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Quantification of Ionic Diffusion in Lead Halide Perovskite Single Crystals

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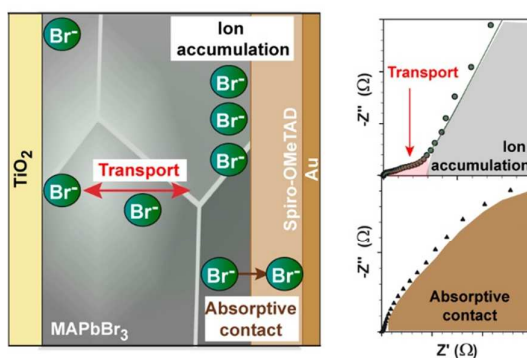
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Abstract

Lead halide perovskites are mixed electronic/ionic semiconductors that have recently revolutionized the photovoltaics field. The physical characterization of the ionic conductivity has been rather elusive due to the highly intermixing of ionic and electronic current. In this work the synthesis of low defect density monocrystalline MAPbBr₃ (MA=Methyl ammonium) solar cells free of hole transport layer (HTL) suppresses the effect of electronic current. Impedance spectroscopy reveals the characteristic signature of ionic diffusion (the Warburg element and transmission line equivalent circuit) and ion accumulation at the MAPbBr₃/Au interface. Diffusion coefficients are calculated based on a good correlation between thickness of MAPbBr₃ and characteristic diffusion transition frequency. In addition, reactive external interfaces are studied by comparison of polycrystalline MAPbBr₃ devices prepared either with or without a HTL. The low frequency response in IS measurements is correlated with the chemical reactivity of moving ions with the external interfaces and diffusion into the HTL.



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4 Hybrid organic-inorganic perovskite materials have revolutionized the photovoltaics
5 field, but they are currently hampered by device performance and degradation issues
6 that stem from a lack of understanding of their ionic conduction properties. Lead halide
7 perovskite materials have long been known to be mixed electronic/ionic conductors^{1,2}
8 however, only recently ionic conductivity has been identified as a key player for
9 operational mechanisms in photovoltaic devices. For example, ion migration has been
10 related to degradation processes,^{3,4} modification in the device operation mechanism
11 affecting the extraction properties of the contacts^{5,6} and inducing a hysteretic behavior
12 during electrical operation.^{7,8} Regardless of the importance of ion migration, a full
13 characterization of the migrating species in these optically active materials has been
14 elusive due to the highly intermixed electronic and ionic currents. In this work, high
15 quality and low defect density monocrystalline devices of MAPbBr₃ have been prepared
16 that enable direct observation of the ionic signal by suppression of the electronic current.
17 The characteristic signature of ionic transport, ion accumulation/diffusion of ions into
18 the external contacts is revealed by using impedance spectroscopy (IS) to investigate
19 both high efficiency MAPbBr₃ monocrystalline and polycrystalline devices.

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21 Ionic migration has been detected in lead halide perovskites by different electrical
22 measurements in operating solar cells, such as chronoamperometry or capacitive
23 methods,^{9,10} which provide limited amount of information. In addition, the use of ex-situ
24 techniques has clearly confirmed the nature of the migrating species. For example,
25 compositional imaging has been obtained using XPS¹¹ and time of flight secondary ion
26 mass spectrometry (TOF-SIMS), in both cases with resolution in the z-axis direction.
27 Robust results using the latest technique have finally clarified that the metal electrode
28 materials and halides are the main migrating species.^{4,12,13} However, none of these
29 techniques offer kinetic information in operating devices such as the ion diffusion
30 coefficients, which are highly valuable material parameters for evaluating the ionic
31 conductivity properties of the material.

