Electronic Supplementary Information

Mixed ionic-electronic conduction in Ruddlesden-Popper and Dion-Jacobson layered hybrid perovskites with aromatic organic spacers

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1. Materials and Methods

Commercial materials: Benzylammonium (BzA) iodide spacers were commercially available and acquired from Sigma Aldrich, whereas 1,4-phenylenedimethyleneammonium (PDMA) iodide spacers were synthesized based on the previously reported procedures.¹ PbI₂ inorganic salt with 99.999% purity was bought from Alfa Aesar and PbBr₂ with >98% purity from TCI. Organic solvents dimethyl sulfoxide (DMSO) with 99.7% purity and dimethylformamide (DMF) with 99.8% purity were acquired from Acros Organics.

Sample preparation: Thin films of layered hybrid perovskites based on n = 1 benzylammonium (BzA) spacer, which results in RP type (BzA)₂PbI₄ structure, and 1,4-phenylenedimethanammonium (PDMA) spacer, forming DJ (PDMA)PbI₄ perovskites were prepared as follows.¹ The corresponding samples were prepared from perovskite solutions, which were obtained by dissolving stoichiometric quantities of (BzA)I and PbI₂ in dimethylformamide (DMF) or (PDMA)I₂ and PbI₂ in 4:1 (v:v) DMF: dimethyl sulfoxide (DMSO) to yield 0.4 M (BzA)₂PbI₄ and (PDMA)PbI₄ solutions, respectively. The precursor solutions were thereafter spin-coated at 1000 rpm for 10 sec and 4000 rpm for 20 sec and subsequently annealed for 10 min at 100 °C (BzA)₂PbI₄ and 150 °C (PDMA)PbI₄ under argon. Quartz substrates with gold interdigitated electrodes were used for the electrical measurements with a total overlap area between electrode fingers of 0.0016 cm² and the distance between each electrode of 10 µm.

X-Ray diffraction measurements were carried out using a PANalytical Empyrean Series 2 instrument in Bragg-Brentano configuration with Cu K α radiation at 40 kV voltage and 40 mA current. A nickel filter was used to reduce the K β contribution.

UV-Vis measurements were performed using a Shimadzu UV-2600 spectrophotometer.

Electrochemical measurements: the electrical properties of the materials were investigated using galvanostatic polarization measurements,² performed with a Keithley 2634B instrument, and impedance spectroscopy, using a Novocontrol impedance analyser. Measurements were performed in the dark under argon or under a fixed iodine partial pressure using argon as carrier gas. The samples were loaded in a quartz cell which enabled control of the temperature and access to the electrodes of the devices. Multiple measurements were taken to ensure stabilization of the sample at any given condition. The interpretation of the data followed previous work.^{3,4} Briefly, the total conductivity of the sample was assessed based on the high frequency feature measured with impedance spectroscopy. As discussed in the main text, such feature did not correspond to a single semicircle. In most cases, two R-C elements (R1-C1 and R2-C2) were fitted to the data, to obtain the total resistance as $R_{tot} = R_1 + R_2$. The total conductivity was then extracted based on $\sigma_{tot} = \frac{1}{R_{tot}} \frac{L}{Wd}$, where W is the total overalp between the Au finger contacts and d is the thickness of the film (about 200 nm, see SEM measurement below). The electronic conductivity was extracted from the long-time scale DC polarization measurement. Finally, the ionic conductivity was estimated based on $\sigma_{ion} = \sigma_{tot} - \sigma_{eon}$.

Measurements performed under controlled iodine partial pressure involved argon used as carrier gas flowing in an evaporator containing iodine pellets. The temperature of the evaporator was controlled with a thermostat and the temperature was adjusted to achieve the desirable thermodynamic iodine vapour pressure. The gas was flown in the measuring cell containing the devices. For the data displayed in Figure 3a–b, the following iodine partial pressure protocol was used: first scan $P(I_2) = (6.9, 25, 82, 6.9) \times 10^{-7}$ bar; second scan (6.9, 3.5, 140, 46, 25, 13, 6.9) × 10⁻⁷ bar. For the data displayed in Figure 3c–d, the samples were measured in argon and at $P(I_2) = 3.3 \times 10^{-7}$ bar and 1.3×10^{-6} bar. The kinetic profiles were then obtained by switching the $P(I_2)$ between 1.3×10^{-7} bar and 1.3×10^{-6} bar and measuring a sequence of DC polarization experiments from which the electronic conductivity as a function of time was extracted.

