Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting Information

Thienoimidazole-pyridine based small molecule hole transport materials for dopant-free, efficient inverted perovskite solar cells

Suri Babu Akula[a], Yogesh S. Tingare[b,*], Chaochin Su[b,*], Chen-Yun Hsu[a], Hong-Jia Lin[b], Chien-Hsiang Lin[a], Mu-Yi Lin[b], Ja-Hon Lin[c], Zhi-Ting Wu[b], Chong-Wei Wu[b], Chi-Ruei Guo[a], Wen-Ren Li[a,*]

[a]Department of Chemistry, National Central University, Zhongli 32001, Taiwan.

[b]Institute of Organic and Polymeric Materials/Research and Development Center for Smart Textile Technology, National Taipei University of Technology, Taipei 106344, Taiwan.

[c]Department of Electro-Optical Engineering, National Taipei University of Technology, Taipei 106344, Taiwan.

*Corresponding Author.

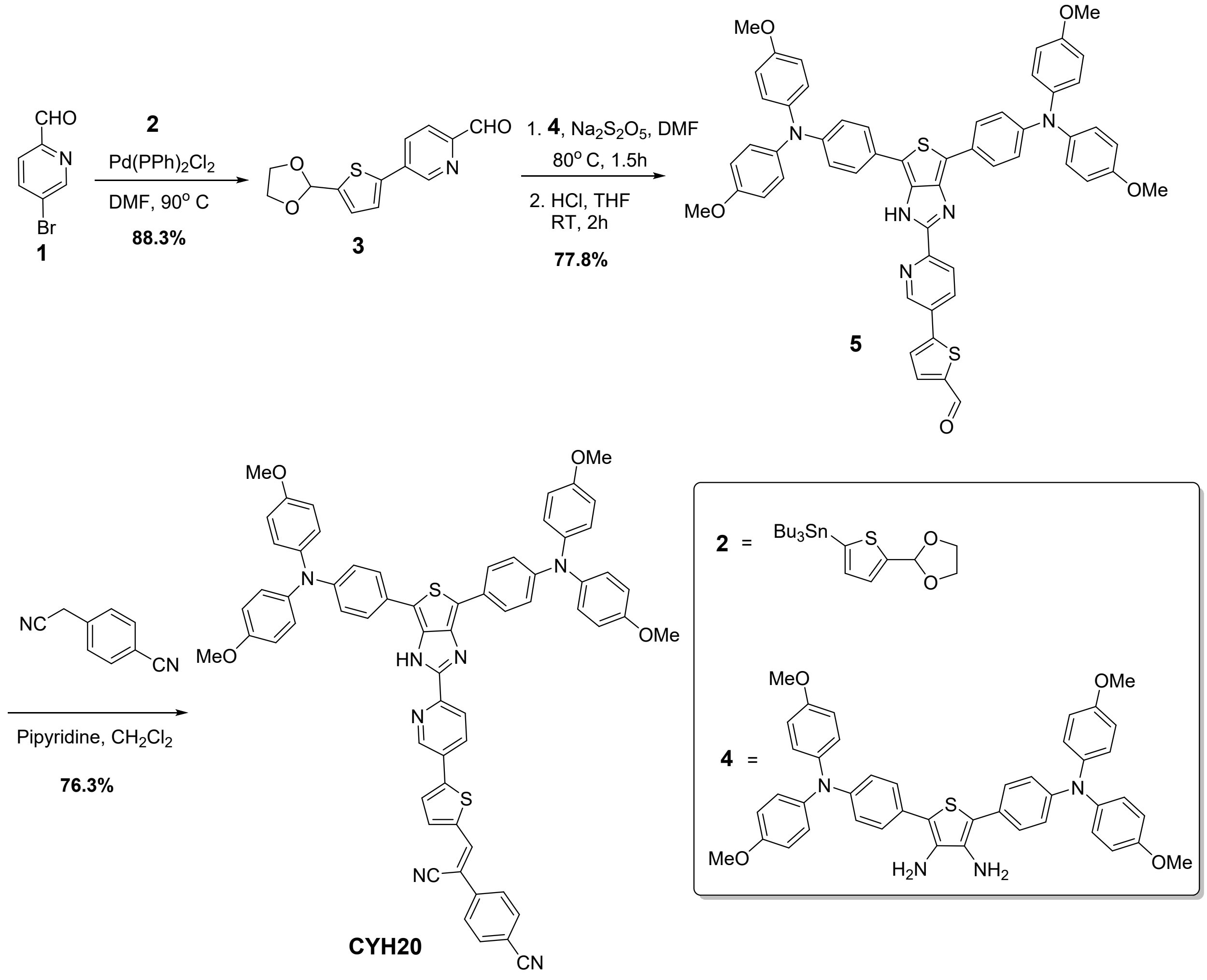
E-mail Address: f12098@ntut.edu.tw (Y.S.Tingare), f10913@mail.ntut.edu.tw (C. Su), ch01@ncu.edu.tw (W.R. Li)

