

Electronic Supplementary Information

Bilayer chlorophyll derivatives as efficient hole-transporting layers for perovskite solar cells

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Materials

The preparation of zinc methyl 3-devinyl-3-hydroxymethyl-pyropheophorbide-*a* (Zn-Chl)^{S1} and methyl 13^l-deoxo-13^l-dicyanomethylene-pyropheophorbide-*a* (H₂-Chl)^{S2} has been reported before. ITO was purchased from Dongguan City Everest Display Technology Co., Ltd. SnO₂ colloidal dispersion (15% in H₂O) was obtained from Alfa Aesar. MoO₃ was

purchased from Sinopharm Chemical Reagent Co., Ltd. Methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$, >99.5%) and lead iodide (PbI_2 , >99.99%) were obtained from Xian Polymer Light Technology Co. The ultra-dry solvents *N,N*-dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.7%), and chlorobenzene (CB, 99.8%) were purchased from INFI. Chloroform (CF, $\geq 99.0\%$) was purchased from BEIJING SHIJI Co., Ltd. Tetrahydrofuran (THF, $\geq 99.9\%$) was obtained from Aladdin Industrial Corporation.

Fabrication of perovskite solar cells (PSCs)

The pre-patterned ITO glass substrates were cleaned with detergent, deionized water, ethanol, acetone, CF, and 2-propanol in sequence in the ultrasonic bath for each step 20 minutes, and then treated under ultraviolet ozone for 30 minutes. Then the diluted SnO_2 colloid dispersion (3% in H_2O) was spin-coated on the prepared ITO substrates at 3000 rpm for 30 s and annealed at 150 °C for 30 minutes in air to form a compact SnO_2 thin layer. Subsequently, the substrates were transferred into the glove box. A perovskite precursor solution was prepared by dissolving $\text{CH}_3\text{NH}_3\text{I}$ (1.3 mol L^{-1}) and PbI_2 (1.3 mol L^{-1}) in DMF:DMSO (4:1, v/v) and stirred for 60 minutes in the glove box at room temperature. Then the perovskite precursor solution was spin-coated on the SnO_2 thin layer at 5000 rpm for 30 s and CB (360 μL) was rapidly dropped on the center of substrates after spin-coating for 5 s, then annealed at 100°C for 10 minutes. For the hole-transporting layers, Zn-Chl was dissolved in the mixed solvents of THF and CF at the volume ratio of 4:1 (10 mg mL^{-1}) and H_2 -Chl was dissolved in CF (8 mg mL^{-1}), then Zn-Chl and H_2 -Chl solutions were spin-coated on top of the perovskite at 2000 rpm for 30 s in sequence, and eventually two layers of complete Chl films (bilayer Chl) were formed.^{S3} Finally, a 100 nm thick Ag electrode was thermally evaporated on top of the bilayer chlorophyll films to compose a complete PSC device.

