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# **Supporting information**

## Blocking Wide Bandgap Mixed Halide Perovskites' Decomposition through Polymer Inclusion

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## **Chemicals**

Lead (II) iodide (PbI<sub>2</sub>, ultradry 99.999 % metals basis) and Gellan Gum (GG) were purchased from Alfa Aesar (Kandel, Germany) while Methylammonium iodide (CH<sub>3</sub>NH<sub>3</sub>I, MAI) and 4-fluoro-phenethylammonium iodide (4FPEAI) were purchased from GreatCell Solar. Dimethyl sulfoxide anhydrous, 99.9 % (DMSO); Toluene anhydrous, 99.8 % (TOL); Chlorobenzene 99.8% 2-propanol (IPA); PTAA anhydrous, (CB):  $[poly(bis \{4-phenyl\} \{2,4,6$ trimethylphenyl}amine)]; Bathocuproine, 96 % (BCP) were purchased from Sigma Aldrich. [6,6]phenyl C<sub>61</sub> butyric acid methyl ester (PCBM) was purchased from Nano-c. The Gellan Gum underwent a drying in process in oven at 60 °C for 5 days before the use. The water concentration was estimated by Thermogravimetric analysis (TGA, SDT Q600, TA instrument). The analysis was conducted heating ~10 g of polymer from room temperature to 900 °C at 10 °C/min speed under nitrogen inert atmosphere, before and after drying process. After the drying the polymer was stored in N<sub>2</sub> filled glove box. All the other materials were used as received without any further purification.

## Perovskite solution preparation

The perovskite solutions for the reference perovskite samples were obtained preparing mother solutions of MAPbI<sub>3</sub> 1M (MAI:PbI<sub>2</sub> = 1:1) and MAPbBr<sub>3</sub> 1M (MABr:PbBr<sub>2</sub> = 1:1) employing an equivalent molar concentration of DMSO and DMF as solvent, which were then stoichiometrically mixed together for the MAPb( $I_{1-x}Br_x$ )<sub>3</sub> formulations.

For the GG additivated perovskite solutions were prepared mother solutions of MAPbI<sub>3</sub> 1M and MAPbBr<sub>3</sub> 1M using DMSO as solvent. Then, these were stoichiometrically mixed together for the MAPb( $I_{1-x}Br_x$ )<sub>3</sub> formulations and at each solution was added GG powder at a concentration of 12 mg/ml leaving under stirring at 80 °C for 3 h.

The solutions were stored in N<sub>2</sub> filled glove box after the preparation.

# Perovskite film deposition and characterization

Reference MAPb $(I_{1-x}Br_x)_3$  solutions were deposited via antisolvent engineering in N<sub>2</sub> filled glove box by spin coating at 4000 rpm for 25 sec (1000 rpm acceleration) using Toluene as antisolvent (at the 10<sup>th</sup> second from the start) followed by an annealing step of 100 °C for 15 min.

 $MAPb(I_{1-x}Br_x)_3$  film produced via Polymer Mediated Crystallisation were obtained depositing the GG additivated solutions by spin coating in N<sub>2</sub> filled glove box at 9000 rpm for 20 sec (1000 rpm acceleration) following an annealing step of 100 °C for 45 or 60 min.

The Scanning Electron Microscopy (SEM) analysis were conducted by Carl Zeiss Auriga40 Crossbeam (Zeiss) instrument in high vacuum and high-resolution mode, equipped with Gemini column and an integrated high efficiency in-lens detector. A 5 kV voltage acceleration was applied. The film thickness was measured using Dektak 150 optical profilometer (Dektak).

The XRD spectra of perovskite films were measured with a PAN analytical X'Pert-PRO Materials Research Diffractometer using graphite-monochromated CuK  $\alpha$  radiation ( $\lambda = 1.5405$  Å). XRD and thickness measurements were carried out at room temperature in ambient air condition.

The absorption spectrum was analysed by PerkinElmer Spectrophotometer (Lambda 1050) in the 400-800 nm range and the Optical Energy Gap was determined by Tauc Plot method.

Digital photo acquired by iPhone XR without any post-production process.

#### Device fabrication and characterization

15x15x1.1 mm ITO patterned glass substrates were cleaned prior to use by ultrasonication baths with deionized water, acetone, 2-propanol, 10 min. at room temperature for each step, and then dried by N<sub>2</sub> flow.

