

Electronic Supplementary Information (ESI)

Large Area Perovskite Light Emitting Diodes by Gas-Assisted Crystallization

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1. Experimental Section

Materials: Small molecule transport materials, Di-NPB and BmPyPhB were purchased from Lumtec Corp.. PEDOT:PSS (Clevios P AI4083) was purchased from Heraeus. Methylammonium bromide (MABr) and Lead(II)bromide (PbBr₂) were purchased from Sigma Aldrich and Greatcellsolar, respectively. All solvents were purchased from Sigma Aldrich. All materials and solvents were used as received.

Perovskite synthesis: The perovskite precursors were prepared by dissolving desired ratios (1:1, 1.5:1, 2:1, 2.5:1 or 3:1) of MABr and PbBr₂ in DMSO resulting in total molar concentrations of 0.27 M (for slot-die coating) or 0.8 M (for spin-coating) solution. The solutions were stirred with a magnetic stirrer at 50°C overnight before using.

Substrates and Device Preparation: Small glass substrates with pre-patterned indium tin oxide (ITO) were purchased from Naranjo B.V. Large area substrates (15.2 × 15.2 cm²) were prepared by sputtering ITO in a KDF 744 to form a 135 nm thick layer with a sheet resistance of 20 Ω/sq. The ITO was then patterned using photolithography, by exposing AZ1518 (Microchemicals GmbH) photoresist to 365 nm UV light (LVA 204, Mega electronics) through a mask. The exposed part was developed with AZ developer (Merck GmbH) and rinsed with water to remove the exposed parts. ITO was etched in a FeCl₃/HCl bath (0.35 M in 18% HCl). Then the remaining photoresist was removed by washing with acetone, resulting in a substrate with 9 ITO patterned devices. The final active area of each device is 4.46 cm². All glass substrates were washed with soap (1% Teepol) and deionized water in an ultrasonic bath followed by a megasonic bath. The substrates were then treated with O₂ plasma for 3 minutes at 900 W in a Branson S2100 Plasma system. The desired amount of PEDOT:PSS was filtered through a 0.45 μm polyvinylidene difluoride filter and used as required. Di-NPB (HTL) was dissolved in toluene at 0.6 wt/v% concentration and filtered through a 0.2 μm PTFE (polytetrafluoroethylene) filter and used as required. The HTL was treated with N₂ plasma for 30 s in case of small substrates and 1 minute for large substrates at 1000 W power in a PVA Tepla 400 plasma system before coating the perovskite layer. After coating the perovskite layer, by either spin-coating or slot-die coating, the substrates were transferred into a thermal evaporator (Lesker) where 30 nm of BmPyPhB, 1 nm of lithium fluoride and 100 nm of aluminum were consecutively deposited through a mask at a pressure of < 1 × 10⁻⁶ mbar.

Small area PeLED Coatings: PEDOT:PSS was spin-coated at 1700 rpm and annealed at 130°C for 15 minutes resulting in a 50 nm dry film. Di-NPB was then spin-coated at 1100 rpm in a glovebox and annealed at 110°C for 15 minutes to result in a ~30 nm film. Then, in a glove box, the perovskite films (0.8 M) were deposited from 70 μL of the precursor solution initially at 1000 rpm. The spin speed was then ramped up to 5000 rpm and while still spinning, the gas-quenching process was initiated using a nitrogen gun held at 3 cm above the substrate at various delay timings as desired, at set gas inlet pressures (2 bar, 4 bar or 6 bar). The coated substrates were immediately annealed at 80°C for 2 minutes in the glovebox.

Large area PeLED Slot-Die Coating: Slot-die coating was done using an nTact nRAD 1 coater. The PEDOT:PSS layer was slot-die coated under ambient environment and dried in a convection oven at 50°C for 7 minutes and then annealed on a hotplate at 130°C for 10 minutes to result in a 100 nm layer. The HTL was slot-die coated using another nTact nRAD 1 coater inside a glovebox

under nitrogen environment and annealed at 110°C for 15 minutes to result in a ~60 nm film. The perovskite precursor (0.27 M) solution was then slot-die coated on top of the N₂ plasma treated HTL using the same equipment, with a clean slot-die head. The slot-die coating speed and flow rate were adjusted as required to tune the final layer thicknesses. Right after the end of the coating, gas quenching was initiated using a 15 cm long air knife (ExAir) held at 3 cm above the substrate at 6 bar gas inlet pressure. The air knife was manually moved back and forth over the substrate area at a rate of ~300 mm/s for 60 s to result in the MAPbBr₃ film. The coated substrates were then annealed at 80°C for 2 minutes inside the glovebox.

