Supporting Information for

The Intrinsic Properties of $FA_{(1-x)}MA_xPbI_3$ Perovskite Single Crystals

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Experiments and Characterization:

Chemicals and Reagents: Lead (II) iodide (PbI_2, Aladdin, 99.9%), methylamine (CH_3NH_2, 40%w/w aq. soln.), formamidine acetate salt (FAAc, Aladdin, 99%), hydriodic acid (HI, Alfa Aesar, 57% w/w aq. soln., stab with 1.5% hypophosphorous acid), gamma-Butyrolactone (GBL, Aladdin, 99%).

Synthesis of CH_3NH_3I and $CH(NH_2)_2I$: MAI was synthesized according to the reference.[1] 30 mL CH_3NH_2 was added into the 250 mL three neck round bottom flask kept at 0 ^oC ice-bath, where the flask was connected with N_2 atmosphere. Then, 32.3 mL HI was added into the flask through injection within 15 minute. The reaction was continued at 0 °C and stoped after 2 h. Subsequently, the solvent was removed at 50 °C by the rotary evaporator, and the yellowish precipitate was washed with diethyl ether and filtrated. Then the product was redissolved into ethanol to form the saturated solution at 80 °C, and the white flake crystal was formed by naturally cooling the solution at room temperature. The crystal was washed, redissolved and recrystallized by three times. The final product was collected after dried at 60 °C in a vacuum oven for 24 h. The synthetic method of FAI was similar to that of MAI, except that 14 g FAAc instead 30 mL CH_3NH_2 was used as the precursor.

Growth of $APbI_3$ ($A = MA^+, FA^+$) Single Crystals: Perovskite single crystals were grown by the HI assisted inverse temperature crystallization in GBL. The total molar ratio of MAI and FAI was the same as that of PbI_2. A given amount of MAI, FAI and PbI_2 were added into GBL to form 1.23 M precursor solution. A proper amount of HI was added into the above solution, e.g. 3μL HI in 1 mL GBL. Then the precursor solution were stirred at 80 °C for 0.5 h. After

dissolution, $FA_{(1-x)}MA_xPbI_3$ (x = 0, 0.05, 0.1, 0.15, 0.2) solutions were transferred into a 90 °C oil bath and 100 °C oil bath for $FA_{(1-x)}MA_xPbI_3$ (x = 0.8, 0.85, 0.9, 0.95, 1). Then the single crystals were collected and dried in the glovebox at 100 °C for 10 min.

Single crystal X-ray Diffraction: Big single crystal particles were measured by Supernova single-crystal diffractometer with graphite monochromator and Mo Kα ray (λ= 0.071073 nm), and SCALE3 ABSPACK was used by absorption correction.

Powder X-ray Diffraction: Crystal powder were grounded from single crystals in the glovebox and measured by the Rigaku D/MAX-2400 diffractometer with step of 0.02 ° and speed of 8 °/min in the air.

Nuclear Magnetic Resonance (NMR): Perovskite single crystals were dissolved in the dimethyl sulfoxide-d6 solvent to form a 25 mg/mL solution at room temperature. The solution was then transfered to the nuclear magnetic tube (America Wimad) with caps. NMR spectra were performed with the Bruker-500 MHz NMR.

Steady-state Photoluminescence (PL): PL spectra of fresh perovskite big single crystal particles were performed by the lifetime and steady state spectrometer FLS980 (Edinburgh Instruments Ltd) with 470 nm excitation wavelength.

Absorption: Absorption of perovskite big single crystal particles were measured by UV-Visible/NIR Spectrophotometer UH4150.

Space-Charge-Limited Current (SCLC) Measurement: The I–V curve was performed with the Keithley 4200 semiconductor characterization system in the dark and room temperature. Both

sides of the single crystals thin films cleaved from big particles (vertical structure) was deposited 80 nm Au to form the hole-only device, or pressed with In to form electron-only devices. For the measurement under vacuum, the device was evacuated under 3×10^{-4} Pa.