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33 IS is a technique that has traditionally been used to characterize ionic transport and
34 electrochemical reactions in a variety of devices such as batteries, dye sensitized solar
35 cells or photoelectrochemical cells.¹⁴⁻¹⁶ This technique measures the electrical response
36 in the frequency/time domain separating resistive and capacitive contributions arising
37 from electronic and ionic processes with different characteristic time/frequencies. In the
38 specific case of solid state ionic diffusion, IS provides a standard and widely used
39 method to identify the main kinetic parameters such as the chemical diffusion
40 coefficient.^{16,17} Depending on the transport properties of the materials, a transmission
41 line can be observed in the complex impedance plot, which accounts for ionic transport
42 in mixed ionic-electronic conductors. Furthermore, IS also provides information on the
43 nature of boundaries and anomalous diffusion phenomena.^{18,19} These methods have been
44 previously applied to determine Li⁺ ion diffusion features in lead halide perovskites,²⁰
45 but not to the displacement of intrinsic defects that are often observed to cause major
46 effects in the photovoltaic perovskite devices. In this work, IS reveals the characteristic
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signature of ionic transport in lead halide perovskite materials. High efficiency monocrystalline MAPbBr₃ solar cells without a hole transport layer (HTL) are an excellent model system that simplifies the electrical response. Using this method, a transmission line characteristic for ion migration is observed together with ion accumulation across the bulk perovskite layer. In addition, polycrystalline MAPbBr₃ devices prepared either with or without Spiro-OMeTAD enables the study of “ion-absorptive” external interfaces. It is shown that in the presence of Spiro-OMeTAD layer free bromide ions do not accumulate at the external interfaces but diffuse into the HTL as a source of chemical reactivity.

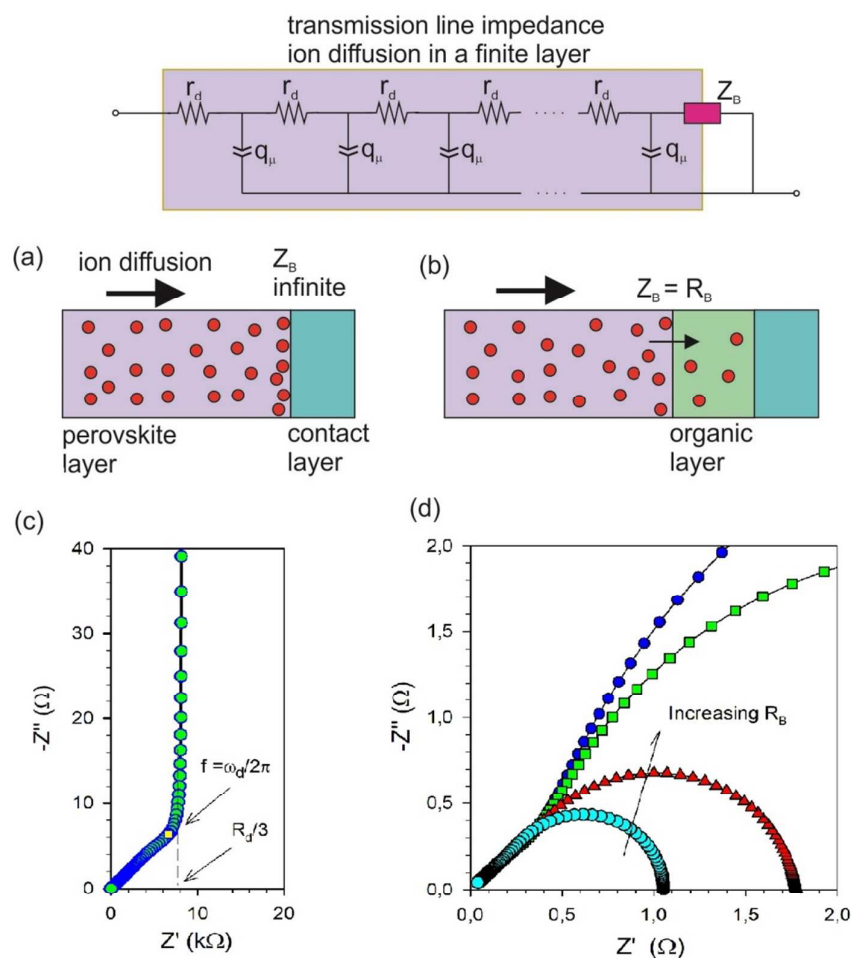


Figure 1: The impedance of ion diffusion in a finite layer is a transmission line composed of a distributed transport resistance and chemical capacitance. The process of termination at the boundary, represented by the boundary impedance, Z_B , changes dramatically the impedance spectra at low frequency. For a blocking boundary shown in (a) the impedance rises vertically (c). For a boundary that allows charge transfer (b) the impedance forms an arc at low frequency, that decreases when the charge transfer rate at the contact increases (d).