Absorption measurement: The absorption spectra were measured in a Cary 5000 UV-Vis-NIR spectrometer at a step rate of 1 nm with a continuous N₂ gas flow in the measurement chamber. MAPbBr₃ films spin-coated using gas-quenching on an ITO deposited small glass substrate were used for this measurement.

Photoluminescence (PL) measurement: The MAPbBr₃ films spin-coated using gas-quenching on an ITO-coated small glass substrate were loaded into a quartz encapsulation box. A 405 nm LED (Thorlabs) with a power of 135 mW/cm² at the substrate; was used to photo-excite the sample inside the quartz box. The PL emission was measured using an Avantes AVS-Desktop spectrometer.

AFM and Thickness: MAPbBr₃ films were spin-coated using the gas-quenching method on a 30 nm layer of Di-NPB to replicate the device morphology. The Dimension Fast Scan (Bruker) AFM sample hood was maintained at a relative humidity level of <0.1 % by continuously flushing with N₂ gas. The samples were then quickly loaded into the hood and the scans were performed, using a Si probe in tapping mode (k 4 N/m, frequency 350 kHz). The perovskite layer thicknesses were measured using a Veeco Dektak150 surface profilometer.

2. Supporting Figures

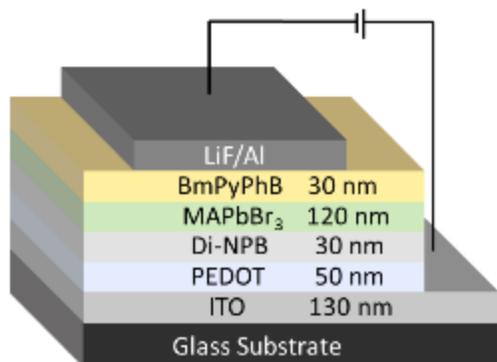


Fig. S1: Schematic illustration of the PeLED device stack used in this work. The PEDOT:PSS, Di-NPB and MAPbBr₃ layers are solution deposited whereas the BmPyPhB layer and the cathode are thermally evaporated for all devices.

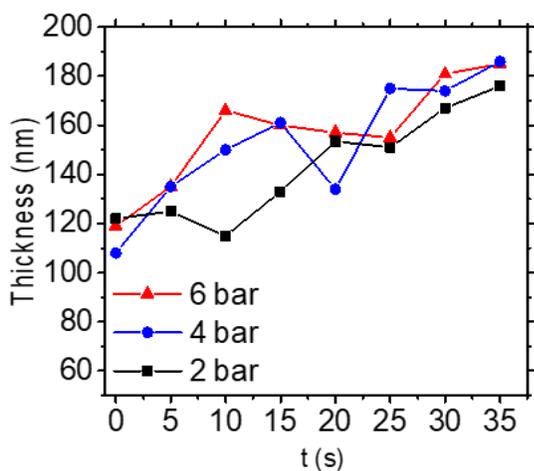


Fig. S2: The thickness of various the MAPbBr₃ films measured using a profilometer as a function of gas-quenching delay timings (t) at three different gas flow pressures.

