

## Supplementary Information

### **Self-Arranged Metal-Organic Polyhedron/Fullerene Asymmetric Structure Improves the Performance of Inverted Perovskite Solar Cells**

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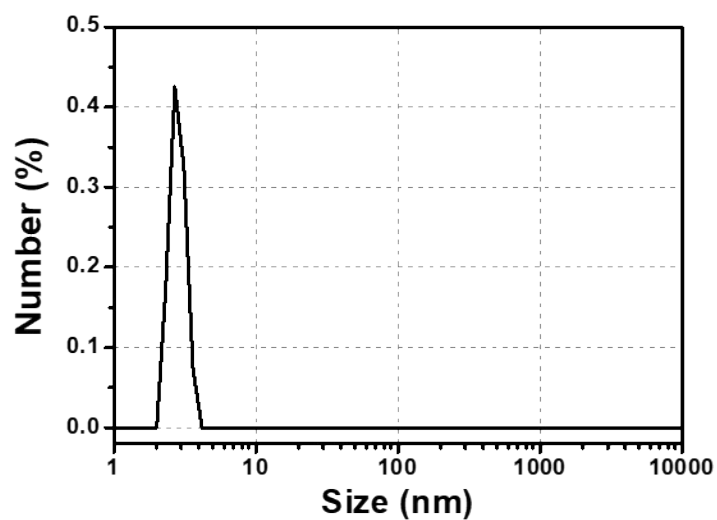
**Keywords:** Metal-organic polyhedron; nanoporous materials; electron transport layer; self-arrange; inverted perovskite solar cells

## Experimental Section

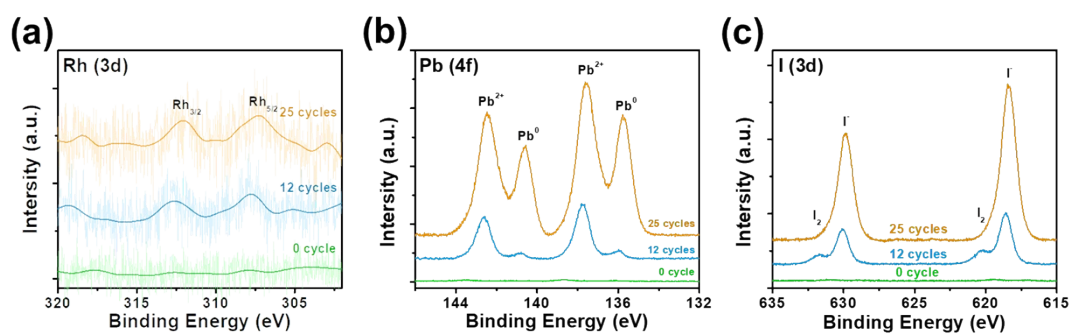
*Materials:* HRhMOP was synthesized according to the methods reported in a previous work,<sup>1</sup> The particle size of HRhMOP used in this study characterized by dynamic light scattering (DLS) of its solution in DMF is ~ 2-4 nm (**Figure S1**). Poly(bis(4-phenyl)(2,4,6-trimethylphenyl)amine) (PTAA) was purchased from Xi'an Polymer Light Technology Corp. Formamidinium iodide (FAI, >99.99%) was purchased from Greatcell Solar Materials. Lead iodide (PbI<sub>2</sub>, 99.99%), lead bromide (PbBr<sub>2</sub>, >98.0%(T)), and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM, >99.5%) were purchased from TCI chemicals. Bathocuproine (BCP) was purchased from UniRegion Bio-Tech (UR). Methylammonium bromide (MABr), cesium iodide (CsI), and all organic solvents for film preparation and device fabrication were purchased from Sigma Aldrich and used without further purification. The PTAA HTL was prepared by dissolving in toluene with a concentration of 2 mg/ml. Perovskite precursor solution was prepared by mixing FAI, MABr, PbI<sub>2</sub>, PbBr<sub>2</sub>, and CsI in DMF:DMSO (v/v = 5:1) with a chemical formula of (FAPbI<sub>3</sub>)<sub>0.83</sub>(MAPbBr<sub>3</sub>)<sub>0.17</sub>(CsPbI<sub>3</sub>)<sub>0.05</sub>. Precursor solutions of PCBM and BCP were prepared by dissolving them in chlorobenzene (CB) and isopropanol (IPA) with concentrations of 20 and 0.5 mg/mL, respectively. HRhMOP was pre-dispersed in CB and added into PCBM precursor solution to form HRhMOP:PCBM hybrid. The concentration for each component in CB is 20 mg/mL for PCBM and 0.5 mg/mL for HRhMOP.