Experimental section

Materials:

All chemical reagents, unless stated otherwise, were purchased commercially from Aldrich, Alfa, and TCI Chemical Company. The solvents (THF, CH_2Cl_2, and DMF) were dried with a VAC purifier (VAC 103991, Vacuum Atmospheres) before being used in air-sensitive processes under an argon atmosphere. The progress of all reactions was closely monitored using thin-layer chromatography on aluminum-coated Merck Kieselgel 60 F254 plates, visualized with I_2 or UV light to ensure the accuracy of our results. The crude chemicals were purified by flash chromatography with silica gel (Scharlau 60, 230-240 mesh). The compounds were characterized using ^1H and ^{13}C NMR, as well as mass spectra obtained with a Bruker Avance 500 MHz spectrometer, Bruker Daltonics Flex Analysis spectrometer, and matrix-assisted laser desorption ionization (MALDI-TOF) investigations. Thermogravimetric analysis (TGA) was carried out using a TA Instruments TGAQ500 at a 10 °C/min ramp rate under N2 from 100 to 600°C. DSC was performed on a Discovery DSC from TA instruments, with two cycles recorded under nitrogen, heating (up to 400 °C), and cooling (50 °C) at a scanning rate of 10 °C/min. The solutions' optical characteristics were examined using a Shimadzu UV3600 UV-vis-NIR spectrophotometer. Cyclic voltammograms of **CHY20** and **CHY23** were recorded using cyclic voltammetry (CV) experiments with a CHI 627C electrochemical setup. The setup 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 at 50 mVs^{-1} 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 **CYH20**.

Synthesis of 5-(5-(1,3-dioxolan-2-yl)thiophen-2-yl)picolinaldehyde (3):