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4 During IS measurement a dc voltage is applied to the sample under either light or dark
5 conditions and a small-signal ac voltage perturbation is superimposed with a wide range
6 of frequencies. The frequency and amplitude of the AC perturbation modulates how
7 much the system is separated from equilibrium and the extent to which carriers/ions will
8 move in the oscillating field.
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10 The impedance of ionic diffusion in solid media has been widely applied in the
11 context of Li ion battery materials.¹⁵ The impedance shows two distinct features that
12 can be obtained from the distributed equivalent circuit of a transmission line as shown in
13 Fig. 1.²¹ At high frequency the ac modulation probes the diffusion unbounded by the
14 contacts. In this domain the representation in the complex impedance plane (Z' , $-Z''$),
15 shows the standard Warburg element, consisting of a line with 45° inclination, Fig. 1c.
16 At low frequency there are different types of behaviors depending on the boundary
17 conditions.²² In the main model the final boundary is a reflecting boundary for ions
18 which cannot enter the other medium at the contact layer, and consequently accumulate
19 at the interface.²³ The low frequency impedance is capacitive, and it shows a vertical
20 line associated to the ionic chemical capacitance, Fig. 1c.²⁴ In between the Warburg and
21 capacitance domains of the impedance response lies the ankle of the characteristic
22 frequency of diffusion, ω_d . When the spectrum is obtained experimentally it is quite
23 straightforward to obtain the ionic chemical diffusion coefficient D_μ by the relation
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$$\omega_d = \frac{D_\mu}{d^2} \quad (1)$$

