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Supporting Information for

Efficient and Stable Perovskite Solar Cells through Electrochemically Polymerized Porphyrin-based Hole-Transporting Materials

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Experimental Section

Materials: Fluorine-doped tin oxide (FTO) glass substrates, fullerene C_{60} (> 99.5%) and bathocuproine (BCP) were purchased from Advanced Election Technology Co., Ltd. Lead iodide (PbI_2, > 99.99%), and methylammonium iodide (MAI, > 99.99%) were purchased from Xi'an e-Light New Material Co. The ultra-dry anhydrous *N,N*-dimethylformamide (DMF, 99.8%), chlorobenzene (CB, 99.8%), dimethyl sulfoxide (DMSO 99.9%) and tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) were purchased from Sigma Aldrich. Free-base porphyrin (**Por**)[S1], zinc porphyrin (**ZnPor**)[S1], and nickel porphyrin (**NiPor**)[S2] were synthesized from natural chlorophyll-*a* according to the literature procedures, as shown in Scheme S1. All of the materials and reagents were used as supplied without further purification.

Synthesis of PolyPor films: Electrochemically polymerized films of **Por**, **ZnPor**, and **NiPor** were prepared in a one-compartment cell under computer control in a three-electrode test system. The working electrode was FTO glass substrate and platinum counter electrode were placed 1.5 cm apart, while an Ag/AgCl electrode was used as reference electrode. The electrolyte solution was CH_2Cl_2 containing 0.1 M Bu_4NPF_6 and 0.5 mM each Por monomer. The thickness of the PolyPor films can be modulated by controlling polymerization time. The electrochemical polymerization was performed by CV. The parameters of the CV were set as follows: the highest potential of 1.3 V, the lowest potential of 0 V, the starting potential of 0 V, and the scanning speed of 0.1 V s^{-1}. After polymerization, the films were thoroughly rinsed with CH_2Cl_2, and then dried in air.

Device fabrication and photovoltaic characterization: FTO glass substrates were ultrasonically cleaned by detergent, deionized water, chloroform, acetone, and ethanol for 20 min and treated with UV-ozone for 20 min before use. The perovskite precursor solution was prepared by mixing PbI_2 (1.4 M), MAI (1.3 M) and NH_4Cl (0.2 M) in DMF/DMSO (4:1 volume ratio), and the solution was stirred at room temperature for 3 hours. The perovskite layer was prepared by spin-coating its precursor solution (80 μL) at 5000 rpm for 30 s onto the HTL, and injecting CB (350 μL) quickly onto the