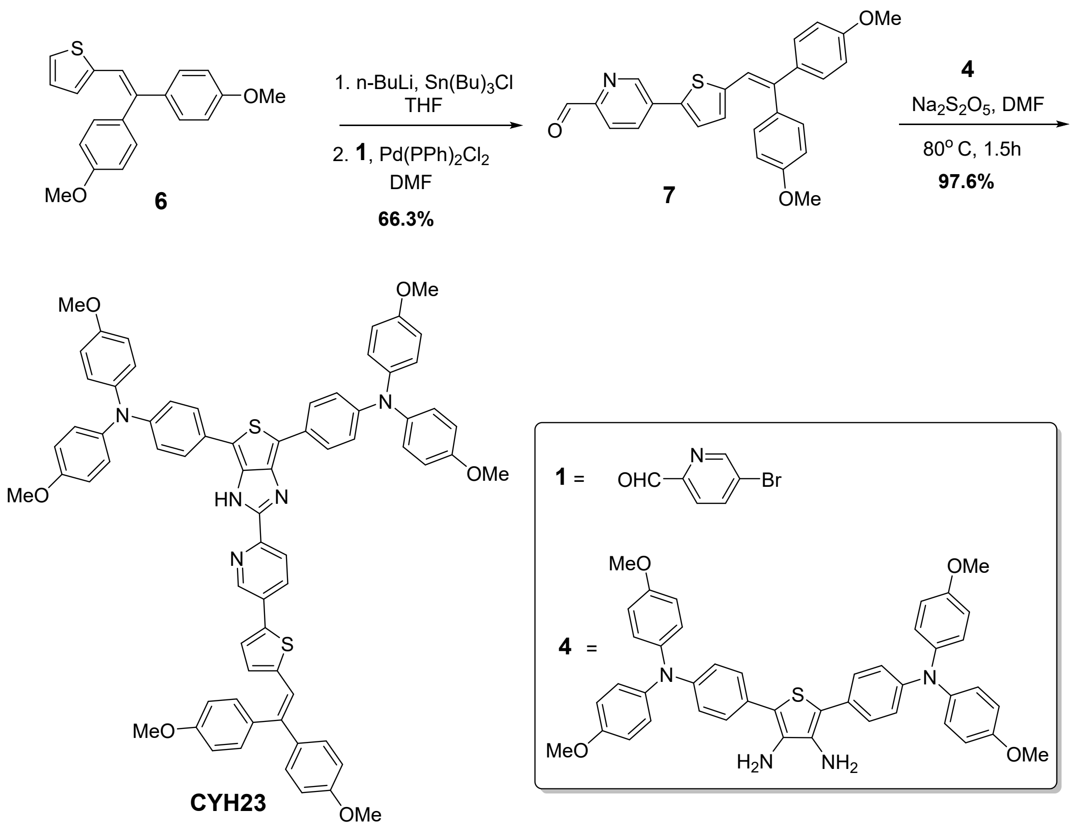
In a 5 mL round-bottomed flask, 5-bromopicolinaldehyde (**1**) (0.1g, 0.54mmol), (5-(1,3-dioxolan-2-yl)thiophen-2-yl)tributylstannane (**2**) (0.263g, 0.59mmol), and $Pd(PPh_3)_2Cl_2$ (0.026g, 0.07mmol) were dissolved in DMF (2.7 mL). The reaction mixture was stirred at 90 °C in an argon atmosphere for 1h. After the reaction was completed, the mixture was filtered through celite, and the solvent was removed under reduced pressure. Finally, the crude residue was purified using gradient column chromatography on SiO_2 with (Ethyl acetate/Hexane = 30%) as the eluant, yielding compound **3** as a light yellow (0.124g, 88.3%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.97 (s, 1H), 9.15 (d, *J* = 1.8 Hz, 1H), 8.28 (dd, *J* = 2 Hz, *J* = 8.1 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 3.8 Hz, 1H), 7.33 (d, *J* = 3.7 Hz, 1H), 6.09 (s, 1H), 4.08~4.03 (m, 2H), 4.00~3.96 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.8, 151.0, 146.5, 144.4, 139.0, 133.4, 133.4, 128.4, 126.7, 122.2, 98.9, 64.8; HRMS (MALDI-TOF) *m/z* calcd for $C_{13}H_{11}NO_3S$ $[M]^+$ 261.0460, found: 261.0454.

Synthesis of 5-(6-(4,6-bis(4-(bis(4-methoxyphenyl)amino)phenyl)-1H-thieno[3,4-d]imidazol-2-yl)pyridin-3-yl)thiophene-2-carbaldehyde (5):