*Device fabrication:* ITO glasses were cleaned in order with detergent, deionized water, acetone, and IPA, followed by plasma treatment for 10 min. All the following film deposition was processed in a N<sub>2</sub>-filled glove box with water and oxygen content under 1 ppm. The PTAA HTL was first spin-coated on the ITO substrates at 5000 rpm for 30 sec and annealed at 100 °C for 10 min. Prior to the deposition of a perovskite layer, 70 μL of DMF was spin-coated at 5000 rpm to attain better wettability. Then, the 45 μL perovskite precursor solution was spin-coated onto it at 5000 rpm for 30 sec and 120 μL anti-solvent CB was added within 1 sec at 10 sec before the end of the spin-coating procedure. The perovskite films were annealed at 100 °C for 30 min. Afterwards, the PCBM and HRhMOP:PCBM layer was spin-coated (at 1000 rpm for 30 sec) onto the perovskite film and the BCP layer was successively coated at 6000 rpm for 15 sec. Finally, silver electrodes (100 nm) were deposited through thermal evaporation under a high vacuum environment ( $< 2 \times 10^{-6}$  Torr) and a metal shadow mask was used to define the active area (0.085 cm<sup>2</sup>).

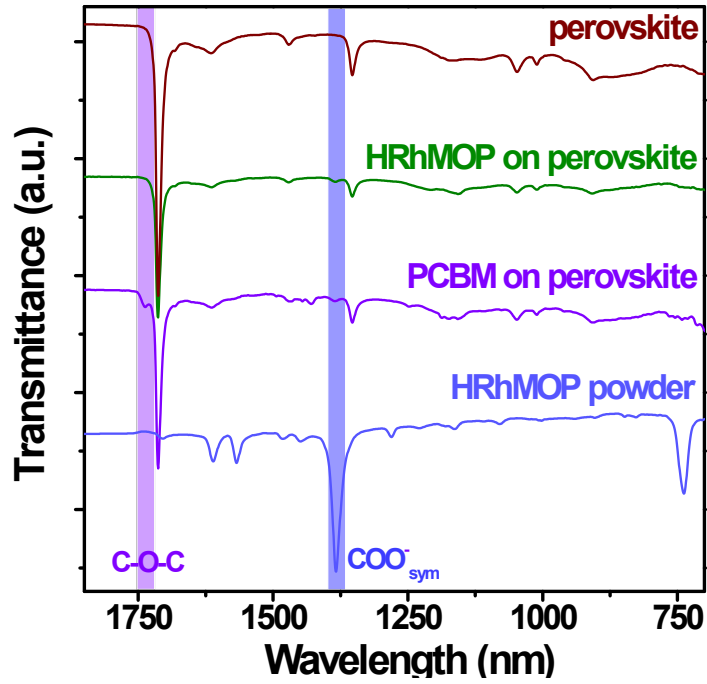
*Characterization:* The infrared spectra were recorded using Fourier Transform IR equipped with an Attenuated Total Reflection (ATR) accessory. Composition analysis was performed using X-ray photoelectron spectroscopy (XPS) PerkinElmer PHI 5400 equipped with monochromatized Al K $\alpha$  X-ray photon discharge lamp. Depth profile was conducted under condition of 2 kV argon ion gun with raster area of 2 mm  $\times$  2 mm, and the time interval of each cycle is set to 1 min. The values of work function (WF) and valence band maximum (VBM) were determined by ultraviolet photoemission spectroscopy (UPS) with He I (photon energy = 21.22 eV) as the excitation source. BET surface areas and porosimetry measurements of the samples (~120 mg) were performed using a BEL Master<sup>TM</sup> instrument and BEL sim<sup>TM</sup> software (v.3.0.0). N<sub>2</sub> adsorption and desorption isotherms were generated through incremental exposure to ultrahigh-purity N<sub>2</sub> (up to ca. 1 atm) in a liquid N<sub>2</sub> (77 K) bath. Surface parameters were calculated using the BET adsorption models in the instrument's software. The pore sizes of the prepared samples were determined using nonlocal density functional theory (NLDFT). The scanning electron microscope (SEM) images were taken from Nova<sup>TM</sup> NanoSEM 230 field-emission SEM. Absorption spectra were measured using Hitachi U-4100 UV–visible spectrophotometer. Steady-state and time-resolved photoluminescence spectra were recorded using Horiba Fluorolog-3 spectrofluorometer system equipped with 450W xenon arc lamp and time-correlated single-photon counting (TCSPC) accessory with 375 nm excitation diode laser. The  $J$ – $V$  curves were measured under AM1.5G illumination (100 mW cm<sup>-2</sup>) by a SS-F5-3A simulator (Enlitech CO., Ltd.) and recorded by a computer-controlled Keithley 2400 source. The EQE spectrum was performed using QE-R (Enlitech Co., Ltd). The spectra for AM1.5G illumination and EQE measurement were calibrated by a single crystal Si photovoltaic cell.