PTAA was selected as hole transporter layer, 4FPEAI as interlayer between PTAA and perovskite while PCBM and BCP were selected as electron transport layer and hole blocking layer, respectively. The deposition parameters were: 6000 rpm for 30 sec followed by 100 °C x 10 min annealing for 1.5 mg/ml Toluene PTAA solution, 4000 rpm for 25 sec followed by 100 °C x 1 min annealing for 20 mM 4FPEAI solution, 1000 rpm for 60 sec for 25 mg/ml Chlorobenzene PCBM solution and 6000 rpm for 20 sec for 0.5 mg/ml 2-propanol BCP solution. All materials were deposited in N<sub>2</sub> filled Glove Box (< 0.1 ppm [O.2], < 0.1 ppm [H<sub>2</sub>O]) except for PTAA. 80 nm Ag were thermally evaporated (Lesker Co. instrument) in high vacuum (5x10<sup>-6</sup> mBar) as cathode top electrode, with a deposition rate of 0.6 A/s and employing a mask that define a 0.04 cm<sup>2</sup> active area.

The photovoltaic device J-V Characteristics were acquired in  $N_2$  atmosphere at 25 °C by a Keithley 2400 Source Measure Unit under an irradiation intensity of 100 mW/cm<sup>2</sup>, employing an Air Mass 1.5 Global (AM 1.5 G) Solar simulator (Newport 91160A, periodically calibrated lamp). J-V scan were performed in voltage ranging from 1.2 V to -0.2 V in both reverse and forward direction.

Maximum Power Point Tracking were carried out in N2 filled glove box under continuous 1 SUN illumination while the External Quantum Efficiency was measured in ambient air condition.

## Photo-stability and halide segregation

Photo-stability was probed by irradiating the sample at a wavelength of 500 nm, by Laser pulses of 7 ns (width) and an average power of 8.4 mW, at a repetition frequency of 20 Hz. Each sample was pumped for 120 minutes. PL spectra were acquired by exciting the sample at a 430 nm, at steps of 20 minutes and at an average light intensity of 2.4 mW.

The measurements were conducted at room temperature in ambient air condition.

## PL Mapping

Room-temperature micro-PL images and spectra were collected in transmission configuration, using a home-built microscope equipped with two objectives. Photoluminescence was excited through a 10X objective with a continuous wave excitation (488 nm) and the PL signal is collected by a 40X microscope objective.

The signal from the sample was projected on the entrance slits of a spectrometer (Acton Spectra Pro SP-2300, Princeton Instruments, USA) and coupled to a Charge Coupled Device (CCD Pixis eXcelon 400, Princeton Instruments, USA), which allows collecting either real space reflectivity/PL maps or energy-resolved maps. The full width half maximum of the excitation spot in real space was ~ 50  $\mu$ m<sup>2</sup> and the laser power was opportunely reduced by using neutral filters, to obtain a density

excitation ~ 0.025 W/mm<sup>2</sup>. Optical measurements were carried out in laboratory environment conditions (temperature = 22 °C; relative humidity = 55%).

## THz time-domain spectroscopy

Terahertz (THz) pulses are generated by optical rectification in a 1mm-thick ZnTe crystal, driven by a Ti:sapphire laser with a repetition rate of 1 kHz. The THz electric field transient transmitted through the sample is reconstructed in the time-domain by electro-optical sampling. Each measurement on the perovskite sample was immediately followed by a measurement on a clean part of the reference fused silica substrate, in order to exclude systematic errors due to fluctuations of the laser spectrum. The setup is closed in a chamber purged with nitrogen gas to minimize the THz absorption by water vapor. The transmitted THz waveforms are then Fourier-transformed, obtaining complex spectra in the frequency domain. The ratio between the sample and the corresponding reference spectrum gives the complex transmission function T. This is eventually used to compute the THz complex conductivity by the thin-film approximation formula:

$$\sigma = \frac{n_a + n_{sub}}{Z_0 d} \left(\frac{1}{T} - 1\right)$$

Where  $n_a = 1$ ,  $n_{sub} = 2.2$  are the refractive indices of air and substrate,  $Z_0 = 376.7 \Omega$  is the impedance of free space and d is the thickness of the film. A correction factor  $exp(i\omega n_{sub}\Delta L/c)$  is applied to the transmission to consider the substrate-thickness mismatch between the sample and reference measurements.



**Figure S0 THz-TDS transmission and conductivity.** (a) Amplitude and phase of the complex transmission function for the sample x=0.4 prepared via PMC. (b) Real and imaginary part of the conductivity retrieved from the transmission in figure (a) by the thin-film approximation formula.