In a 5 mL round-bottomed flask, **3** (0.142g, 0.54mmol), 2,5-bis(4-(bis(4-methoxyphenyl)amino)phenyl)thiophene-3,4-diamine (**4**) (0.392g, 0.54mmol), and sodium metabisulfite (0.155g, 0.81mmol) were dissolved in DMF (2.7 mL). The reaction was monitored using a 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. Next, the solid obtained was dissolved in THF and treated with a 3 M aqueous hydrochloric acid solution at room temperature. After the reaction was completed, 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 (Ethyl acetate/Hexane = 40%) to obtain compound **5** as a dark brown solid (0.407g, 77.8%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.62 (s, 1H), 9.96 (s, 1H), 9.14 (s, 1H), 8.42~8.36 (m, 2H), 8.12 (d, *J* =3.8 Hz, 1H), 8.00 (d, *J* =3.6 Hz, 1H), 7.89 (d, *J* = 7.55 Hz, 2H), 7.65 (d, *J* = 7.3 Hz, 2H), 7.04 (d, *J* = 7.85 Hz, 8H), 6.92 (d, *J* = 8.35 Hz, 8H), 6.86~6.8 (m, 4H), 3.75 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.57, 160.32, 156.17, 149.07, 148.39, 147.21, 146.97, 146.82, 143.79, 140.48, 139.28, 135.24, 134.87, 129.94, 127.59, 126.90, 126.58, 125.30, 123.04, 120.40, 115.42, 55.73. HRMS (MALDI-TOF) *m/z* calcd for $C_{55}H_{43}N_5O_5S_2$ [M] $^+$ 917.2706, found: 917.2700.

Synthesis of HTM CYH20:

Compound **5** (0.03g, 0.033mmol) and 4-cynophenylacetonitrile (0.0056g, 0.036mmol) were dissolved in CH_2Cl_2 (0.163mL, 0.2M) in the 25mL round bottom. Piperidine (0.0071mL, 0.072 mmol) was added to the above mixture and refluxed for 8h. After completion of the reaction, the solvent was reduced under pressure, and the residue was extracted with CH_2Cl_2 and a 5% $HCl_{(aq)}$ solution. 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 (Ethylacetate/Hexane = 50%) to yield a solid dark yellow-green product, **CYH20**. ^{1}H NMR (500 MHz, $CDCl_3$, 298K) δ 9.79 (s, 1H), 8.90, (s, 1H), 8.43 (d, *J* = 6.7 Hz, 1H), 8.05 (d, *J* = 6.1 Hz, 1H), 7.93 (s, 2H), 7.77-7.72 (m, 5H), 7.68 (d, *J* = 3.2 Hz, 1H), 7.51 (d, *J* = 4.0 Hz, 1H), 7.38 (s, 2H), 7.09 (d, *J* =7.7 Hz, 8H), 7.00, (d, J = 7.5 Hz, 4H), 6.85 (t, J = 5.3 Hz, 8H), 3.81 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, 298K) δ 156.0, 147.6, 146.9, 145.8, 145.3, 140.8, 140.5, 137.8, 137.7, 135.7, 135.6, 133.3, 132.7, 129.7, 126.7, 126.6, 126.2, 125.9, 125.6, 125.0, 123.1, 122.0, 120.8, 118.3, 117.2, 114.8, 112.2, 106.2, 55.6. HRMS (MALDI-TOF, m/z): calculated for = $C_{64}H_{47}N_7O_4S_2$, $[M]^+$ = 1041.3125, found: 1041.3125.



Scheme 2. Synthesis of final HTM **CYH23**.

Synthesis of 5-(5-(2,2-bis(4-methoxyphenyl)vinyl)thiophen-2-yl)picolinaldehyde (7):

To a solution of 2-(2,2-bis(4-methoxyphenyl)vinyl)thiophene (**3**) (0.5g, 1.55 mmol) in dry THF (3.5 mL), *n*-BuLi (2.5 M in hexane, 2.4mL, 1.86 mmol) was added dropwise at -78 °C. After stirring for 1 h, tributyltin chloride (0.442mL, 1.63 mmol) was added while stirring the solution at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. After quenching with a small amount of water, the resulting mixture was concentrated and diluted with ethyl acetate. The solution was washed with brine and water, and the aqueous phase was extracted twice with ethyl acetate. The combined organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. Next, the crude product (0.6g, 0.98 mmol), 5-bromopicolinaldehyde (**1**) (0.166g, 0.89 mmol), bis(triphenylphosphine)palladium(II) dichloride

