

Electronic Supplementary Information

for

Effect of guanidinium on mesoscopic perovskite solar cells

Xiaomeng Hou, Yue Hu, Huawei Liu, Anyi Mei, Xiong Li, Miao Duan, Guoan Zhang, Yaoguang Rong, Hongwei Han**

School of Chemistry and Chemical Engineering, Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wuhan 430074, Hubei, P. R. China.

**E-mail: hongwei.han@mail.hust.edu.cn; ygrong@hust.edu.cn*

Experimental section

Synthesis of methylammonium iodide. $\text{CH}_3\text{NH}_3\text{I}$ was synthesized according to previous literatures as follow: Methylamine (40 wt.% in methanol, TCI) hydroiodic acid (57 wt.% in water, Aldrich) with a mole ratio of 1:1 was added into a round-bottom flask in an ice bath and stirred for 2 h. After evaporated the solvent at 50 °C, the yellowish raw product of $\text{CH}_3\text{NH}_3\text{I}$ was obtained. Subsequently the precipitate was filtered and washed three times with diethyl ether. After that, the white solid was collected and dried in a vacuum oven for 24 h.

Device fabrication. FTO glass substrates were patterned with a laser and then ultrasonically cleaned with detergent, deionized water and ethanol. A c- TiO_2 layer was deposited on the FTO-coated glass by spray pyrolysis deposition with diisopropoxytitaniumbis (acetyl acetonate) solution at 450 °C. Subsequently *ca.* 1.0 μm mesoporous TiO_2 (PASOLHPW-18NR, JGC Catalysts and Chemicals Ltd., Japan) layers, *ca.* 1.0 μm ZrO_2 spacer layers and *ca.* 10.0 μm carbon layers were deposited by screen-printing on the substrates layer by layer, which were sintered at 500 °C, 500 °C and 400 °C for 30 min, respectively. After cooling down to room temperature, 2.0~2.5 μL perovskite precursor solution was dripped on the top of the carbon layer in ambient air. After annealing at 100 °C for 5 min, the color of the perovskite precursor changed from yellow to dark brown. The perovskite precursor solution was prepared as follows: 0.159 g $\text{CH}_3\text{NH}_3\text{I}$, 0.461 g PbI_2 and appropriate quantities of guanidinium chloride were dissolved in 1.0 ml DMF, and stirred at 60 °C overnight.

Characterization. The X-ray diffraction (XRD) spectra were measured with a Bruker D8 Advance X-ray diffractometer with Cu $\text{K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The absorption spectra

of the perovskite films were deposited on the TiO₂ sca and recorded by a UV-Vis-NIR spectrophotometer (UV-3600, Shimadzu Scientific Instruments). The Fourier transform infrared (FT-IR) spectra were collected using a VERTEX 70 from Bruker Company. The scanning electron microscopy (SEM) tests were performed on a field-emission SEM (FEI Nova NanoSEM 450). Perovskite films for top-view SEM tests were prepared on FTO substrates *via* spin-coating. The cross-sectional SEM images were obtained with perovskites infiltrated mesoscopic scaffolds of TiO₂ (*ca.* 500 nm)/ZrO₂ (*ca.* 500 nm)/Carbon on FTO substrates. The steady-state Photoluminescence (PL) spectra were measured by LabRAM HR800 Raman Microscope. Perovskite films prepared on quartz were excited by laser beam at 532.16 nm. Time-resolved PL was measured at 760 nm using excitation with a 478 nm laser at a frequency of 4 MHz from the Horiba Jobin Yvon Fluoromax-4 fluorimeter. The lifetime was obtained by fitting an exponential decay function.

Photocurrent density-voltage (*J-V*) characteristics were measured using a Keithley 2400 sourcemeter under simulated AM1.5 one sun illumination (100 mW cm⁻²). A black mask with a circular aperture (0.126 cm²) was applied on the top of the device. The incident photon-to-current conversion efficiency (IPCE) was measured using a 150 W xenon lamp (Oriol) fitted with a monochromator (Cornerstone 74004) as a monochromatic light source. Impedance spectroscopy (IS) measurements were carried on a potentiostation (ZAHNER) in the frequency range 100 m Hz to 4 M Hz with 10 mV AC amplitude under dark condition.

Table S1. Photovoltaic parameters of devices fabricated with MAPbI₃·xGuCl

MAPbI ₃ ·xGuCl	V_{OC} (mV)	J_{SC} (mA cm ⁻²)	FF	PCE (%)
$x = 0$	880 ± 20	14.16 ± 0.85	0.66 ± 0.04	8.14 ± 0.96
$x = 0.25$	1000 ± 20	17.06 ± 2.24	0.74 ± 0.04	13.24 ± 1.20
$x = 0.5$	1050 ± 15	14.61 ± 1.03	0.72 ± 0.02	10.73 ± 0.62
$x = 0.75$	840 ± 17	4.33 ± 0.78	0.68 ± 0.01	2.47 ± 0.2
$x = 1.0$	820 ± 15	2.74 ± 0.35	0.51 ± 0.05	1.15 ± 0.1