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31 Note that D_μ is a quantity that depends on composition.²⁵ However, in a highly
32 diluted system, as expected in the low concentration of mobile defects in lead halide
33 perovskites, the chemical diffusion coefficient should be a constant characteristic of the
34 specific material environment of the moving ions.
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36 Another important point is that the impedance spectroscopy will respond to the global
37 transport properties of the system. It has been established that hybrid perovskites may
38 contain a variety of carriers, electronic and ionic. The observation of ionic diffusion
39 demands a specific system with a low density of electronic carriers, otherwise the ionic
40 transport resistance will be masked by a parallel pathway of low electronic resistance. In
41 our experimental system we have specifically addressed this issue.
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44 In addition, it has been widely recognized that the impedance spectra can be
45 drastically modified by the carrier boundary condition of the transport layer.²² Systems
46 with different contact layers are compared in Fig. 1a and b, accordingly with different
47 specific contact boundary impedance Z_B . If the final boundary is perfectly blocking,
48 the impedance rises in a capacitive vertical line as mentioned previously. However, for
49 an absorptive interface that transfers or allows the diffusion of ions into a neighbor layer
50 as occurs in Fig. 1b, an arc at low frequency will appear, Fig. 1d, with a total resistance
51 determined by the charge transfer rate of the injection process.¹⁸ This remark provides a
52 useful criterion to derive the nature of the boundaries from the observed impedance
53 spectra.¹⁸
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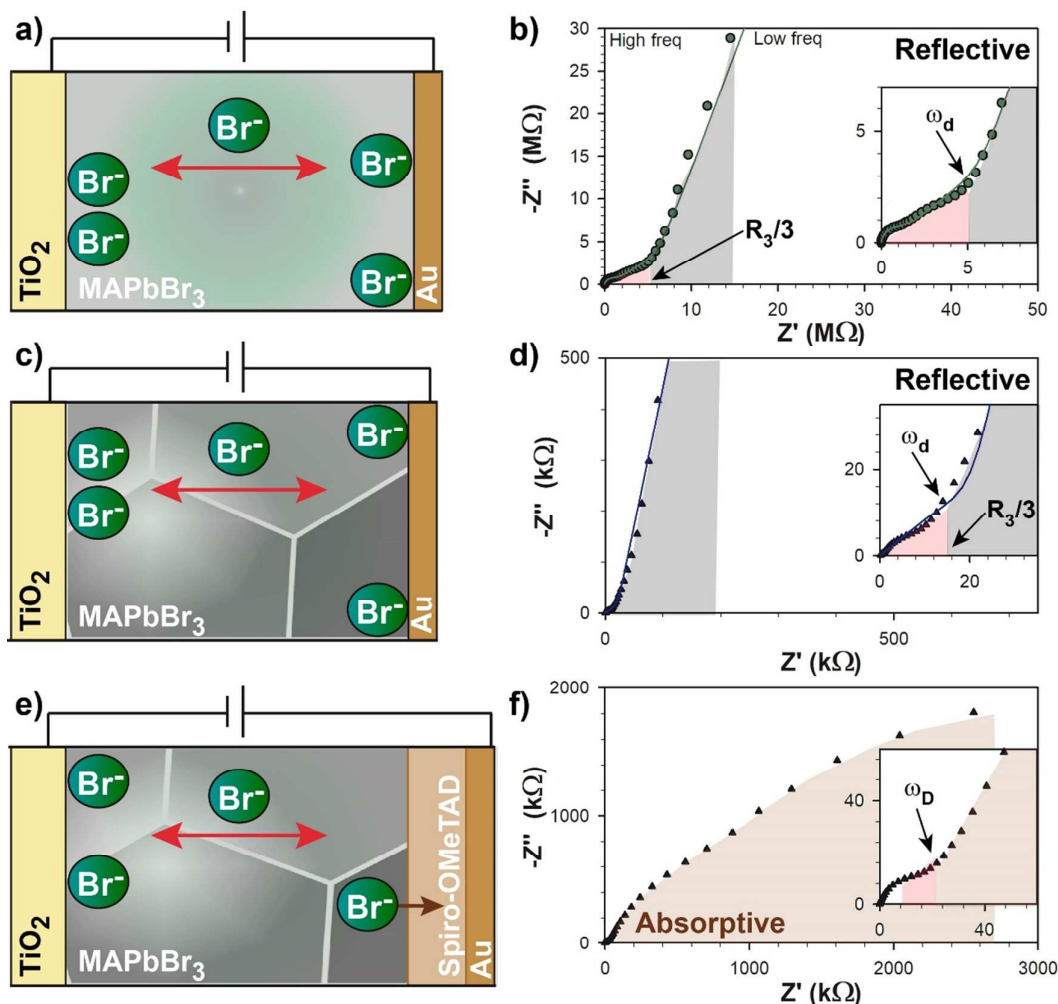
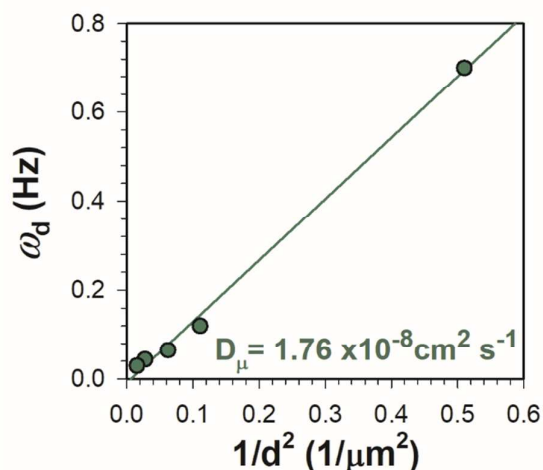


Figure 2: Different configurations used for devices containing MAPbBr₃: a) Monocrystalline, c) and e) Polycrystalline. b), d), f) Complex plane impedance plots extracted from impedance measures in the dark at 0 V for configurations shown on their left. Solid lines correspond to fitting results using equivalent circuit shown in Fig. 1). Ionic processes are highlighted with different colors: ionic transport (red), charge accumulation (grey) and diffusion into absorptive contacts (brown).

A series of high efficiency photovoltaic devices are prepared using either monocrystalline or polycrystalline MAPbBr₃. A photovoltaic configuration containing monocrystals of MAPbBr₃ (Fig. 2a) offers an excellent model system with low defect densities of $1.8 \times 10^{12} \text{ cm}^{-3}$, see supporting information for Mott-Schottky analysis. In addition, this configuration does not contain the commonly used hole transport layer Spiro-OMeTAD simplifying the electrical response as this layer contains different additives (i.e. LiTFSI) that could lead to ion migration of additional species (i.e. Li⁺).²⁶ Power conversion efficiencies depend on the thickness of the MAPbBr₃ monocrystals but are in the range of 2-5 % with a remarkably high V_{oc} close to 1.4 V, representative