(0.044g, 0.062 mmol) in DMF (4.45mL, 0.2M) was refluxed at 90° C under argon for 8 h. After cooling down the reaction to room temperature, the mixture was extracted with ethyl acetate and washed with water. The organic layer was collected and evaporated under reduced pressure. The crude product was purified by column chromatography (Ethyl acetate/Hexane= 30%) to obtain compound **7** (0.253g, 66.3%) as a yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.90 (s, 1H), 8.87 (d, J = 1.8 Hz, 1H), 7.93 (d, J = 1.9 Hz, J = 8.15 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.66 (d, J = 3.8 Hz, 1H), 7.38 (s, 1H), 7.26 (d, J = 8.7 Hz, 2H), 7.16~7.10 (m, 5H), 6.91 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H), 3.75 (s, 3H) ; ^{13}C NMR (125 MHz, DMSO-d_6) δ 192.6, 159.5, 159.1, 150.4, 145.9, 144.1, 140.5, 137.4, 133.6, 132.5, 131.0, 130.7, 130.5, 127.9, 126.5, 122.3, 118.6, 115.0, 113.9, 55.2, 55.2; HRMS (MALDI-TOF) *m/z* calcd for $C_{26}H_{21}NO_3S$ $[M]^+$ 427.1242, found: 427.1237.

Synthesis of HTM CYH23:

In a 5 mL round-bottomed flask, **7** (0.087g, 0.2 mmol), 2,5-bis(4-(bis(4-methoxyphenyl)amino)phenyl)thiophene-3,4-diamine (**4**) (0.146g, 0.2 mmol), and sodium metabisulfite (0.033g, 0.3 mmol) were dissolved in DMF (1.01 mL). The reaction was monitored using a 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. The crude product was purified by column chromatography (THF/Hexane= 40%) to obtain **CYH23** (0.224g, 97.6%) as a dark red solid. ^{1}H ^{1}H NMR (500 MHz, $CDCl_3$, 298K) δ 9.76 (s, 1H), 8.65 (s, 1H), 8.32 (d, J = 8.3 Hz, 1H), 7.92 (s, 2H), 7.79 (d, J = 6.2 Hz, 1H), 7.37 (s, 2H), 7.28 (d, J = 8.8 Hz, 2H), 7.23 (d, J = 3.9 Hz, 1H), 7.21 (d, J = 8.6 Hz, 2H), 7.15 (s, 1H), 7.09 (d, J = 8.2 Hz, 8H), 7.04 (d, J = 8.6 Hz, 2H), 6.99 (d, J = 7.4 Hz, 4H), 6.94 (d, J = 3.8 Hz, 1H), 6.84 (t, J = 6.8 Hz, 10H), 3.91 (s, 3H), 3.82 (s, 12H), 3.81 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 298K) δ 159.9, 159.4, 156.0, 155.8, 148.4, 146.9, 146.2, 145.6, 143.6, 140.7, 138.8, 134.6, 134.1, 132.8, 131.5, 131.3, 129.7, 128.3, 126.5, 124.2, 122.0, 121.3, 118.9, 114.9, 114.7, 113.8, 55.6, 55.5, 55.4. HRMS (MALDI-TOF, m/z): calculated for = $C_{70}H_{57}N_5O_6S_2$, $[M]^+$ = 1127.3745, found: 1127.3745.

Device fabrication:

The surface of the conducting glass substrate, indium tin oxide (ITO), was cleaned in an ultrasonic cleaner using detergent, deionized water, acetone, and isopropanol every 20 minutes for 1 hour at 110 degrees Celsius. The substrates were then dried and treated with ultraviolet ozone (UV-ozone) for 15 minutes before being transported to a glovebox. In an N_2-filled glovebox, chlorobenzene solutions of HTM **CYH20** (conc. 1 mg/mL) and **CYH23** (conc. 1 mg/mL) were produced. 50 µL/cell solution was spin-coated on ITO substrates at 3000 rpm for 30 s and then annealed at 110 °C for 30 min. The film thickness obtained for **CYH20** and **CYH23** were 2.26 nm and 2.04 nm, respectively. 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 $MAPb(I_{0.9}Cl_{0.1})_3$ solution used was prepared by mixing MAI (206.65 mg), PbI_2 (509.52 mg), and $PbCl_2$ (54.23 mg) in 1000 µL of DMF: DMSO (885:115) mixed solvent and stirred at 70 °C inside the N_2-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_2 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_{61}-butyric acid methyl ester (PCBM, 20 mg mL^{-1} 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^{-1} 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^{-7} 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 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.