Current-voltage hysteresis Measurement: Ohmic contacts were deposited by thermal evaporation of 80 nm Au on one side of big single crystal particles with intervals. Then the devices were measured with the electrochemical workstation CHI660E in the dark. The voltage scan started from the initial voltage (0 V) to the high voltage (2 V), and then the low voltage (–2V), and ended at 0 V finally. The scan rate was 0.1 V/s and the sample interval was 0.001 V.

Photodetector I–V Curve: Au/big perovskite single crystal particles /Au planar photodetectors were illuminated with an Oriel 300 W solar simulator (Thermo Oriel 91160-1000) as an excitation source. KG5 silicon solar cell was used to calibrate the light intensity. Neutral density filters (Newport) with different OD value were employed to adjust the illumination intensity. The I–V relationship was recorded on a Keithley 2400 source meter.

Wavelength dependent photoresponsivity measurement: The big single crystal particles was performed by an Enli Technology (Taiwan) EQE measurement system, and the incident wavelength varied from 300 nm to 1000 nm with +2 V bias voltage.

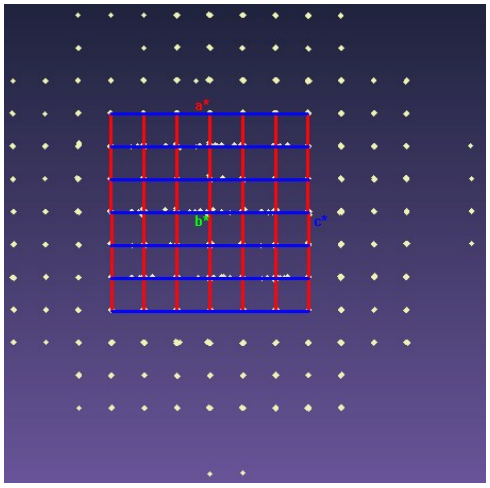

Figure S1. The *h0l* plane reflection of $FAPbI_3$ single crystal at 300K.

Table S1 The crystal data and structure refinement for $FAPbI_3$, $FA_{0.85}MA_{0.15}PbI_3$ and $FA_{0.15}MA_{0.85}PbI_3$.

Chemical formula	$FAPbI_3$
Formula weight /g mol^{-1}	632.96
Temperature /K	300
Crystal color	Black
Wavelength /Å	0.71073
Crystal system	Cubic
Space group	P-43m
a /Å	6.3691 (2)
b /Å	6.3691 (2)
c /Å	6.3691 (2)
□ /°	90
□ /°	90
□ /°	90
Volume /$Å^3$	258.365 (14)
Z	1
F(000)	266.0
Theta range (data collection)	4.53 to 29.52°
Limiting indices	−8 < = h < = 7, −8 < = k < = 8, −8 < = l < = 8
Reflections collected/unique	2719/165 [$R_{(int)}$ = 0.0344]
Completeness	98% (1.60 Å)
GOF on F^2	1.235
Absorption correction	Multi-scan
Data/restraints/parameters	165/1/8
R_1, wR_1 [I > 4σ(I)]	0.0125
R_1 (all data)	0.0125
wR_2	0.0343

$W = 1/[s^2(F_o^2) + (0.0190P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Chemical formula	$FA_{0.85}MA_{0.15}PbI_3$
Formula weight /g mol^{-1}	631.01
Temperature /K	300
Crystal color	Black
Wavelength /Å	0.71073
Crystal system	Cubic
Space group	pm-3m
a /Å	6.3749(4)
b /Å	6.3749(4)
c /Å	6.3749(4)
α /°	90
β /°	90
γ /°	90
Volume /Å^3	259.07(3)
Z	1
F(000)	265.0
Theta range (data collection)	5.54 to 26.04°
Limiting indices	−4 < = h < = 7, −7 < = k < = 7, −3 < = l < =7
Reflections collected/unique	407/76 [$R_{(int)}$ = 0.0332]
Completeness	97.4%
GOF on F^2	1.199
Absorption correction	spherical harmonics
Data/restraints/parameters	76/1/7
Refine 1s R factor all	0.0281
Refine 1s R factor gt	0.0281
Refine 1s wR factor ref	0.0595
$W = 1/[s^2(F_o^2) + (0.0391P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$.	