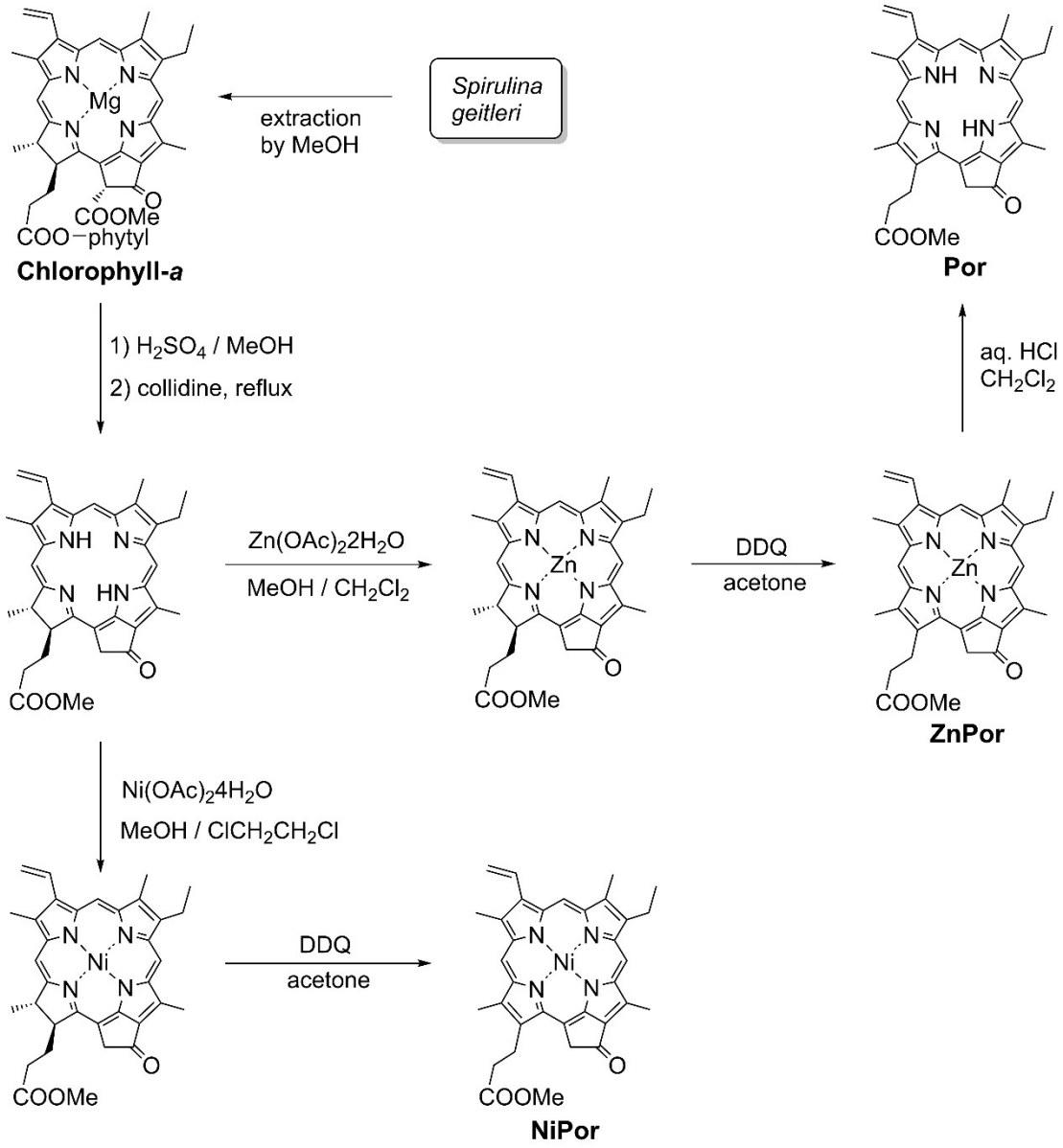
spinning film for 5 s during the spin-coating process. The obtained film was then heated at 100 ℃ for 10 min. In the final step of device fabrication, 20 nm of C_{60}, 7 nm of BCP and 100 nm of Ag electrode were thermally evaporated under high vacuum conditions (≈10^{-4} Pa). The active area of this electrode was fixed at 0.04 cm^2.

Characterizations: The UV-ozone treatment was employed by a BZS250GF-TS UV-ozone cleaner. UV-vis absorption spectra were recorded using a Shimadzu UV-1900 spectrophotometer. X-ray diffraction (XRD) patterns of various films were measured by a Bruker D8 X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) at room temperature. The data was collected with a 0.02° step size (2θ) for 0.2 s. The top view and cross-section were obtained through a field emission scanning electron microscopy (SEM, Regulus 8100) image. The current density–voltage (*J–V*) curves of the PSCs were monitored using a Keithley 2400 source meter under AM 1.5 solar simulator with an irradiation of 100 mW cm^{-2}. The effective area of the cells was confirmed to be 0.04 cm^2 using a non-reflective metal mask. The incident photon-to-current conversion efficiency spectra were measured in air under short-circuit conditions using SOFN 7-SCSpecIII equipped with a 100 W Xe arc lamp, a filter wheel, and a monochromator. Monochromatic light was chopped at a frequency of 80 Hz and photocurrents were measured using a lock-in amplifier. The time-resolved photo-luminescence (TRPL) was measured by using Fluorolog-3 spectrometer (Horiba Jobin Yvon, America) monitoring at 770 nm. The steady-state photoluminescence (PL) spectra were tested by a spectrometer (IHR550, HORIBA) excited by He-Cd laser (325 nm). The electrochemical impedance spectroscopy (EIS) spectra were measured by PMC-1000 in the range from 100,000 to 0.1 Hz. Ultraviolet photoelectron spectroscopy (UPS) results were recorded by ThermoFisher ESCALAB 250Xi (hν = 21.22 eV). Atomic force microscopy (AFM) images were obtained with Bruker Dimension Icon. The Energy Dispersive X-ray Spectroscopy (EDS) instrument used is a BRUKER QUANTAX 200 with an XFlash 6I60 detector. The electron beam energy was set to 15 keV and the take-off angle was 26°.

References

S1. H. Tamiaki, K. Fukai, S. Nakamura, Intramolecular interaction of synthetic chlorophyll heterodyads with different π-skeletons, Photochem. Photobiol. Sci. 19 (2020) 332-340.