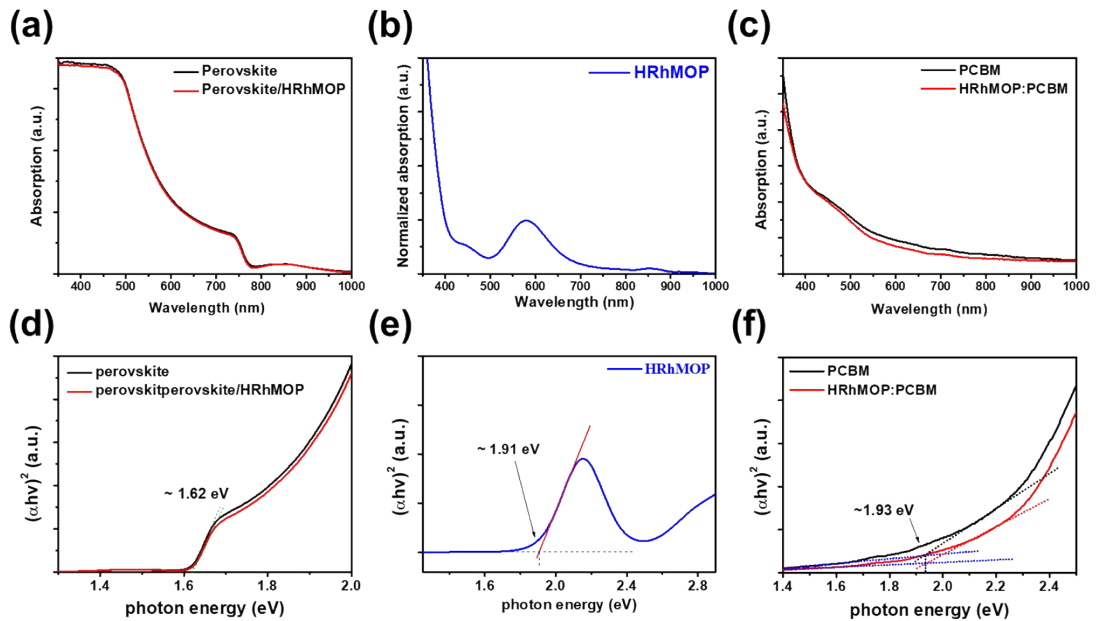
**Figure S1.** The size distribution plot of HRhMOP characterized by dynamic light scattering (DLS).



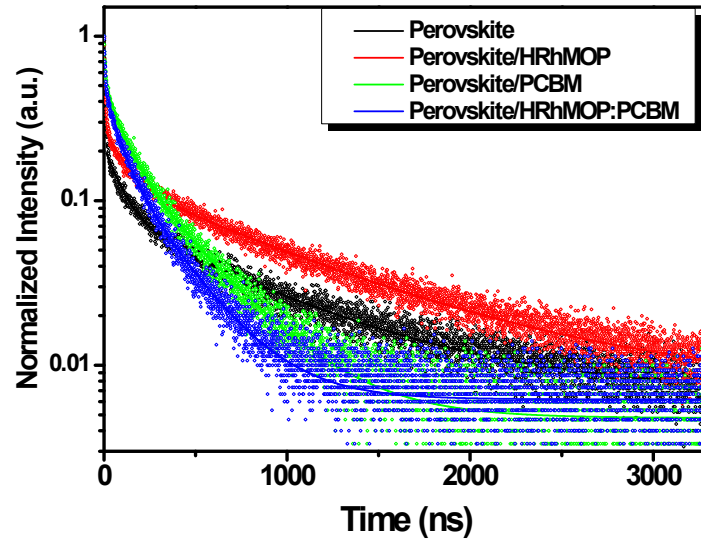
**Figure S2.** XPS spectra of (a) Rh (3d), (b) Pb (4f), and (c) I (3d) after argon ion sputtering with 0, 12, 25 cycles, representing region I, II, and III, respectively.



