

Formamidinium Lead Halide Perovskite Crystals with Unprecedented Long Carrier Dynamics and Diffusion Length

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Supporting Information

Materials and Methods

Chemicals and reagents. Lead bromide ($\geq 98\%$), lead iodide (99.999% trace metal basis), DMF (anhydrous, 99.8%) and GBL ($\geq 99\%$) were purchased from Sigma Aldrich. MABr, FABr and FAI were purchased from Dyesol Limited (Australia). All salts and solvents were used as received without any further purification.

MAPbBr₃, FAPbBr₃ and FAPbI₃ single crystals were grown by Inverse Temperature Crystallization (ITC) technique from 1 M solution of PbBr₂/MABr in DMF, 1 M solution PbBr₂/FABr in DMF:GBL (1:1 v/v) and 0.8 M solution of PbI₂/FAI in GBL, respectively, as it was previously reported by *Saidaminov et al.*^{1,2}

Powder X-ray diffraction was performed on a Bruker AXS D8 diffractometer using Cu-K α radiation.

The steady-state absorption was recorded using a Cary 6000i UV-Vis-NIR Spectrophotometer with an integrated sphere in diffuse-reflectance mode.

The steady-state photoluminescence of FAPbBr₃ crystals was recorded using an Edinburgh Instruments FLS920 Spectrofluorometer, with 500 nm excitation wavelength.

The steady-state photoluminescence of FAPbI₃ crystals was recorded using a femtosecond laser system with ocean optics coupled fiber detector, with 1300 nm laser excitation pulse.

Photo-electron spectroscopy in air (PESA) was carried out on FAPbX₃ single crystals fixed on a glass substrate, using a Riken Photo-electron Spectrometer (Model AC-2). The power number was set at 0.5.

Space-charge-limited current (SCLC) measurement. The transport properties of FAPbX₃ single crystals were obtained by SCLC technique. Hole only devices were obtained by sputter

deposition of 80 nm gold electrodes on both sides (sandwich configuration) of the FAPbBr₃ (4.5 × 4.5 × 1.2 mm³) and FAPbI₃ (4.2 × 4.2 × 1.2 mm³) single crystals. The SCLC measurement was performed on the hole only device in the dark, under vacuum using a Keithley 2635A source-meter.

Time-resolved photoluminescence measurement on FAPbBr₃ crystals was performed using an Ultrafast Systems HALCYONE femtosecond fluorescence spectrometer, with 800 nm excitation wavelength.

High-Resolution X-ray diffraction (Rocking curves) on FAPbBr₃ and MAPbBr₃ single crystals was performed with a Bruker D8 Discover X-ray diffractometer.

Single crystal X-ray diffraction measurement was collected at 298(2) K, performed on a Bruker D8 Venture diffractometer with PHOTON 100 CMOS detector with an microfocus source (Cu-K α radiation, $\lambda = 1.54178$ Å). The computing cell refinement and data reduction were processed using APEX2 software. [SAINT-Plus; APEX2; SADABS, Bruker-AXS Inc.:Madison, Wisconsin, 2004] Crystal data, data collection parameters, and structure refinement details are given in **Table S1**. The structure was solved by direct methods with SHELXT.³ Subsequent difference Fourier calculations and full-matrix least-squares refinement against F² were performed with SHELXL using Olex2.^{3,4} All non-hydrogen atoms were refined with anisotropic displacement parameters.