Measurements of materials and devices

The ultraviolet–visible–near infrared (UV-VIS-NIR) absorption spectra of Zn-Chl and H₂-Chl dissolved in THF and Zn-Chl, H₂-Chl, Zn-Chl/H₂-Chl films spin-coated on glass were recorded by a Shimadzu UV-3100 spectrophotometer. The scanning electron microscope (SEM) images of Zn-Chl, H₂-Chl, and Zn-Chl/H₂-Chl thin films spin-coated on ITO and the cross-sectional SEM image of the devices, ITO/SnO₂/MAPbI₃/Zn-Chl and ITO/SnO₂/MAPbI₃/Zn-Chl/H₂-Chl, were obtained from a Hitachi SU8000 field emission scanning electron microscope. The X-ray diffraction (XRD) patterns of these films deposited on glass were measured by using the Bruker D8 X-ray diffractometer at room temperature. The photo-electron spectroscopic data of Zn-Chl and H₂-Chl films were measured by ionization energy photoelectron yield spectroscopy (IPS) in the vacuum. The hole mobilities of Zn-Chl, H₂-Chl, and Zn-Chl/H₂-Chl were measured by the dark current density-voltage ($J-V$) curves of the hole-only devices (ITO/MoO₃/Chls/MoO₃/Ag) using space charge limited current (SCLC) method. And the dark $J-V$ characteristics of the hole-only devices were measured by forward scanning from 0~10 V using a computer-controlled Keithley 2400 source meter measurement system. The $J-V$ characteristics of the PSCs were measured by a computer-controlled Keithley 2400 source meter measurement system with an AM 1.5G filter at a calibrated intensity of 100 mW cm⁻² illumination, as regulated by a standard silicon reference cell (91150V Oriel Instruments). The incident photon-to-electron conversion efficiency (IPCE) responses of these PSCs were measured under standard measurement conditions by using a commercial IPCE setup (CrowntechQTest Station 1000AD, SOFN INSTRUMENTS CO., LTD). The working area of these PSCs was controlled by a metal mask at 0.04 cm². The steady-state photoluminescence (PL) spectra of these devices (glass/MAPbI₃, glass/MAPbI₃/Zn-Chl, and glass/MAPbI₃/Zn-Chl/H₂-Chl) were carried out on a PL spectrometer (Shimadzu, RF-530PC) with the excitation wavelength at 403 nm. The electrochemical impedance spectroscopy (EIS) was recorded by using a VSP multichannel potentiostatic-galvanostatic system (Bio-Logic Science Instruments) with the frequency

ranging between 1 MHz and 10 Hz under illumination (AM 1.5G, 100 mW cm⁻²) at 0 V relative to the open-circuit potential. The fitting data of the equivalent circuit model for the impedance spectra were calculated by computer simulation using the Z-view software. The device stability at their maximum power points (MPP) under 1-sun illumination in air was compared using the same galvanostatic-potentiostatic system.

Table S1 Photovoltaic parameters of the ITO/SnO₂/MAPbI₃/H₂-Chl/Ag device.^{a)}

HTM	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
H ₂ -Chl	0.87±0.06	0.52±0.09	35.0±1.3	0.16±0.06

^{a)} The average values measured for ten independently fabricated devices with standard deviation.

Table S2 Photovoltaic parameters of the PSC based on Zn-Chl treated with neat CF.^{a)}

HTM	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
Zn-Chl	0.92±0.03	22.2±0.5	56.8±1.6	11.6±1.0

^{a)} The average values measured for ten independently fabricated devices with standard deviation.

Table S3 Fitting parameters for EIS data of the PSCs based on Chls.

HTMs	R_s [Ω]	R_{rec} [Ω]	CPE-T [F]	CPE-P
Zn-Chl	40.1	115	6.11×10^{-9}	0.992
Zn-Chl/H ₂ -Chl	43.3	261	7.72×10^{-9}	0.967

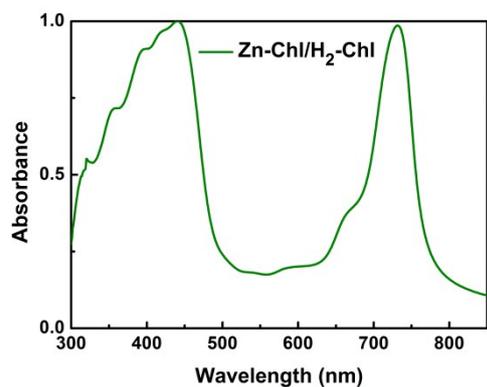


Fig. S1 UV-VIS-NIR absorption spectrum of bilayer film (Zn-Chl/H₂-Chl) spin-coated on the glass substrate.