The results of multiple scans are then averaged in the frequency domain and the standard errors on the real and imaginary parts are computed and represented in the plots by error bars. An example of the (corrected) transmission function and of the corresponding conductivity is reported in the figure. The samples are irradiated using a continuous-wave laser at 532 nm. The average power impinging on the sample is 0.1 W distributed on a spot with a diameter of  $\sim$ 5 mm. The 532 nm beam is kept open during the whole data acquisition.



Figure S1. SEM analysis of reference MAPb( $I_{1-x}Br_x$ )<sub>3</sub>, images at low magnification. Scale bar 1  $\mu$ m



Figure S2. SEM analysis of reference MAPb(I<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub>, images at high magnification. Scale bar 300 nm.



Figure S3. SEM analysis of via PMC MAPb(I\_1-xBr $_x$ )<sub>3</sub>, images at low magnification. Scale bar 20  $\mu$ m



Figure S4. SEM analysis of via MAPb(I<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub>, images at high magnification. Scale bar 300 nm



Figure S5. XRD analysis of MAPb( $I_{1-x}Br_x$ )<sub>3</sub> via PMC at 30 min. of annealing.



**Figure S6. XRD analysis of MAPb**( $I_{1-x}Br_x$ )<sub>3</sub> via PMC to evaluate the best annealing condition. At a) 30 min. are detected signals referred to PbI<sub>2</sub> and adducts between PbI<sub>2</sub> and DMSO, at b) 45 min. occur the complete conversion from perovskite precursors to perovskite while at c) 60 min. is starting the perovskite degradation.



Figure S7. XRD analysis of MAPb( $I_{1-x}Br_x$ )<sub>3</sub> via PMC based on the proper annealing condition.



**Figure S8. Estimation of optical bandgap.** a-f) Absorption spectra of Reference mixed halides perovskite obtained via antisolvent engineering. The Energy Gap of each formulation based on the different I:Br ratio was determined applying the Tauc Plot method.

	MAPb(I <sub>1-x</sub> Br <sub>x</sub> ) <sub>3</sub>			
x	Eg (eV)			
	Refence	Via PMC		
0	1.6	1.6		
0.1	1.64	1.65		
0.2	1.7	1.7		
0.3	1.77	1.76		
0.4	1.83	1.83		
1	2.32	2.3		

Figure S9. Eg values of reference and via PMC perovskite.

		FF (%)	Voc (V)	Jsc (mA/cm²)	PCE (%)	
x= 0	Reference	73.1	1.058	21.41	16.56	Best
		73.10	1.03	20.33	15.26	Average
		2.78	0.03	1.35	0.91	Dev. St.
	via PMC	74.6	1.072	21.24	16.98	Best
		75.05	1.06	19.64	15.60	Average
		2.19	0.02	1.03	0.99	Dev. St.
x= 0.1	Reference	78.2	1.045	20.57	16.82	Best
		77.84	1.04	18.74	15.18	Average
		1.17	0.02	1.77	1.31	Dev. St.
	via PMC	77	1.097	20.95	17.69	Best
		73.39	1.09	19.74	15.72	Average
		2.28	0.03	1.19	1.09	Dev. St.
x= 0.2	Reference	80	1.12	20.02	17.94	Best
		77.84	1.07	19.43	16.19	Average
		2.70	0.05	1.34	0.79	Dev. St.
	via PMC	72.8	1.104	20.36	16.37	Best
		73.64	1.09	18.99	15.24	Average
		2.70	0.04	0.98	0.65	Dev. St.

Figure S10. Best, average, and standard deviation values of performance recorded from x= 0, x= 0.1, x= 0.2 perovskite for both Reference and via PMC formulations. Data from 60 devices.



**Figure S11. Figure of merit and performance analysis.** a) J-V scans of MAPb $(I_{1-x}Br_x)_3$  based device at x=0, acquired in both reverse and forward condition; b) Maximum Power Point Tracking under continuous illumination (1 sun) of device based on different Br concentration; c) Incident Photon to Current Efficiency and integrated short circuit current.



**Figure S12.** Photoaging of x= 0.4 a) reference and b) via PMC perovskite. Unnormalized data of the recorded blue-shift emission.



Figure S13. Perovskite degradation and irreversible blueshift under pulsed light illumination. Reference perovskite analyzed after one week of storage in  $N_2$ -dark condition.



**Figure S14. Reversible redshift emission under continuum light illumination.** Data of both a) reference and b) via PMC perovskite from initial state, after 135 s of illumination and keeping the sample in dark for 2 minutes after the illumination (recovery). The curves have been rescaled for a better visualization.



**Figure S15. Focus on the centroid position of emissions' peaks cropped from Fig. 3.** A slightly different behavior is shown between reference e via PMC perovskite.