Supporting Information

Effective Ion Mobility and Long-Term Dark Current of Metal-Halide Perovskites of Different Crystallinity and Composition

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| Table S1. Characteristics of the samples studied | | | | | | | |
|--|-------------------------|---------------|----------------------|-----------------------------|--|--------------------------|---------------------------------|
| Sample Composition | Number of samples | Cristallinity | Dimensions | Sample thickness (µm) | Electrode configuration and area | Picture of the sample | Picture of the electrodes |
| MAPbI ₃ | 6 | МС | diameter ~15 mm | ~1000 | Pt/Cr ~ 1cm ² | \mathbf{O} | Cr/Au Pt |
| MAPbBr ₃ | 2 | МС | diameter ~15 mm | ~1560 | Pt/Cr ~ 1cm ² | \bigcirc | Pt Ċr/Au |
| MAPbBr ₃ | 2 | SC | 3.93 mm × 3.87 mm | ~2000 | Cr/Cr ~ 0.12 cm ² | Cr | Cr |



Figure S1 Example on current transient response to short-circuit condition (0 Vbias voltage) of a a) MAPbI₃ MC sample contacted with Pt/Cr electrodes b) a MAPbBr₃ SC symmetrically contacted with evaporated Cr electrodes. Short circuit current



Figure S2. Protocol of measurement based on long-time current transient's response to different voltage steps of a) a 2.2 mm MAPbBr₃ SC- symmetrically contacted with evaporated Cr electrodes and two samples of b) MAPbBr₃ MC and c) MAPbI₃ MC contacted with Pt/Cr electrodes. Note the reproducibility between cycles.



Figure S3. Long-time current transient response to different voltage steps during the 1^{st} and b) 2^{nd} cycle of measurement of a 2 mm-thick MAPbBr₃ SC.



Figure S4. Long-time current transient response to different voltage steps during the 2^{nd} and b) 3^{rd} cycle of measurement of a 1.5 mm-thick MAPbBr₃ MC.



Figure S5. Long-time current transient response to different voltage steps during the 2^{nd} and b) 3^{rd} cycle of measurement of a 1 mm-thick MAPbI₃ MC.



Figure S6. Current–voltage characteristics (*j*-*V*) with scan rate of a) 500 mV/s and step of 1 V of 1 mm-thick MAPbI₃ MC sample b) 500 mV/s and 100 mV/s and step of 1 V of firstly, a 2 mm-thick MAPbBr₃ SC and secondly a 1.5 mm-thick MAPbBr₃ MC. In Fig b it is remarkable the ohmic character of the characteristics *j*-*V* curve, in agreement with previous analysis on Cr-contacted perovskite device¹



Figure S7. Rotation XRD spectra along α cell axis of a crystal measured with Cu radiation. In here only dots appear and the absence of concentric circles supports the

monocrystalline nature of the crystal. However, is evident the high symmetry observed in the material around one axis



Figure S8. a) Absorbance spectra of MAPbI₃ MC sample Inset: Tauc-plot of the pellet (thickness ~1000 μ m), showing the typical absorption edge of MAPbI₃ in 1.60 eV b) PXRD pattern of MAPbI₃-MC sample confirming a single-phase sample with tetragonal symmetry at room temperature. The film show the (110), (220), and (310) peaks at 14.1°, 28.4°, and 32.1°, respectively. These values are in good agreement with the reported values²⁻³ c) and d) SEM images of the top view of a MAPbI₃ thick pellets showing the microcrystalline nature of the sample at different magnified areas.



Figure S9. a) Image of the PXRD diffractogram of MAPbBr3-MC sample showing cubic crystal lattice (Pm3m space group). The diffractogram show the (100), (110), and (200) (210) peaks at 15.0°, 21.21°, and 30.12 ° and 33.78 ° respectively. These values agree with those found in the literature.⁴⁻⁶ SEM images of the top view of a b) of MAPbBr3-SC sample after a polishing procedure and a c) of MAPbBr3-MC sample

showing a different surface morphology d) Transmittance spectra of MAPbBr3-SC via UV-visible spectroscopy (SC thickness = 2.0 mm) In the inset: Tauc plot of MAPbBr3-SC for band gap determination ($E_q = 2.18 \text{ eV}$)

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