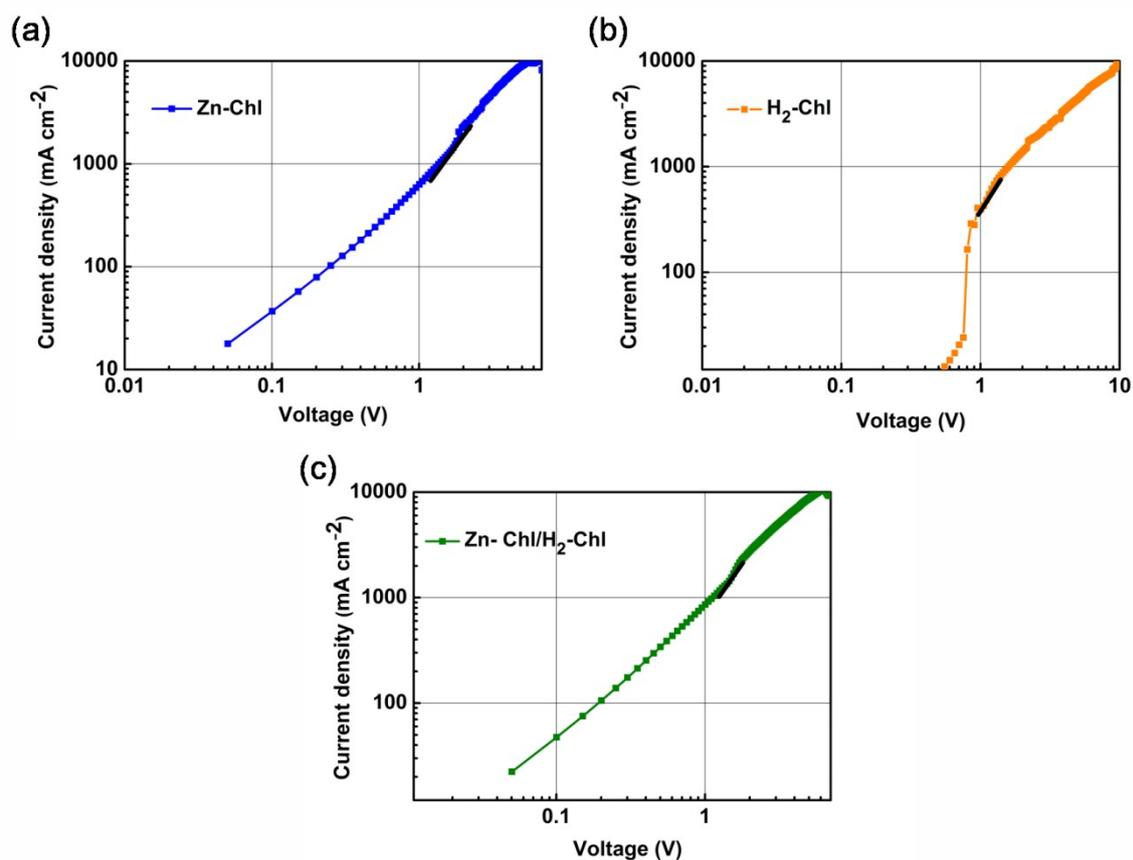


Fig. S2 J - V curves of the hole-only devices based on (a) monolayer Zn-Chl or (b) H₂-Chl and (c) bilayer Zn-Chl/H₂-Chl in the dark.

The hole mobilities were calculated using the following equation: ^{S4}

$$J = 9\varepsilon_0\varepsilon_r\mu V^2(2L)^{-3} \quad (S1),$$

where μ is the hole mobility, ε_0 is the permittivity of free space, ε_r is the relative dielectric constant (assumed to be 3), L is the thickness of HTLs thin film, J and V are the values corresponding to the point of slope=2 in the dark-state J - V curves (Fig. S2).