S2. R. J. Abraham, A. E. Rowan, K. E. Mansfield, K. M. Smith, NMR spectra of the porphyrins. Part 40. Self-aggregation in zinc(II) and nickel(II) 2-vinylphyllperythrins, J. Chem. Soc., Perkin Trans. 2 (1991) 515-521.



Scheme S1. Synthesis of **Por**, **ZnPor**, and **NiPor** from natural chlorophyll-*a*.

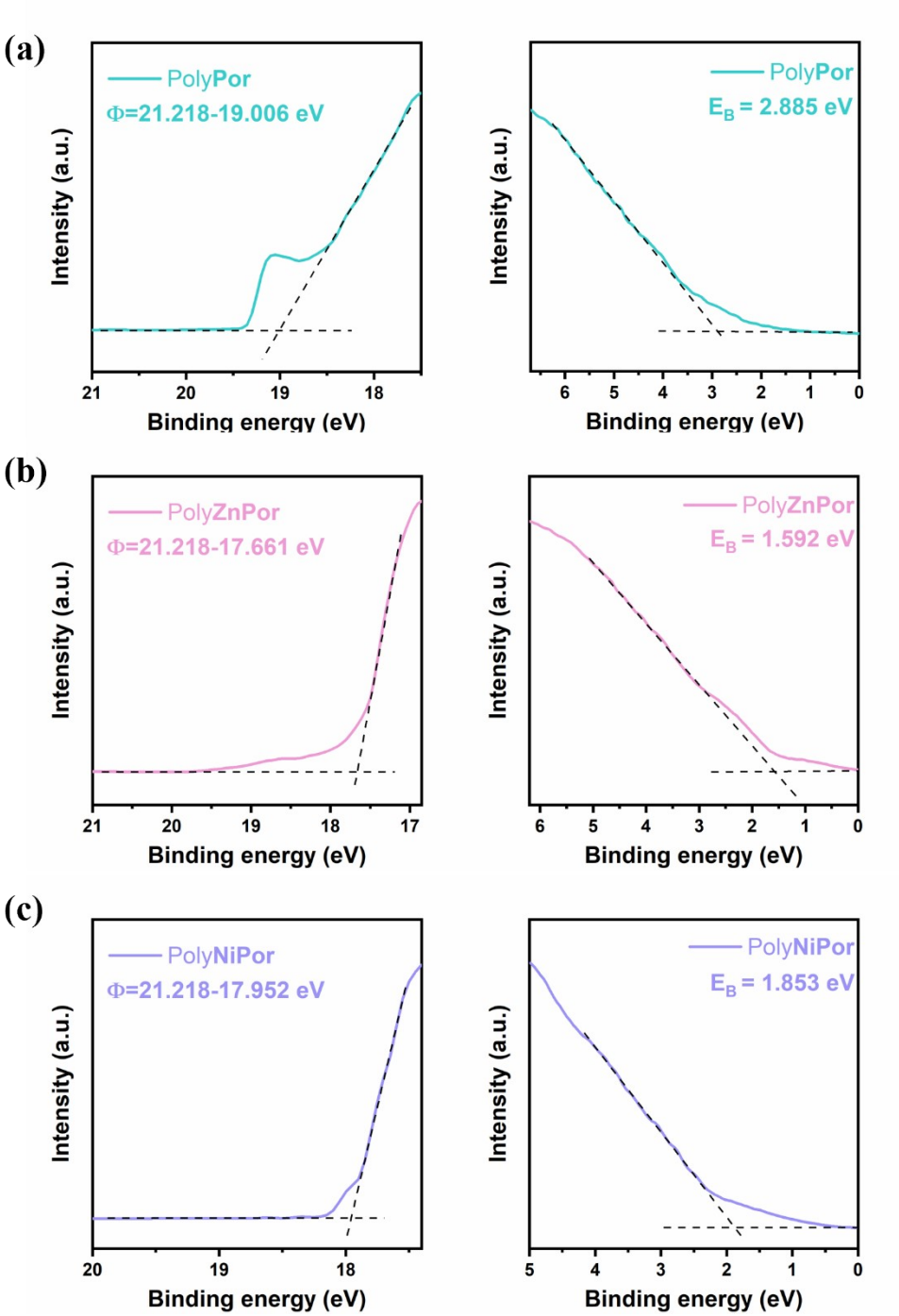


Figure S1. UPS spectra of FTO substrates covered by (a) Poly**Por** film, (b) Poly**ZnPor** film and (c) Poly**NiPor** film. (Left) UPS spectra around the secondary electron cutoff; (right) UPS spectra in the valence band (VB) region. Φ represents the work function (WF), and E_B=VB−WF.