2. Supplementary Data



Figure S1. (a) UV-vis absorption spectra of $(BzA)_2PbI_4$ and of $(PDMA)PbI_4$ thin films. (b) XRD patterns of $(BzA)_2PbI_4$ (RP) and $(PDMA)PbI_4$ (DJ) thin films deposited on glass substrates and on quartz substrates with Au interdigitated contacts for conductivity measurements (device). The diffraction patterns with and without the electrodes show comparable structural characteristics. All peaks for the RP samples can be attributed to the (001) orientation (lattice parameter c = 28.6 Å), while for the DJ samples peaks refer to the (h00) orientations (lattice parameters a = 12.08 Å and b = 7 Å) and (hk0) orientations.



Figure S2. Device gap length dependence of the electronic and ionic properties for (PDMA)PbI₄ (left column) and (BzA)₂PbI₄ (right column) measured under argon and under fixed iodine partial pressure $P(I_2) = 3.3 \times 10^{-7}$ bar. (a, b) Electronic resistance and (c, d) ionic resistance normalized by the interdigitated contacts overlap *W*. The lines represent linear fits to the data (see text below for discussion). Deviation from the linear trend in the DJ sample for gap length of 40 μ m, might be due to a contribution from grain boundaries to the resistance (see SEM images in Figure S3 and supplementary discussion), which would become more pronounced the wider the gap between contact fingers, *L*. (e, f) Time constant τ extracted from the DC polarization experiment at long time scales. (g, h) Conductivity values extracted for each device (see discussion in the text).

Table S1. Relations obtained from the linear fits shown in Figure S2 for the 2D DJ and RP perovskite films. Here *L* is the gap width in centimeters (L/cm). We expect the negative values for the intercepts to be due to experimental error.

	(PDMA)PbI4		(BzA) ₂ PbI ₄	
Condition	$R_{eon}/(\Omega \mathrm{cm})$	$R_{ion}/(\Omega \mathrm{cm})$	$R_{eon}/(\Omega \mathrm{cm})$	$R_{ion}/(\Omega \mathrm{cm})$
argon	$1.0 \times 10^{15}L + 2.6 \times 10^{12}$	$2.2 \times 10^{15} L - 4.2 \times 10^{11}$	$8.6 \times 10^{14} L + 6.1 \times 10^{11}$	$6.7 \times 10^{15} L - 2.0 \times 10^{12}$
P(I ₂)	$3.8 \times 10^{14}L + 1.3 \times 10^{11}$	$7.2 \times 10^{14} L - 7.7 \times 10^{10}$	$4.5 \times 10^{14}L + 1.8 \times 10^{11}$	_



Figure S3. SEM images recorded for the four devices with different value of the gap width between the gold interdigitated contacts: (a) $L = 5 \ \mu m$, (b) $L = 10 \ \mu m$, (c) $L = 20 \ \mu m$, (d) $L = 40 \ \mu m$. The grain size for the (PDMA)PbI₄ film deposited on top of the substrate is in the order of 10–30 μm .



Figure S4. Cross-section SEM of a (PDMA)PbI₄ film deposited on a quartz substrate with Au interdigitated contacts. The edge of the Au finger slightly bent upward is a result of the lift-off process used to fabricate the electrodes. Note that the Cr adhesion layer is applied before deposition of gold on the substrate. In the SEM image, the top platinum coating applied before the measurement is also visible.



Figure S5. Kröger-Vink diagrams of defect concentrations as function of P(I₂) for (a) (PDMA)PbI₄ and (b) (BzA)₂PbI₄, considering Schottky disorder involving iodide vacancies and spacer cations (assuming Pb defects are frozen-in).



Figure S6. (a) XRD peak intensity change over time of (BzA)₂PbI₄ sample in the temperature range of 90–100 °C. (b) XRD diffraction of graphs of (BzA)₂PbI₄ before (black) and after exposure to 60 °C in nitrogen for 42 days (blue). (c– d) Temperature-dependent XRD patterns for (c) RP and (d) DJ samples performed in nitrogen atmosphere.