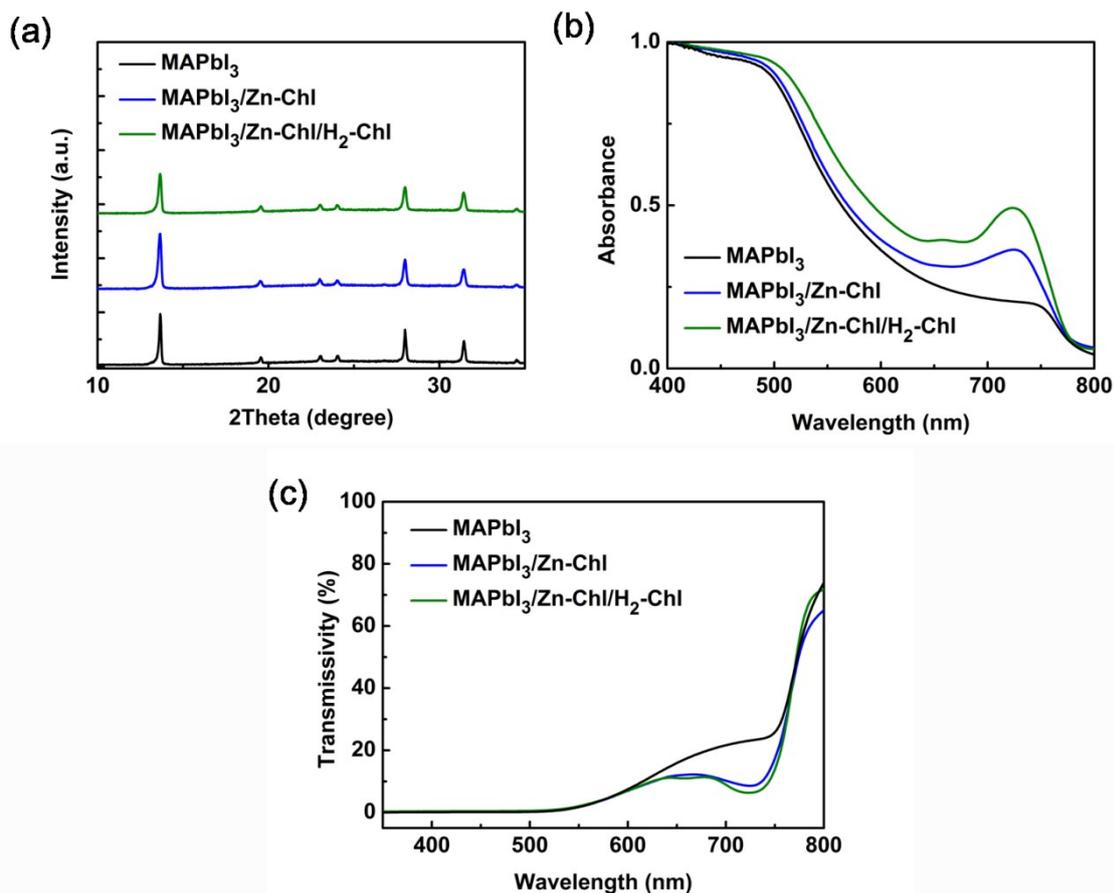


Fig. S3 (a) The XRD patterns, (b) normalized UV-VIS-NIR absorption spectra, and (c) normalized UV-VIS-NIR transmission spectra of glass/MAPbI₃, glass/MAPbI₃/Zn-Chl, and glass/MAPbI₃/Zn-Chl/H₂-Chl.

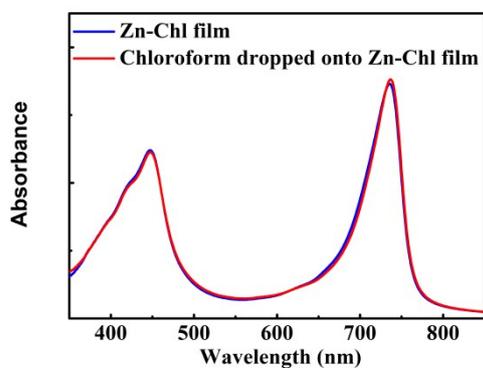


Fig. S4 Absorption spectra of Zn-Chl thin film (blue line) and the already formed Zn-Chl thin film treated with neat solvent CF only (red line).

