 911.3136.

Synthesis of final HTM WWC106: In another round bottom flask, carbon tetrabromide (0.2 g, 0.86 mmol) and triphenylphosphine (0.45 g, 1.71 mmol) were dissolved in dichloromethane and placed in an ice bath under an argon atmosphere for 10 minutes. Both the above mixtures were mixed together and stirred for 10 minutes. The temperature was brought to room temperature, and stirring was continued for 3 hours. Following the completion of the reaction, the solid was filtered, and the filtrate was dried and mixed with K_2CO_3 (68 mg, 0.4 mmol), THF (0.55 mL, 0.15 M) and H_2O (0.49 mL, 1M). 4-methoxyphenylboronic acid (31.1 mg, 0.2 mmol) was added and the reaction was purged three times with argon. $Pd(PPh_3)_4$ (5mg, 0.0004 mmol) was quickly added to the reaction, and mixture was refluxed for 24 hours. Following the completion of the reaction, the mixture was filtered through celite and the solvent was reduced under pressure to yield a yellow solid product **WWC106**. (70 mg, yield: 55.7%).^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 12.36(s, 1H), 8.14(d, 2H, J = 9Hz), 8.07(d, 1H, J = 7Hz), 7.97(d, 1H, J = 7.21), 7.94(d, 1H, J = 7.7), 7.53(d, 2H, J =8.5), 7.44(d, 2H, J =7.3), 7.37(s, 1H), 7.25(d, 2H, J = 8.4), 7.21(d, 2H, J =8.0), 7.15(d, 2H, J =9.0), 7.09(d, 10H, J =8.2), 6.96-6.87(m, 12H), 3.75(s, 18H) ; ^{13}C NMR (125 MHz, DMSO-d_6, ppm): δ 156.45, 152.15, 149.97, 148.53, 148.45, 141.97, 140.66, 140.52, 140.38, 140.18, 140.01, 138.55, 134.90, 133.10, 131.76, 131.54, 130.38, 129.98, 129.93, 129.57, 129.33, 128.61, 128.21, 128.04, 127.64, 127.48, 127.34, 125.59, 125.48, 123.69, 123.61, 120.54, 120.23, 120.05, 119.54, 119.39, 118.59, 115.49, 114.31, 55.74. (HRMS (MOLDI) m/z calculated for $C_{72}H_{59}N_5O_6S$ $[M]^+$: 1121.4186, found: 1121.4181.

Table S1: Electrochemical properties of **WWC106** HTM.

HTM	λ_{onset} (nm)	E_g (eV)	E_{onset}^{ox} (eV)	E_{HOMO} (eV)[a]	E_{LUMO} (eV)[b]	Hole-mobility (10^{-4} cm^2 v^{-1} s^{-1})[c]
WWC106	485	2.56	0.387	-5.34	-2.78	3.58

[a] $TBAPF_6$ (0.1 M) was used as electrolyte in DCM. Potential vs. ferrocene/ferrocenium redox couple. $E_{HOMO} = -5.1 - (E_{onset}^{ox} - E_{onset}^{Fc})$. [b] $E_{LUMO} = E_{HOMO} + E_g$. [c] $\mu = J \times 8/9 \times d^3 V^2 \times 1/\varepsilon_0\varepsilon_r$ (Where, ***J*** is current = 26.25 mA/cm^2; ***d*** is the thickness of the HTM layer = 49 nm; $\boldsymbol{\varepsilon_0}$ is the permittivity of free space = 8.854 x 10^{-4} F/cm; $\boldsymbol{\varepsilon_r}$ is the relative permittivity of the material = 3; ***V*** is the effective voltage = 0.17 V.)

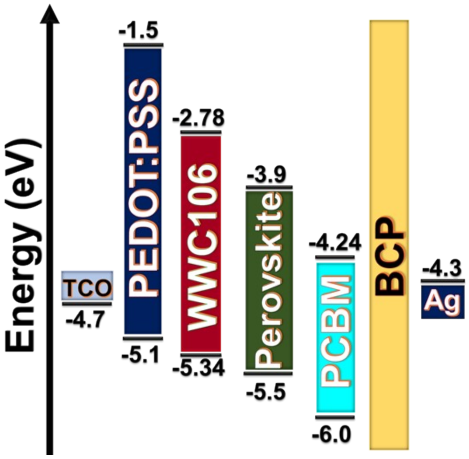


Figure S1. Energy levels of the PSC device in this study.