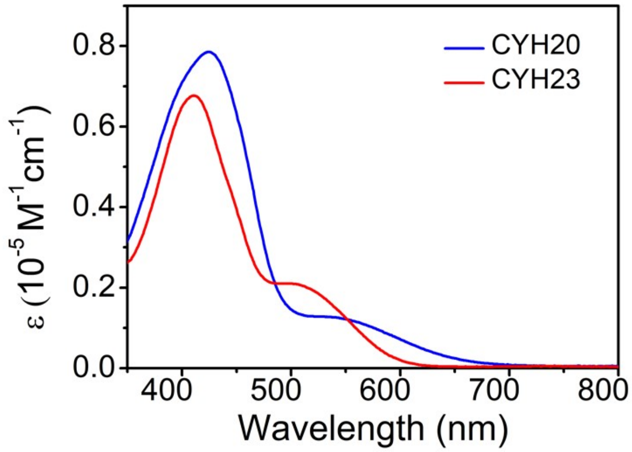


Figure S1. UV-vis absorption spectra of HTM **CYH20** and **CYH23** in CH_2Cl_2 solutions.

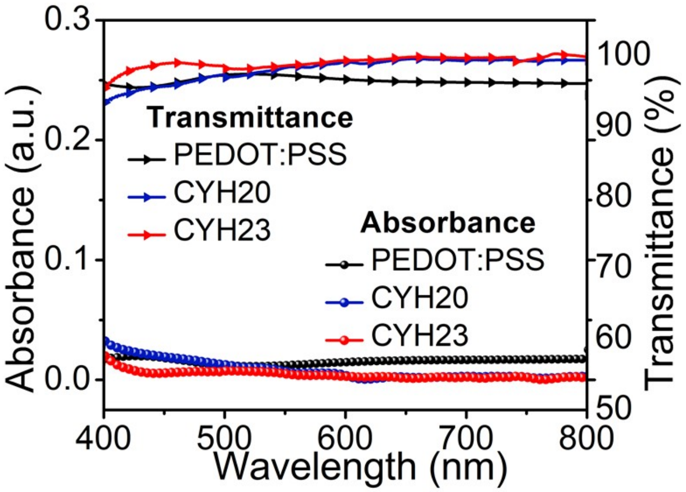


Figure S2. UV-vis absorption and transmittance spectra of **CYH20** and **CYH23** films.

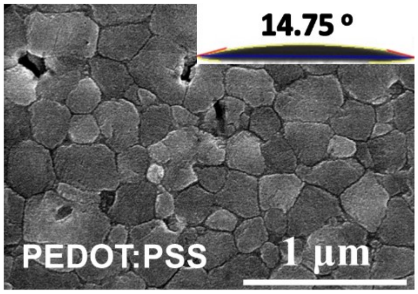


Figure S3. Scanning electron microscopy (SEM) top-view image, with inset water contact angle, of **PEDOT:PSS** film

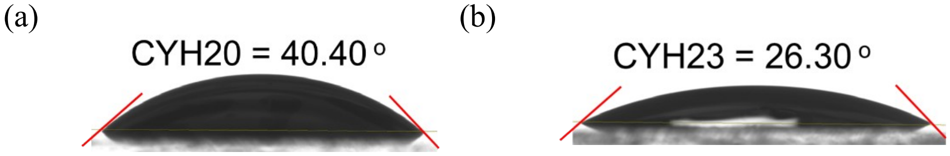


Figure S4. Contact angles of **CYH20** and **CYH23** in DMSO.

Table S1. The detailed parameters of PL obtained by fitting the TRPL of **PEDOT:PSS**, **CYH20**, and **CYH23**.