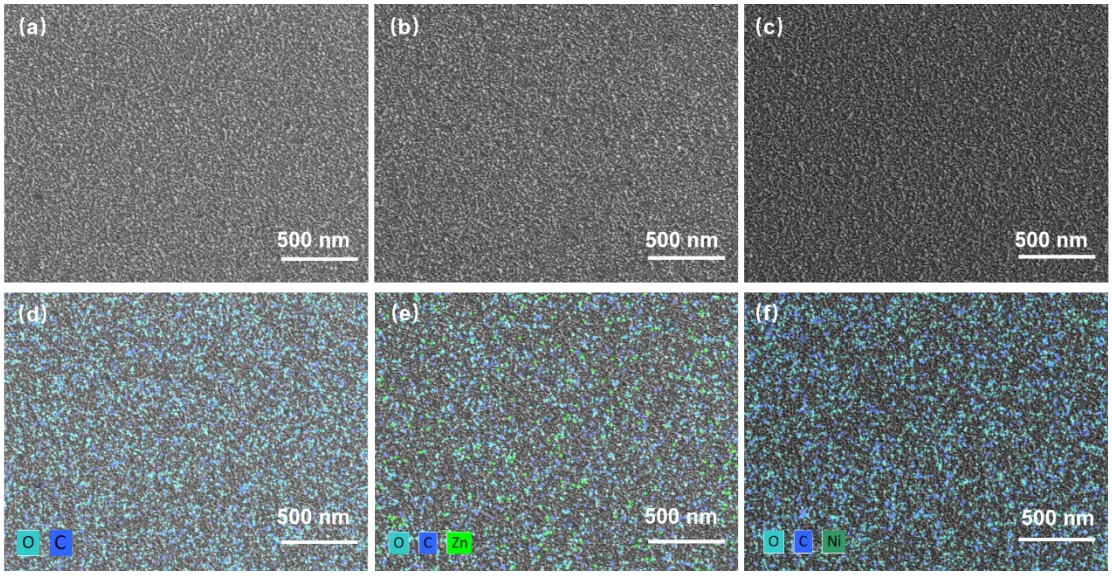


Figure S2. SEM images of (a) Poly**Por** film, (b) Poly**ZnPor** film and (c) Poly**NiPor** film. EDS images of (d) Poly**Por** film, (e) Poly**ZnPor** film and (f) Poly**NiPor** film.

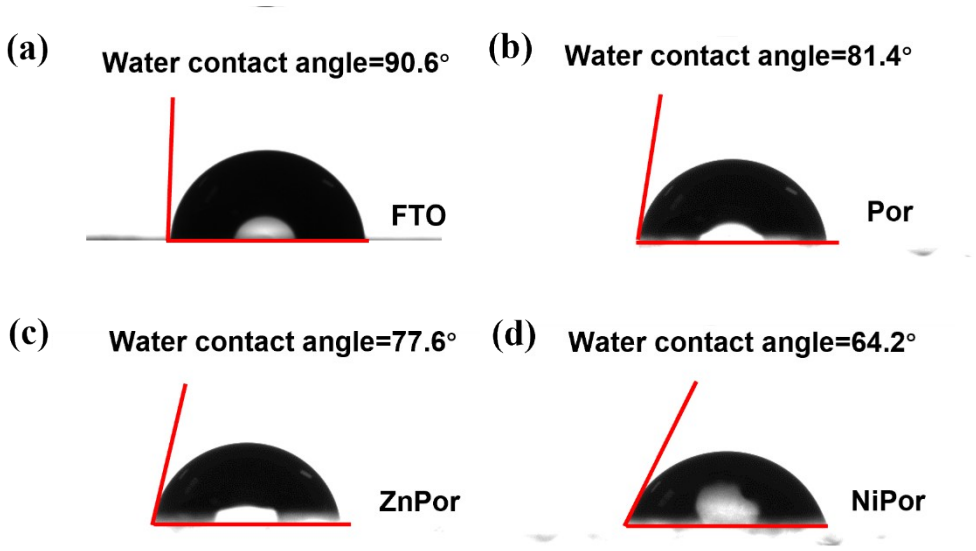


Figure S3. Water contact angles of (a) FTO substrate, (b) Poly**Por** film, (c) Poly**ZnPor** film and (d) Poly**NiPor** film.