**Figure S3.** Comparison of the FTIR spectra of the pristine perovskite film, HRhMOP/perovskite film, and PCBM/perovskite film on the glass substrate and HRhMOP powder.



**Figure S4.** UV-Vis spectra with the respective Tauc plots of the (a, d) perovskite and HRhMOP passivated perovskite films, (b, e) HRhMOP powder, and (c, f) PCBM and HRhMOP:PCBM hybrid films.



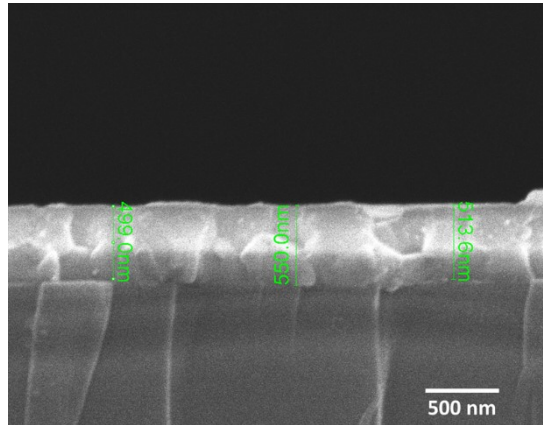
**Figure S5.** Time-resolved photoluminescence spectra (TRPL) of the films of pure perovskite, HRhMOP-passivated perovskite, bilayer perovskite/PCBM, and bilayer perovskite/HRhMOP:PCBM.

**Table S1.** Fitted carrier lifetimes from TRPL spectra based on a biexponential decay

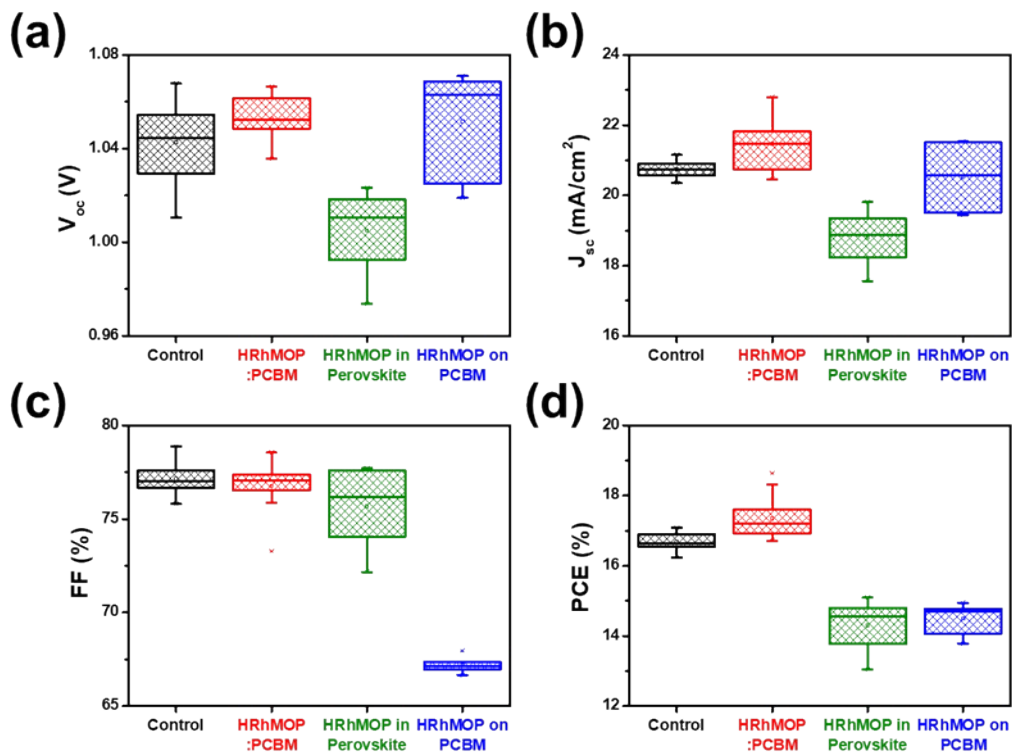
equation:  $y = y_0 + A_1 e^{-\frac{x}{\tau_1}} + A_2 e^{-\frac{x}{\tau_2}}$ . The average carrier lifetime is calculated from:  