Chemical formula	$FA_{0.15}MA_{0.85}PbI_3$
Formula weight /g mol^{-1}	621.91
Temperature /K	300
Crystal color	Black
Wavelength /Å	0.71073
Crystal system	Cubic
Space group	pm-3m
a /Å	6.3191(2)
b /Å	6.3191(2)
c /Å	6.3191(2)
α /°	90
β /°	90
γ /°	90
Volume /Å^3	252.328(14)

Z	1
F(000)	261.0
Theta range (data collection)	4.56 to 29.57°
Limiting indices	−8 < = h < = 7, −8 < = k < = 8, −8 < = l < = 8
Reflections collected/unique	2576 /100 [$R_{(int)}$ = 0.0426]
Completeness	97.1%
GOF on F^2	1.182
Absorption correction	spherical harmonics
Data/restraints/parameters	100/1/7
Refine 1s R factor all	0.0259
Refine 1s R factor gt	0.0259
Refine 1s wR factor ref	0.0608

$W = 1/[s^2(F_o^2) + (0.0480P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$.

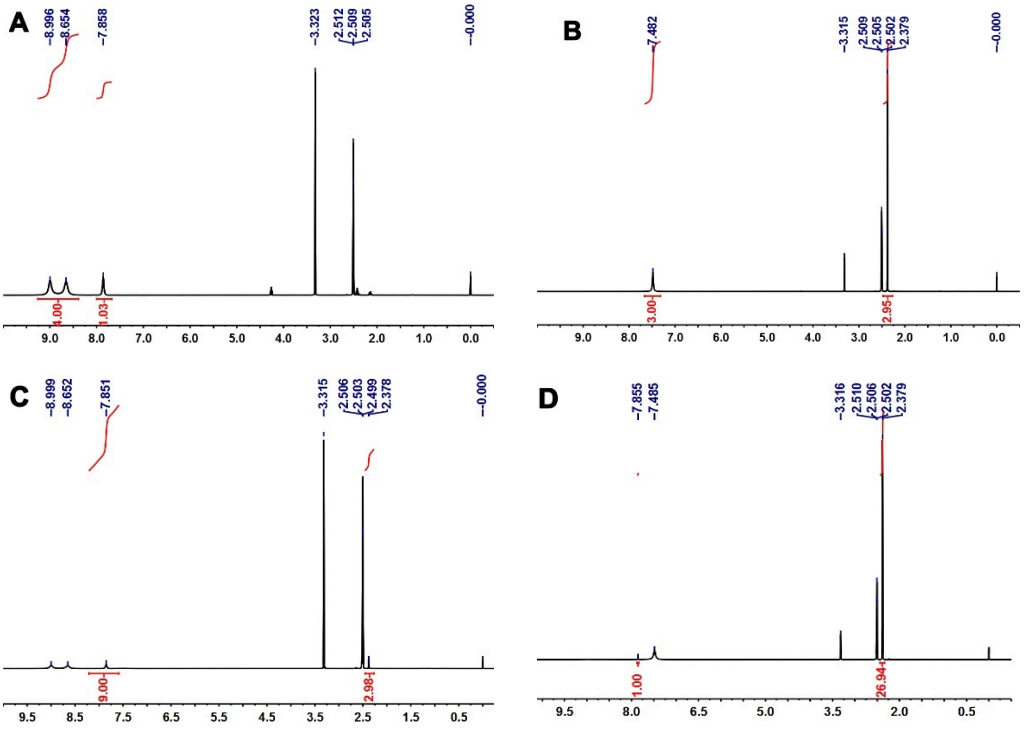

Figure S2. The HNMR spectra of (A) $FAPbI_3$ single crystal and (B) $MAPbI_3$ single crystal. (C) $FA_{0.9}MA_{0.1}PbI_3$, (D) $FA_{0.1}MA_{0.9}PbI_3$.