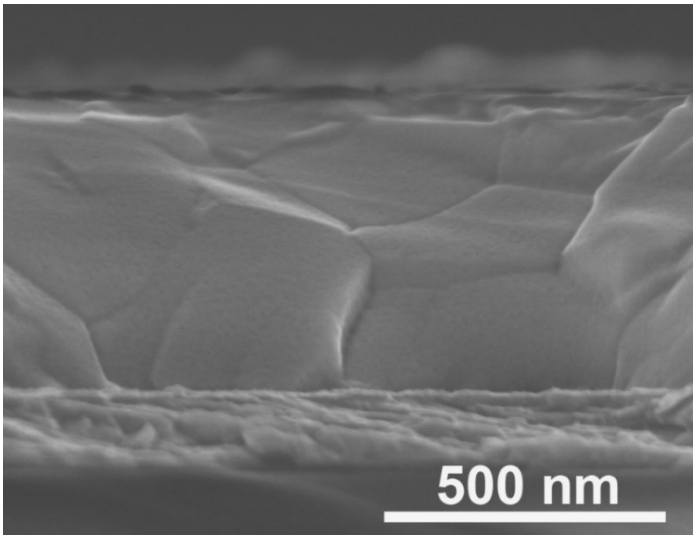


Figure S4. Typical cross-sectional SEM image of PSC based on the porphyrin HTMs.

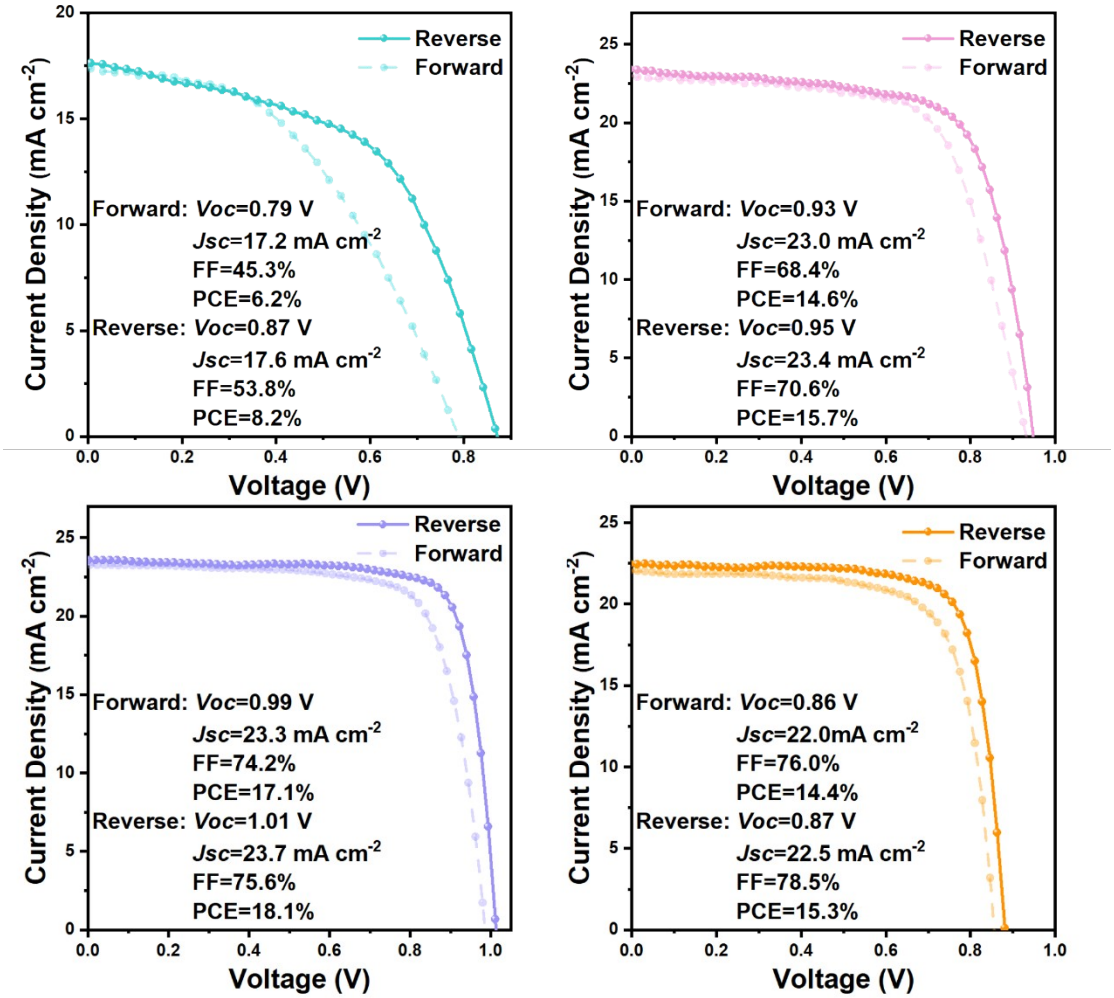


Figure S5. *J-V* curves of devices with Poly**Por**, Poly**ZnPor**, Poly**NiPor**, and PEDOT as HTLs, obtained through reverse and forward scans.