3. Supplementary Discussion

Device gap length dependence of the electronic and ionic properties: Figure S2 shows the extracted values for the electronic and ionic resistance (normalized by the contact overlap) for a (PDMA)PbI₄ and a (BzA)₂PbI₄ thin films as function of the length of the gap between the contacts, L. In absence of interfacial resistance, such parameters should scale linearly with L, with a slope that is related to the relevant resistivity (σ^{-1}). The fits to the data yield the relations shown in Table S1. We note that, for Reon associated with the (PDMA)PbI4 film, a significant value of the intercept is detected when measurements are performed under argon. This observation points towards a significant contribution from an interfacial resistance. We find that such contribution decreases when measurements under fixed $P(I_2)$ are conducted. For the data in argon, we extract a value of electronic conductivity of $\sigma_{eon} = 5.0 \times 10^{-11} S \ cm^{-1}$ by considering the slope of the linear fit. This value is slightly higher than the values obtained by analyzing each data point individually (Figure S2g). We also note that for the Reon dataset recorded for the (PDMA)PbI4 film under argon, the value measured for the device with $L = 40 \ \mu m$ significantly deviates from the trend outlined by the other devices with shorted gap length. In addition, a similar deviation is observed for the R_{ion} data, despite there being a negligible intercept associated with the linear fit. These observations could be explained in terms of grain boundary contribution to the resistance. As shown in the SEM images displayed in Figure S3, the grain size in the film is in the order of 10-30 μm . It is evident that the longer the gap width L, and the more likely it is to have at least one grain boundary affecting charge carrier transport from one contact to the other. For Reon associated with the (BzA)₂PbI₄ film, a negligible intercept is found for both measurements under argon or under fixed iodine partial pressure. This may be related to the smaller grain size of such films, which would provide multiple contact points to the gold electrodes, mitigating the presence of grains with unfavorable orientation in proximity of the perovskite/metal interface. The evaluation of the ionic properties for this film proved challenging for devices with large L, due to the high resistance nature of the configuration used. In Figure S2d, only data for the shorter L devices is shown. Figure S2e and f display the dependence of the time constant extracted from the DC polarization measurements on the two films on L. In both cases, a slope below 1 is found. This clearly shows that the stoichiometric polarization occurring during the measurement does not represent the rate determining mechanism. Space charge polarization would yield a slope of 1, as it has been reported for the case of the 3D perovskite MAPI. We are not able to explain the lower slope observed here, however we point out that the determination of τ becomes challenging when the mixed conductor presents $\sigma_{eon} > \sigma_{ion}$. As this is especially the case for the (BzA)₂PbI₄ film measured here, the data in Figure S2f may have an even larger degree of inaccuracy. While these data already highlight a large error, the analysis of the DC measurement might be neglecting polarization feature that occurs at even longer time scales, which are not detectable under these conditions.

Discussion of P(I₂) dependence: The results presented in Figure 3a–b can be discussed based on possible defect chemical models describing the DJ and RP layered perovskites investigated here. Previous studies on MAPbI₃ confirmed that iodide vacancies are ionic majority carriers in this material.^{2,3} While there is no

consensus on the dominant disorder type in hybrid perovskites, Schottky disorder is often invoked, based on the observation of MA diffusion as well as from calculations of defect formation energies.^{4,5} Assuming that Schottky disorder is relevant also to (PDMA)PbI₄ and (BzA)₂PbI₄ we can write the ionic disorder reactions involving iodide vacancies and spacers.

$$\phi \rightleftharpoons V_{PDMA}^{\prime\prime} + 2V_{I}^{\cdot} \tag{E1}$$

$$\phi \rightleftharpoons V'_{BzA} + V'_{I} \tag{E2}$$

These can be coupled with the electronic disorder reaction and the iodine exchange reaction at equilibrium

$$\emptyset \rightleftharpoons e' + h^{\cdot}$$
 (E3)

$$\frac{1}{2}I_2 + V_I \rightleftharpoons I_I^{\times} + h^{\cdot}$$
(E4)

From the system of equations resulting from the mass-action law associated with reactions (E1–E4) and the electroneutrality condition, we obtain possible P(I₂) defect concentration dependence, which we display in Kröger–Vink diagrams (Figure S5). Assuming that the charge carrier mobility is independent of defect concentration in the P(I₂) range explored here, we conclude that the obtained slopes of ionic and electronic conductivities (Figure 3) are generally consistent with both DJ and RP films operating in the intrinsic (I) region.^{6,7} We note that, even when considering the anti-Frenkel reaction involving iodide vacancies and interstitials as the dominant ionic disorder, this would not change our conclusion. We also point out that, given the incomplete reversibility observed for the ionic conductivities, more complex interaction of ionic defects with the incorporated iodine might occur. Further studies on the electrical properties of quasi-layered hybrid perovskites (n > 1) might clarify this question, as their compositions involve both spacer molecules and the A cations (MA, FA or Cs) used in 3D compositions.

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