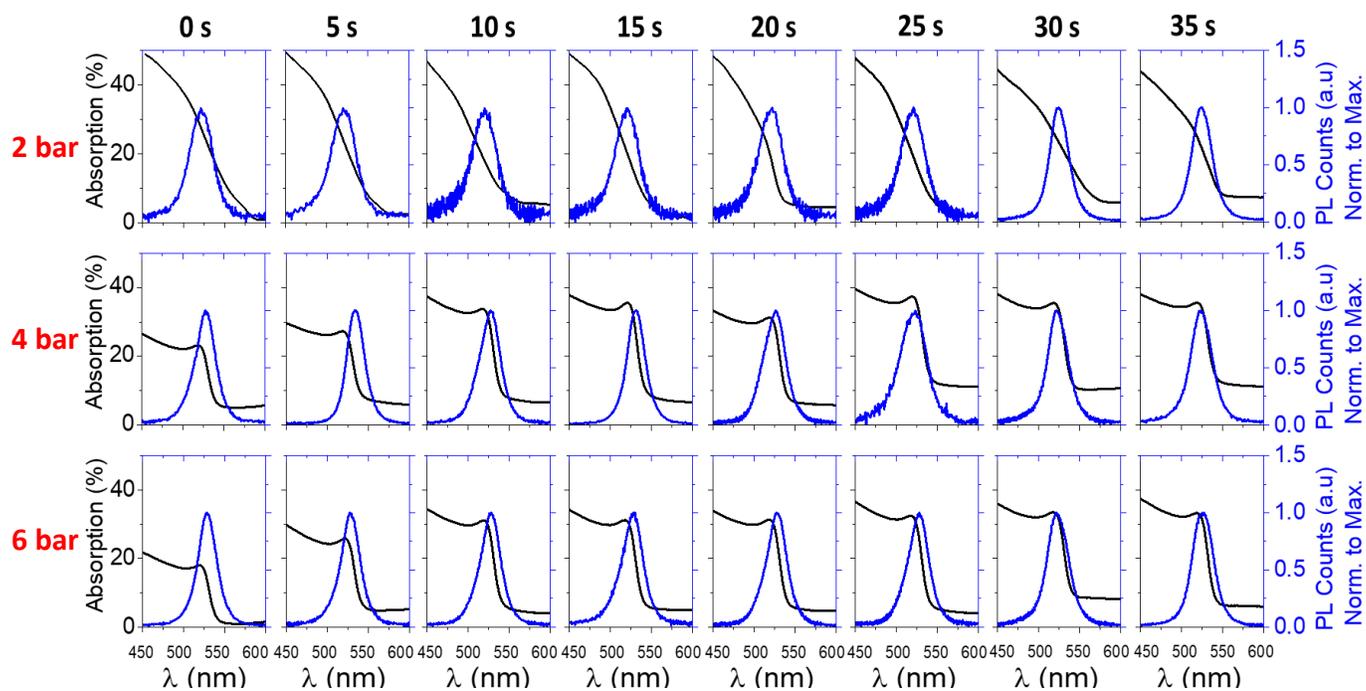


Fig. S3: Absorption (black line, left axis) and photoluminescence (PL) spectra (blue line, right axis) of the MAPbBr₃ films used in this work. The various delay timings are indicated at the top of the images in black color. The various gas-pressures are indicated on the left side in red color.

The absorption band edges of all the films are located at ~540 nm and an excitonic absorption peak is visible at 520 nm for 4 and 6 bar gas-pressures. The excitonic absorption feature is absent for the 2 bar gas-pressure. There is no shift in the band edge with varying delay timings and gas-pressures. The PL peaks have their maxima at around ~530 nm for all delay timings and gas-pressures.