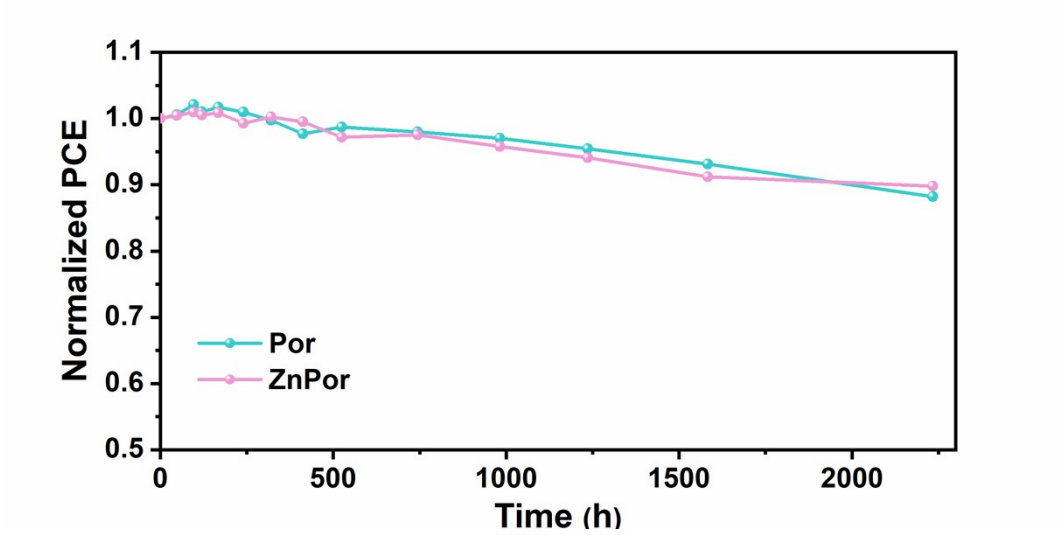


Figure S6. The stability test in ambient air under Relative Humidity (approximately 20%) of the unencapsulated PSCs based on Poly**Por** and Poly**ZnPor** HTL.

Table S1. PL decay lifetimes (τ_1, τ_2 and $\tau_{average}$) of the $MAPbI_3$ films coated on different substrates from Figure 4f.

Sample	τ_1(ns)	τ_1 ratio (%)	τ_2(ns)	τ_2 ratio (%)	$\tau_{average}$(ns)
Poly**Por**-$MAPbI_3$	31.0	2.03	1160.0	97.97	1137.08
Poly**ZnPor**-$MAPbI_3$	97.6	7.02	959.6	92.98	899.09
Poly**NiPor**-$MAPbI_3$	58.9	18.60	782.4	81.40	666.43

Table S2. Fitting parameters of the equivalent circuit of the Nyquist plot of the PSCs from Figure 4g.

Sample	R_s (ohm)	R_{rec} (k ohm)
Poly**Por**	68.5	0.61
Poly**ZnPor**	85.1	2.5
Poly**NiPor**	39.2	3.4

Table S3. Photovoltaic parameters of the best-performing devices based on Poly**NiPor** and PEDOT HTL.

HTLs	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)
Poly**NiPor**	23.7	1.01	75.6	18.1
PEDOT	22.5	0.87	78.5	15.3

Table S4. Fitting parameters of the equivalent circuit of the Nyquist plot of the PSCs from Figure 5f.

Sample	R_s (ohm)	R_{rec} (k ohm)
Poly**NiPor**	35.6	3.1
PEDOT	47.6	2.8

Table S5. Average photovoltaic parameters of the PSC (10 devices).

HTLs	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)
PolyPor	16.60±0.89	0.85±0.018	51.28±3.91	7.22±0.78
PolyZnPor	23.09±0.27	0.94±0.011	68.70±1.42	14.93±0.50
PolyNiPor	23.51±0.18	0.99±0.014	72.21±0.86	16.73±0.43