HTMs	τ_1	**A$_1$**	τ_2	**A$_2$**	τ_{Averege}
ITO	2.62	53.33%	9.16	44.18%	5.58
PEDOT:PSS	2.27	67.34%	8.38	34.10%	4,32
CYH20	1.25	60.87%	5.07	36.58%	2.68
CYH23	0.81	70.49%	4.03	31.15%	1.80

Table S2: Parameters of **CYH20**-Based Inverted PSC.

CYH20	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF*	PCE (%)
0 mg/mL	1.05	13.48	34.70	4.87
0.5 mg/mL	1.04	20.07	65.42	13.61
1 mg/mL	1.08	20.24	72.72	15.84
1.5 mg/mL	1.06	18.77	74.87	14.86
2 mg/mL	1.09	16.64	74.18	13.41

Table S3: Parameters of **CYH23**-Based Inverted PSC.

CYH23	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF*	PCE (%)
0.5 mg/mL	1.07	18.80	69.92	14.02
1 mg/mL	1.09	20.32	76.51	16.94
1.5 mg/mL	1.07	19.42	75.72	15.74
2 mg/mL	1.04	19.85	70.14	14.44

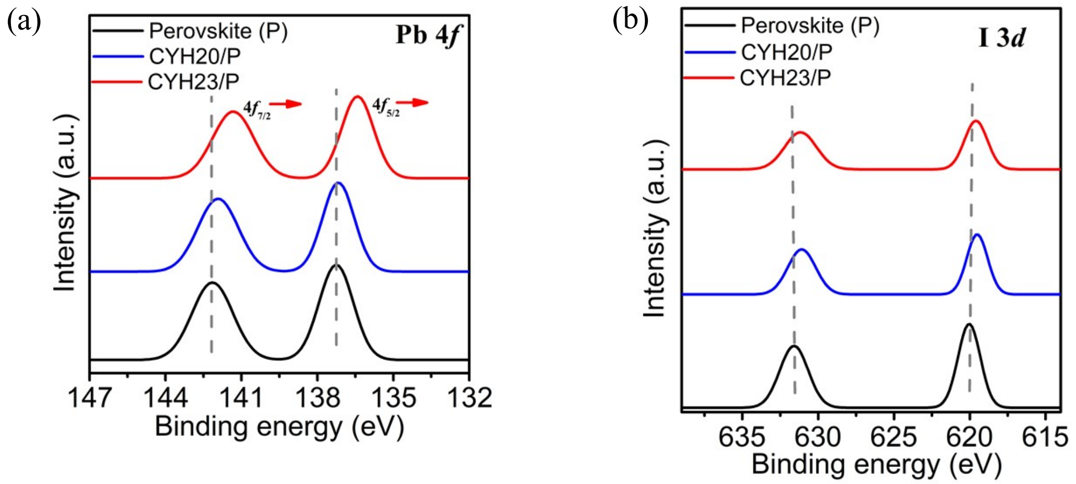


Figure S5. XPS (a) Pb 4*f* and (b) I 3*d* of FTO/HTM/perovskite.

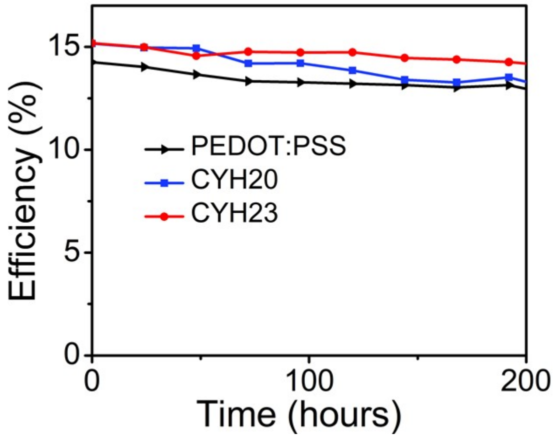


Figure S6. The stability testing of the PSCs incorporated with **PEDOT:PSS**, **CYH20**, and **CYH23**.