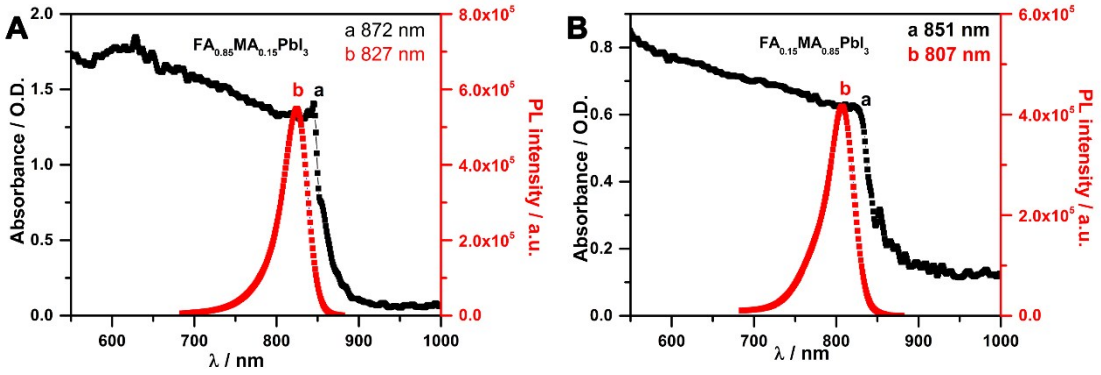

Figure S3. The PL emission spectrum and absorption spectrum of (A) $FA_{0.85}MA_{0.15}PbI_3$ and (B) $FA_{0.15}MA_{0.85}PbI_3$.

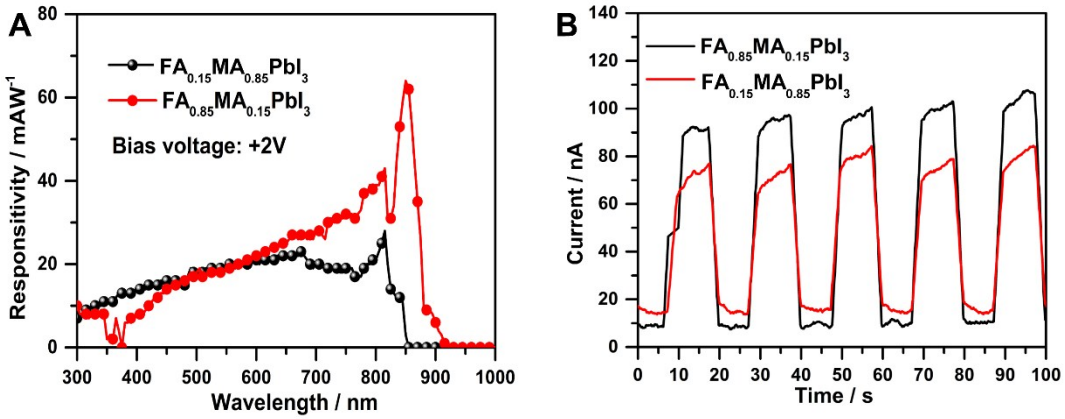

Figure S4. (A) Photoresponse of $FA_{0.85}MA_{0.15}PbI_3$ and $FA_{0.15}MA_{0.85}PbI_3$ photodetector under bias voltage of + 2V, (B) photoresponse to white light (91.2 mW/cm^2) under 0.05 Hz on/off frequency.

Reference

1. L. Etgar, P. Gao, Z. Xue, Q. Peng, A. K. Chandiran, B. Liu, M. K. Nazeeruddin and M. Gratzel, *J. Am. Chem. Soc.*, 2012, **134**, 17396-17399.