$$\tau_{avg} = \frac{A_1 \tau_1 + A_2 \tau_2}{A_1 + A_2}$$

Films	$A_1$	$\tau_1$ (ns)	$A_2$	$\tau_2$ (ns)	$\tau_{avg}$ (ns)
Perovskite	0.611	95.6	0.389	741.0	346.7
Perovskite/HRhMOP	0.510	108.2	0.490	896.1	494.3
Perovskite/PCBM	0.571	88.1	0.429	337.2	195.0
Perovskite/HRhMOP:PCBM	0.574	69.0	0.426	260.0	150.4

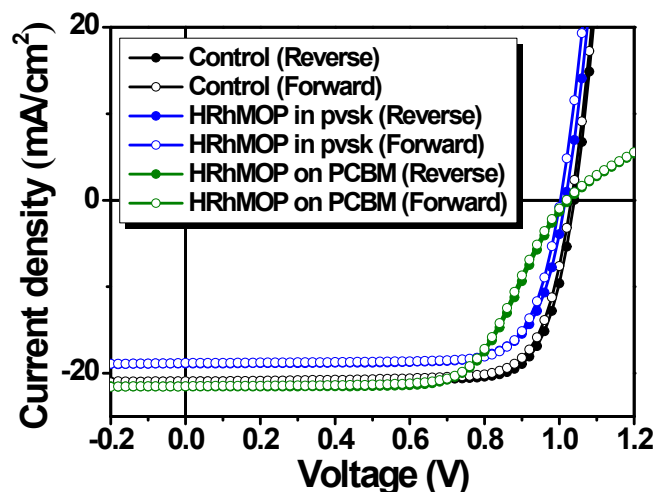


**Figure S6.** Cross-section SEM image of perovskite film deposited on glass.



**Fig**

**Figure S7.** Box charts of the  $V_{oc}$ ,  $J_{sc}$ , FF, and PCE values of the studied devices.



**Figure S8.**  $J$ - $V$  characteristics of the devices with different HRhMOP modifications as indicated.

**Table S2.** Photovoltaic performance of the devices with different HRhMOP modifications as indicated. The hysteresis index (HI) is calculated from the definition:  $HI = |PCE(\text{reverse}) - PCE(\text{forward})| / PCE(\text{reverse})$ .

Device	Scan	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	$FF$ (%)	HI (%)	PCE (%)
<b>Control</b>	<i>Forward</i>	1.032	20.94	77.21	2.7	16.67
	<i>Reverse</i>	1.040	20.97	78.61		17.14
<b>HRhMOP:PCBM</b>	<i>Forward</i>	1.049	22.78	76.63	1.7	18.32
	<i>Reverse</i>	1.061	22.80	77.01		18.64
<b>HRhMOP in perovskite<sup>a</sup></b>	<i>Forward</i>	1.003	18.82	77.72	0.5	14.67
	<i>Reverse</i>	1.016	18.89	76.08		14.60
<b>HRhMOP on PCBM<sup>b</sup></b>	<i>Forward</i>	1.019	21.51	66.98	0.7	14.68
	<i>Reverse</i>	1.025	21.53	66.96		14.78

<sup>a</sup> Concentration of HRhMOP as additive: 0.2 mg/mL in the perovskite precursor solution. <sup>b</sup> Concentration of HRhMOP on PCBM: 0.5 mg/mL in IPA with same coating procedure as the BCP buffer layer.



## References

1. S. Furukawa, N. Horike, M. Kondo, Y. Hijikata, A. Carne-Sanchez, P. Larpent, N. Louvain, S. Diring, H. Sato, R. Matsuda, R. Kawano and S. Kitagawa, *Inorg Chem*, 2016, **55**, 10843-10846.