Device fabrication and characterizations: The fluoride-dope tin oxide (FTO) conducting glass substrates was cleaned in an ultrasonic cleaner for 15 minutes, each with detergent, deionized water, acetone, and isopropanol. The cleaned substrates was then exposed to UV-ozone for 15 minutes before moving to a glovebox. Inside the N_2-filled glovebox, anhydrous chlorobenzene solvent was used to make **WWC106** solutions (conc. 1 mg/mL). The solutions were spin-coated at 4000 rpm for 30 seconds on the FTO substrates before being annealed at 100 °C for 10 minutes. The **PEDOT:PSS** stock solution was filtered through a 0.22 m PVDF filter before being spin-coated on the FTO at 5000 rpm for 30 seconds and heated at 120 °C for 20 minutes before being transferred the glovebox. To make the mixed cation perovskite solution, MAI (206.65 mg), PbI_2 (509.42 mg), and $PbCl_2$ (54.23 mg) were mixed in DMF:DMSO (4:1) and stirred at 50 °C inside the N_2-filled glove box. The perovskite thin films were produced using the anti-solvent process. Generally, the prepared perovskite solution (80 µL) was then spin-coated in two steps at 1000 and 6000 rpm for 10 and 20 s, respectively. 200 µL of chlorobenzene was dropped on the perovskite layer in the last 5 s of the procedure. The resulting perovskite film turned transparent brown after applied anti-solvent, which turned darker after annealing at 100 °C for 1 hour in a nitrogen-filled glove box. After cooling down, 50 µL of [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM, 20 mg mL^{-1} in chlorobenzene) was filtered through a 0.45 µm PTFE and spin-coated at 1000 rpm for 60 s before drying for 30 minutes. A ~3 nm thick finishing bathocuproine (BCP) layer was vapor-deposited on top of the PCBM layer. Finally, a 100 nm thick Ag electrode was deposited by thermal evaporation in a vacuum deposition chamber with 10^{-7} torr pressure. The *J-V* characteristics were determined in a glovebox using Keithley 2400 measurement source units kept at room temperature. The photovoltaic testing was carried out using a calibrated solar simulator (Class 3A, SS-F5-3A, Enli Technology) at 100 mW cm^{-2} and a shadow mask of 0.24 cm^2. The light intensity was calibrated with a standard photovoltaic reference cell (SRC-2020 series, Enli Technology). The light intensity test was changed through the software (IVS-KA6000) from Enli Technology. The EQE spectrum was measured using a QE-R Model of Enli Technology.

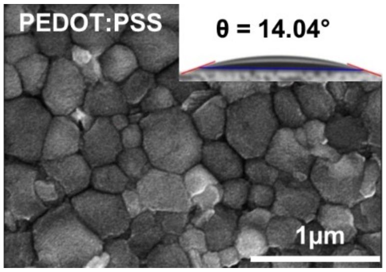


Figure S2. SEM characterizations for surface views of perovskites layer with **PEDOT:PSS**. The inlet in the surface SEM images is the contact angles of **PEDOT:PSS**.

Table S2. FWHM values of **PEDOT:PSS** and **WWC106**.

HTM	2θ	Standard deviation	Diffraction intensity
PEDOT:PSS	13.3	0.86	9623
WWC106	14.15	0.97	11121

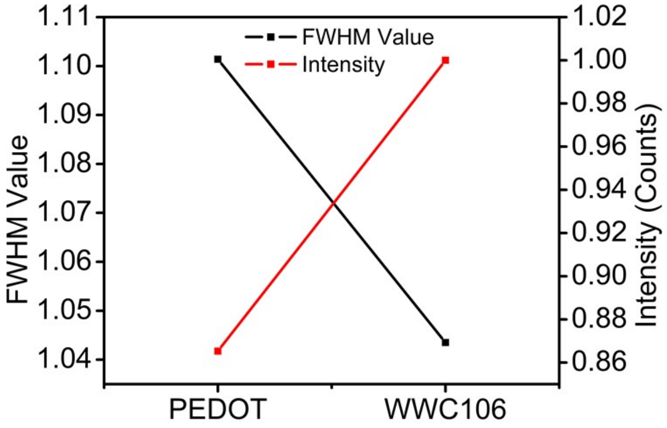


Figure S3. FWHM of dominant peaks of **PEDOT:PSS** and **WWC106**.

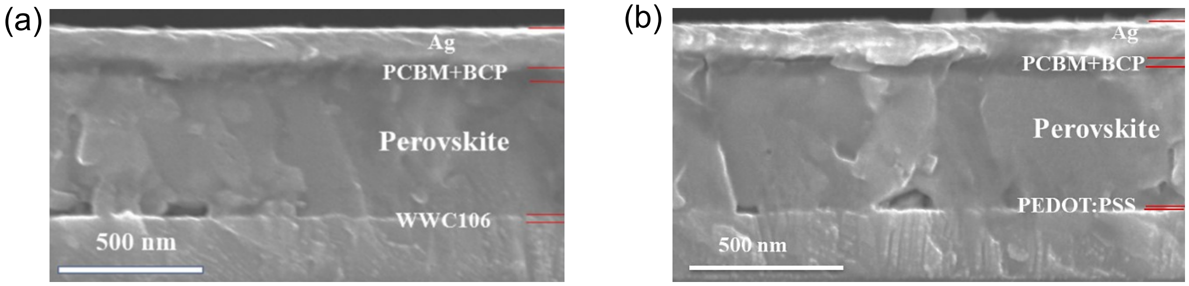


Figure S4. SEM cross-sectional view of perovskites devices with (a) **WWC106** and (b) **PEDOT:PSS** HTMs.