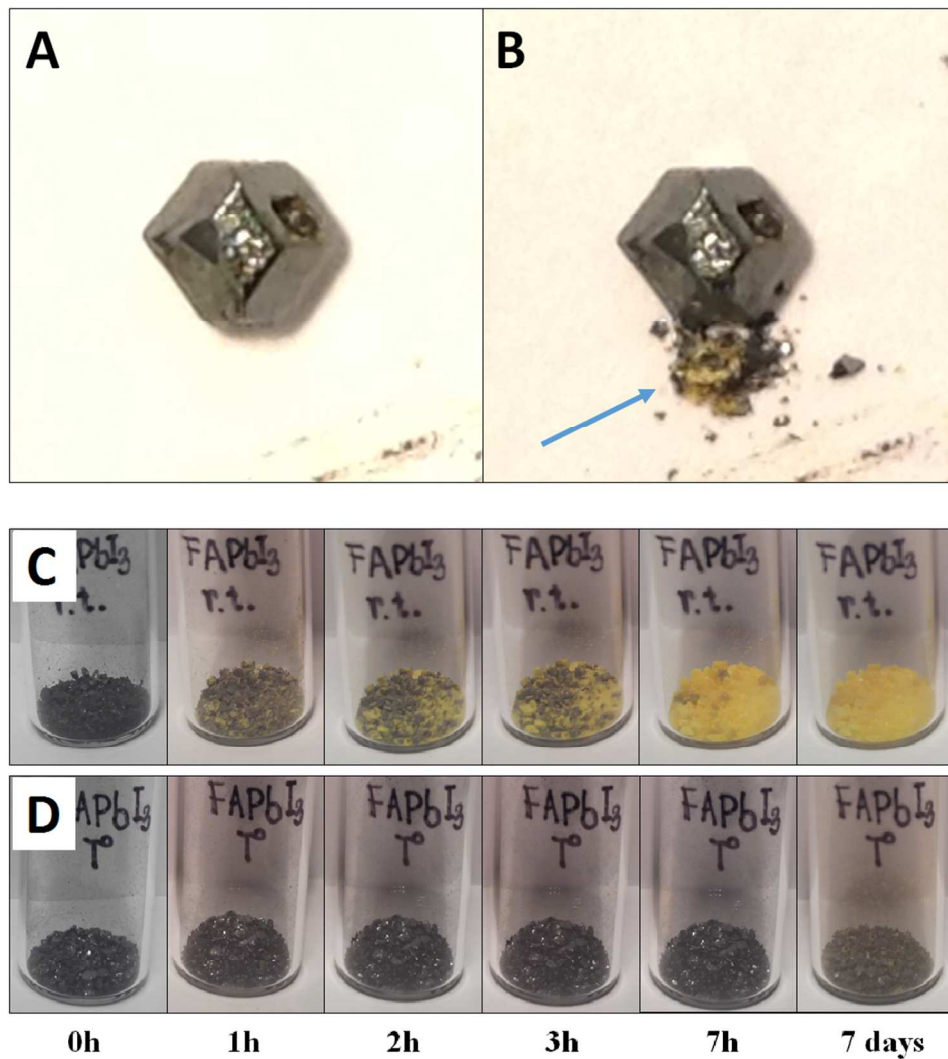


Figure S1. Crystal after 18 hours in the air: (A) before cutting and (B) after cutting from the edge. The yellow δ -FAPbI₃ non-perovskite phase is present in the bulk of the crystals (blue arrow). The color evolution of crashed (C) non-stabilized and (D) stabilized FAPbI₃ crystals with time.