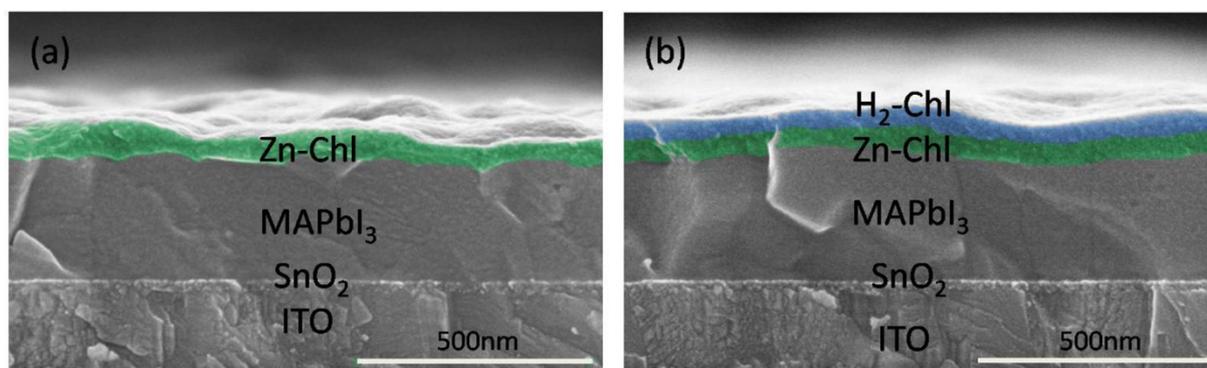


Fig. S5 The cross-sectional SEM images of the device with structures of (a) ITO/SnO₂/MAPbI₃/Zn-Chl and (b) ITO/SnO₂/MAPbI₃/Zn-Chl/H₂-Chl.

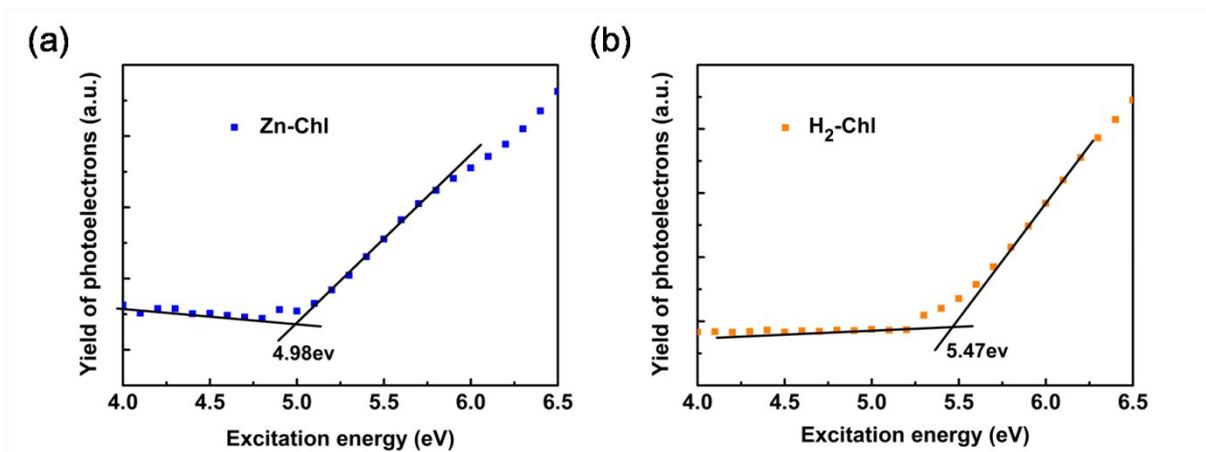


Fig. S6 The HOMO energy levels of (a) Zn-Chl and (b) H₂-Chl thin films examined by IPS.