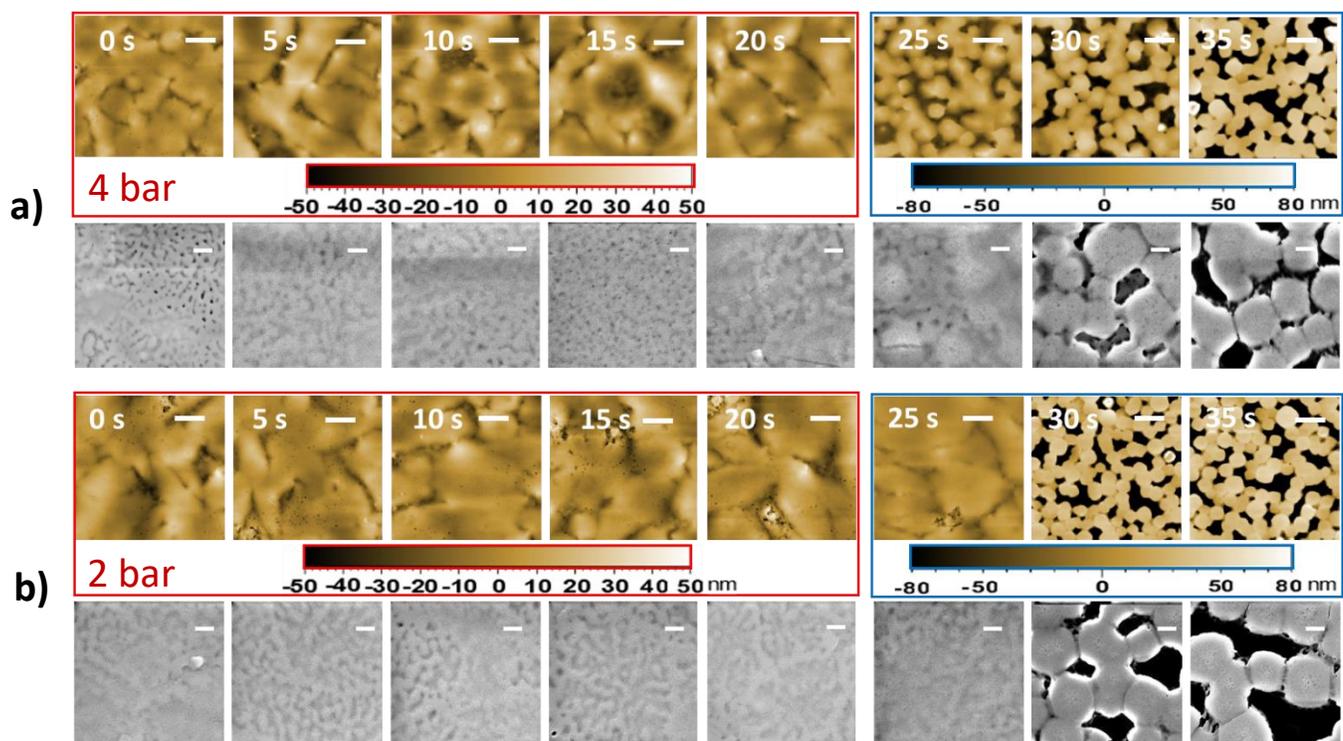


Fig. S4: AFM images of the MAPbBr₃ films prepared by gas-quenching and their corresponding SEM images placed underneath for various delay timings, marked on the top left corner of the AFM images for (a) 4 bar gas pressure and (b) 2 bar gas pressure. The scale bars in the AFM images represent 2 μm. The z-axis roughness scale is provided at the bottom of the images grouped together by the colored box (red or blue). The scan area of the images is 10 μm × 10 μm. The scale bars in the SEM images represent 400 nm.