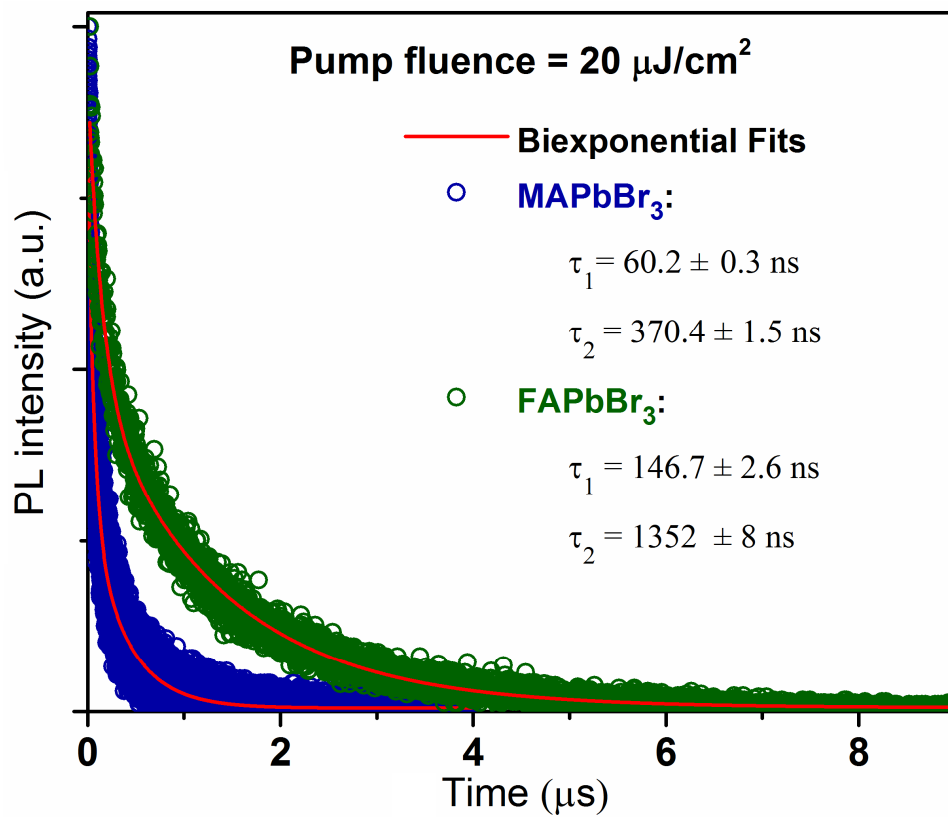


Figure S2. PL time-decay traces of FAPbBr₃ (green) and MAPbBr₃ (blue) crystals after 800 nm excitation with a pump fluence of 20 $\mu\text{J}/\text{cm}^2$.

Table S1. Single crystal XRD data.

Chemical formula	Pb₁I₃CN₂H₅	Pb₁Br₃CN₂H₅
M_r	632.98	491.98
Crystal system, space group	Cubic, $Pm-3m$	Cubic, $Pm-3m$
Temperature (K)	298	298
a (Å)	6.3573 (5)	5.9944 (12)
V (Å ³)	256.93 (4)	215.40 (7)
Z	1	1
Z'	0.02083	0.02083
$\Theta_{min,max}$ (°)	7.0, 72.7	7.4, 74.2
Radiation type	Cu-K α	Cu-K α
Crystal size (mm)	0.20×0.15×0.10	0.15×0.15×0.10
Diffractometer	Bruker <i>APEX</i> -II CCD diffractometer	Bruker <i>APEX</i> -II CCD diffractometer
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	658, 78, 78	406, 66, 66
R_{int}	0.078	0.064
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.619	0.624
Largest peak	19.23	3.77
Deepest hole	-8.98	-4.31
GooF	2.271	1.890
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.150, 0.395, 2.271	0.098, 0.183, 1.890
No. of parameters	11	14
No. of restraints	14	3

Computer programs used: SHELXS and SHELXL, OLEX2.^{3,4}

Single crystals of both materials have been obtained and their unit cells have been verified by single crystal X-ray diffraction. The unit cell dimensions as well as the space groups (for FAPbBr₃: cubic, space group $Pm-3m$, $a = 5.9944(12)$ Å; for FAPbI₃: cubic, space group $Pm-3m$, $a = 6.3573(5)$ Å) are in excellent agreement with literature reports.^{5,6}

References:

1. Saidaminov, M. I.; Abdelhady, A. L.; Murali, B.; Alarousu, E.; Burlakov, V. M.; Peng, W.; Dursun, I.; Wang, L.; He, Y.; Maculan, G.; Goriely, A.; Wu, T.; Mohammed, O. F.; Bakr, O. M. *Nat. Commun.* **2015**, *6*, 7586.
2. Saidaminov, M. I.; Abdelhady, A. L.; Maculan, G.; Bakr, O. M. *Chem. Commun.* **2015**, *51*, 17658.
3. Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122.
4. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339-241.
5. Hanusch, F. C.; Wiesenmayer, E.; Mankel, E.; Binek, A.; Angloher, P.; Fraunhofer, C.; Giesbrecht, N.; Feckl, J. M.; Jaegermann, W.; Johrendt, D.; Bein, T.; Docampo, P. *J. Phys. Chem. Lett.* **2014**, *5*, 2791-2795.
6. Weller, M. T.; Weber, O. J.; Frost, J. M.; Walsh, A. *J. Phys. Chem. Lett.* **2015**, *6*, 3209-3212.