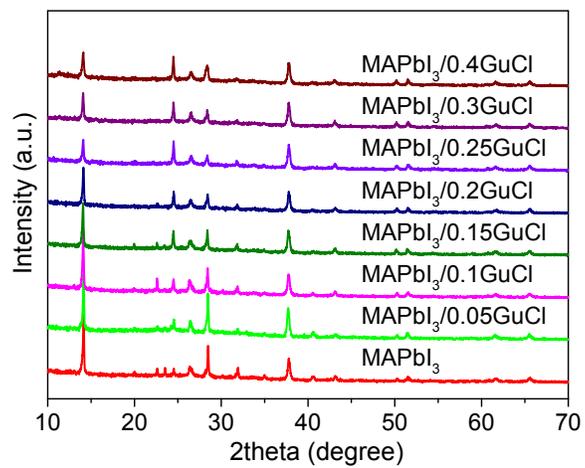


Figure S1. XRD patterns of MAPbI₃·xGuCl on glass substrates ($x = 0.05 \sim 0.4$).

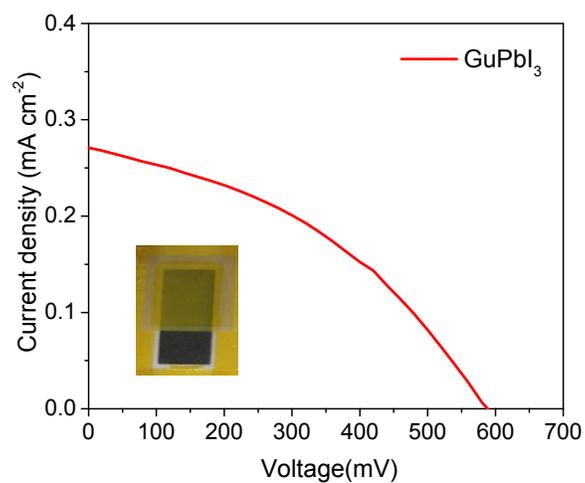


Figure S2. The J - V curve of the device fabricated with pure GuPbI₃. The inset shows the digital image of the pure GuPbI₃ based hole-conductor-free MPSC with the architecture of TiO₂/ZrO₂/Carbon.

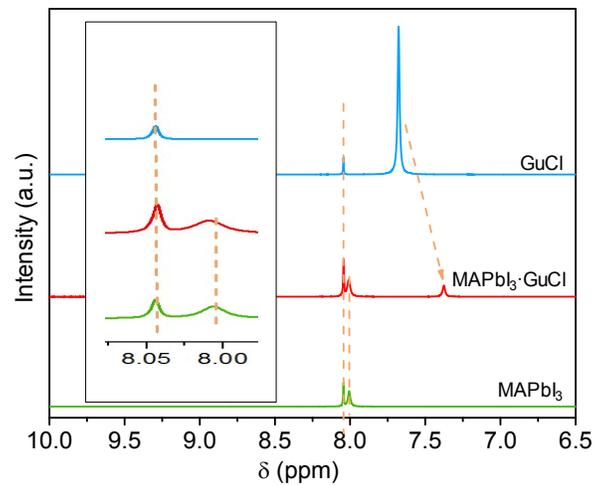


Figure S3. ¹H NMR spectra of GuCl, MAPbI₃ and MAPbI₃·*x*GuCl solution in deuterated *N, N*-dimethylformamide-*d*₇ (DMF-*d*₇) at 295 K.

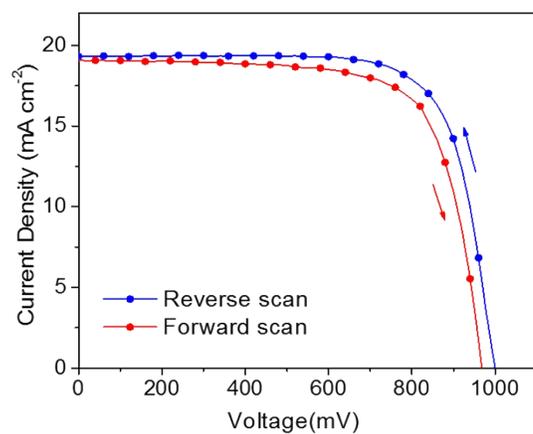


Figure S4. J - V curves of $\text{MAPbI}_3 \cdot x\text{GuCl}$ ($x = 0.25$) based device measured with reverse scan and forward scan.

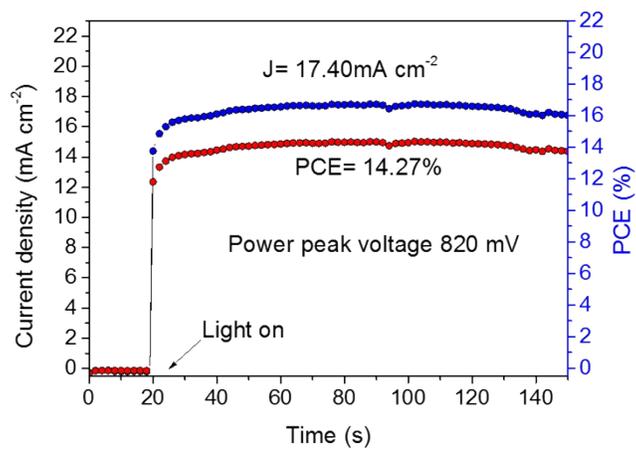


Figure S5. The current of the device measured at a bias of 0.82 V, corresponding to a PCE of ~14.27%.