Table S3. The detailed parameters of PL obtained by fitting the TRPL of **PEDOT:PSS** and **WWC106**.

HTMs	τ_1	A_1	τ_2	A_2	$\tau_{averege}$[a]
PEDOT:PSS	1.15	6810	4.3	3333	2.19
WWC106	0.58	6564	2.4	3314	1.19

[a] Average lifetime is calculated according to the equation of $\tau_{average} = (A_1\tau_1^2+A_2\tau_2^2)/(A_1\tau_1+A_2\tau_2)$

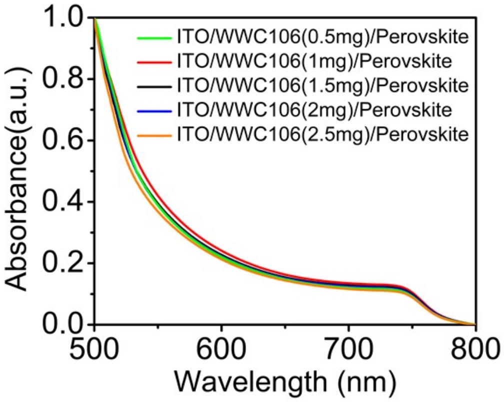


Figure S5. Absorption spectra of perovskite films deposited on top of **WWC106** films with different concentrations.

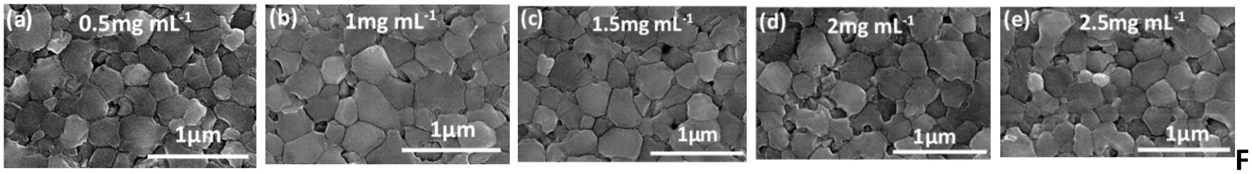


Figure S6. SEM top-views of perovskite on top of **WWC106** films with different concentrations.

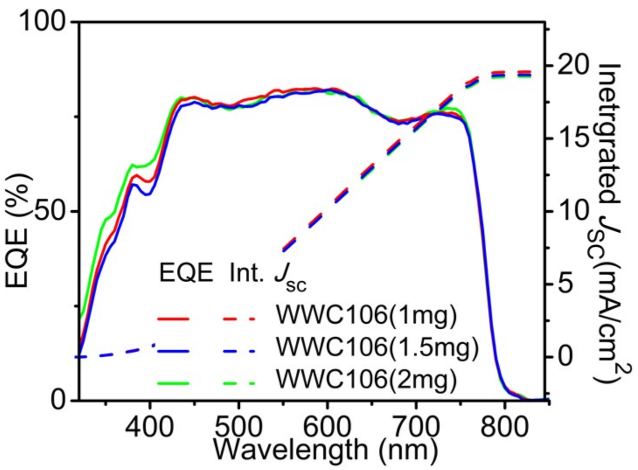


Figure S7. EQE spectra with integrated J_{SC} of the PSCs with different concentrations of **WWC106**.

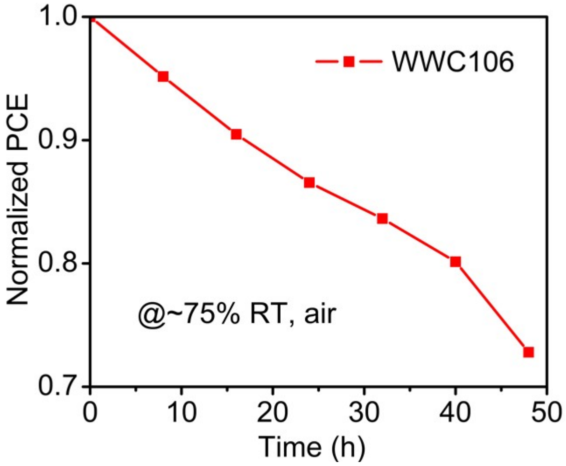


Figure S8. Humidity stability test result of **WWC106** with a relative humidity of 75% at RT in the air under interior lighting.