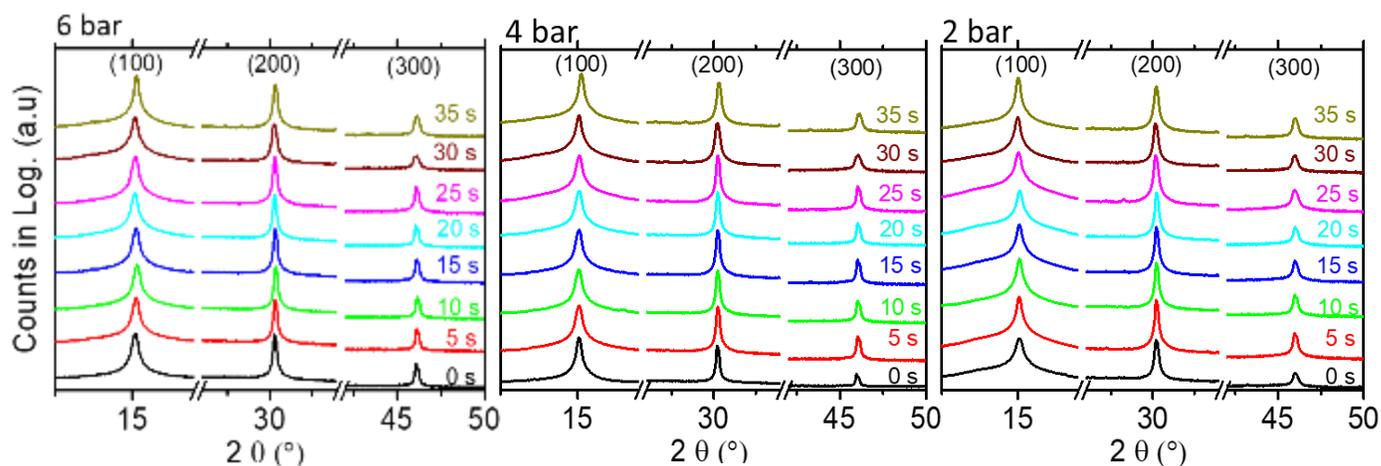


Fig. S5: XRD spectra of the MAPbBr₃ films prepared by gas-quenching used in this work plotted in logarithmic scale. The gas pressures are indicated on the top left corner of the images and the delay timings are indicated in the plot with different colors. The XRD spectra were collected from perovskite films coated on top of a PEDOT:PSS/Di-NPB bilayer to mimic the device morphology.

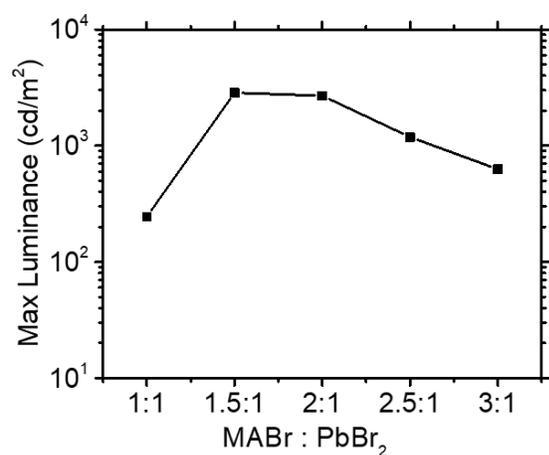


Fig. S6: Maximum luminance obtained from the PeLEDs as a function of the ratio of MABr:PbBr₂ in the precursor solution. The PeLEDs were made by gas-quenching with a delay time of 15 s and at a gas pressure of 6 bar. Each data point represents the mean value over 3 different devices.