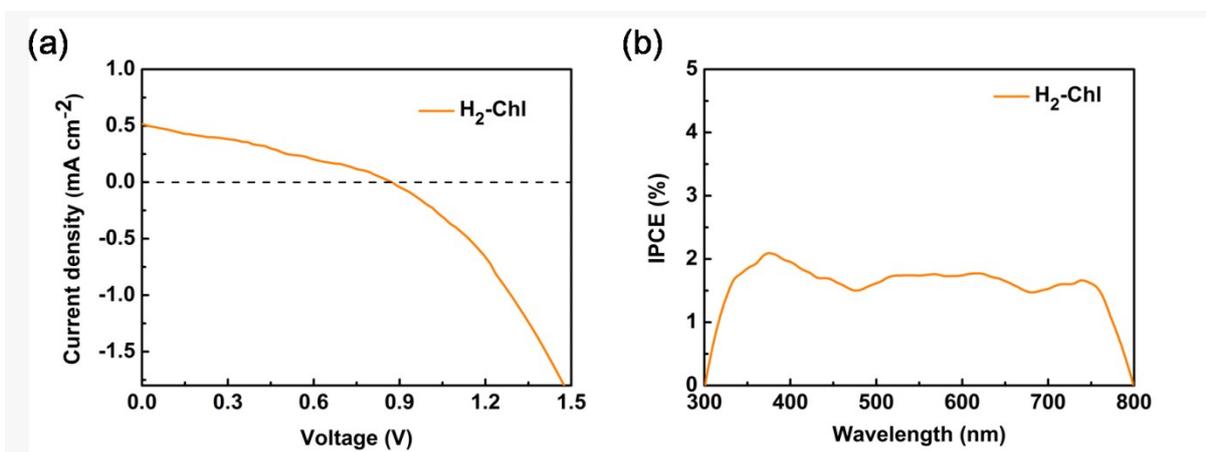


Fig. S7 (a) J - V curve and (b) IPCE spectra of the ITO/SnO₂/MAPbI₃/H₂-Chl/Ag device under standard AM1.5G illumination.

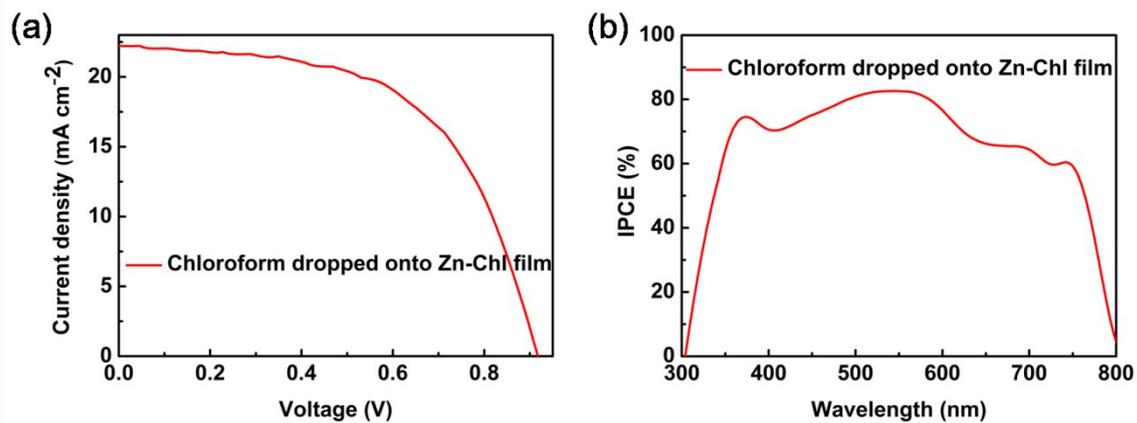


Fig. S8 (a) $J-V$ curve and (b) IPCE spectra of the PSC based on Zn-Chl treated with solvent CF only under standard AM1.5G illumination.

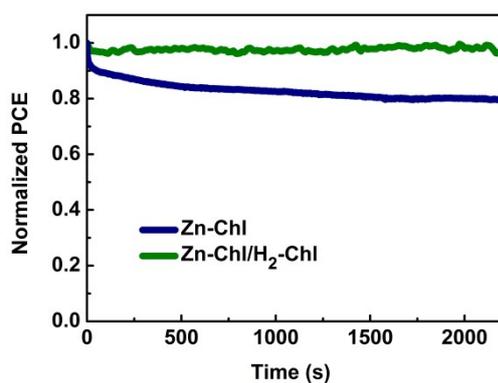


Fig. S9 Stability tracking over time of unencapsulated PSCs based on Zn-Chl and Zn-Chl/ H_2 -Chl at MMP under 1-sun illumination in air.

References

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