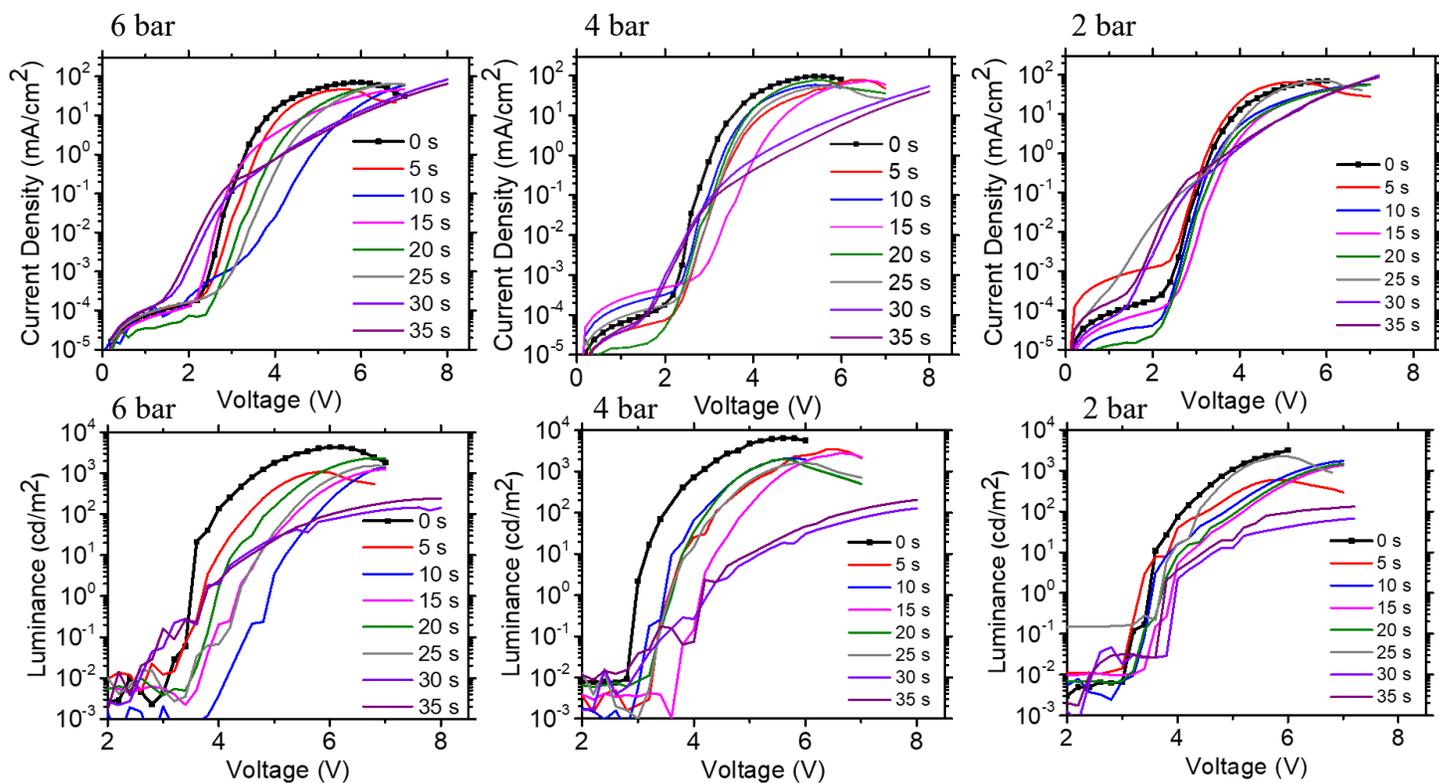


Fig. S7: The current density-voltage and luminance-voltage characteristics of the spin-coated small area (16 mm²) PeLEDs made by gas-quenching at various gas pressures and delay timings. The data of one representative PeLED is shown for each case. The gas pressures are indicated on the top left corner of the images and the delay timings are indicated within the plot with different colors. The best performing devices, those with delay time of 0 s, are highlighted (black line with marker). The current density and the luminance drops gradually with increase in delay timings from 0 s to 35 s for all cases. Particularly in the case of delay timing above 25 s the luminance drops to insignificant values and a large leakage current below 2 V is visible.

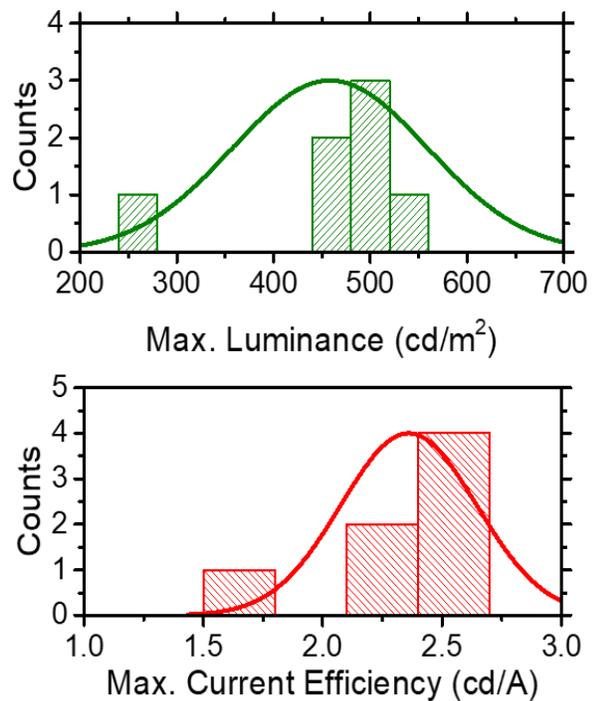


Fig. S8: Histograms of maximum luminance and maximum current efficiencies measured for 7 working PeLEDs (out of 9) from a single slot-die coated substrate.