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4 photovoltaic performance data is shown as supporting information.²⁷ In order to study
5 the effect of the HTL during ion migration, a polycrystalline MAPbBr₃ configuration is
6 tested with and without Spiro-OMeTAD. Polycrystalline devices (Fig. 2c and 2e) have
7 been developed in this work with improved solvent formulation leading to pinhole-free
8 devices with an impressive morphology. Polycrystalline devices without HTL show low
9 efficiencies of 0.3 % with photocurrent being the most affected parameter while
10 efficiency dramatically increases to 2.0 % with the presence of Spiro-OMeTAD.²⁸ In
11 summary mono- and polycrystalline devices are of high quality ensuring that the system
12 is not limited by transport of electrons or holes that would ultimately lead to
13 recombination of carriers.²⁹

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17 Monocrystalline MAPbBr₃ devices with different active layer thickness were
18 measured by IS under the dark condition at 0 V (Fig. 2b). In these conditions we expect
19 only the native mobile defects in diluted conditions so that the chemical diffusion
20 coefficient should be the same for the different samples. The complex impedance plot
21 clearly shows a transmission line at intermediate frequencies (red region) covering more
22 than two orders of magnitude in the frequency scale (0.5-200 Hz). As can be observed in
23 Fig. 2b, there is a very good agreement between the fitting results (solid lines) with the
24 impedance data obtained for reflective boundary conditions. The observation of tilted
25 lines in the low frequency range indicates anomalous diffusion patterns as explained in
26 the supporting information. For example, for a perovskite thickness of 1.4 micron, ω_d is
27 0.91 Hz and accumulation of ions at the contacts is observed at lower frequencies
28 leading to an almost vertical line (grey region), typical for reflective contacts. The fact
29 of observing a blocking boundary for a diode configuration indicates that the impedance
30 for electron transport is extremely large and does not shunt the device. This feature
31 corresponds to a sample with extremely low doping level, as reported previously.³⁰ This
32 is the reason why the impedance of pure ionic diffusion can be clearly observed in these
33 monocrystal samples.
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55 **Figure 3:** Dependency of characteristic frequency with the monocrystal thickness and
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4 extracted diffusion coefficient.
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7 As the monocrystal thickness is increased, ω_d decreases, corresponding to the
8 increase of the transit time for ions to reach the external interfaces, according to the
9 classical diffusion theory explained above (see Fig. 1). Very importantly, there is a
10 balance between the ionic migration kinetics and the thickness of the sample that allows
11 the observation of the complete transmission line pattern. For example, a monocrystal of
12 50 microns only shows the Warburg part and does not reveal ion accumulation at
13 frequencies as low as 1 mHz (see supporting information). Diffusion coefficients of
14 $D_{\mu} = 1.8 \times 10^{-8}$ cm²/s can be calculated for Br⁻ from the correlation of the frequency of
15 the ankle to the thickness of the perovskite layer (Fig. 2c) and using Equation (1), see
16 Fig. 3. Note that in this device configuration there is no Spiro-OMeTAD or additives
17 containing small ions like Li⁺ which could also be transported through the perovskite
18 matrix.²⁶ In addition, the large size of the methyl ammonium (MA⁺) cation in
19 comparison to the halides has been reported to be the factor why migration in MAPbI₃ is
20 dominated by I⁻ vacancies.³¹ In this work, Br⁻ is even smaller than the I⁻ analogue. For
21 these reasons, we propose that Br⁻ diffusion is measured in this device configuration. It
22 is important to highlight that migration of Br⁻ in monocrystalline devices is related to
23 transport *via* vacancies/interstitial defects of the crystalline structure, not the grain
24 boundaries. Finally, the impedance data can be fitted using the equivalent circuit
25 described in Fig. 1.
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30 Understanding the effect of the external interfaces is essential as highest efficiencies
31 in photovoltaic devices are typically obtained using adequate HTL and electron
32 transport layers (ETL). In addition, degradation processes in perovskite devices has
33 recently been connected with reactivity at the perovskite/contact interfaces.^{3,5,32}
34 Unfortunately, using our process it is not possible to prepare monocrystalline devices
35 with different HTL materials offering homogeneous thickness. Therefore we turn to
36 polycrystalline MAPbBr₃ for comparing by IS a system free of HTL and a system
37 containing HTL. The complex plane impedance plots are shown in Fig. 2d and 2f,
38 respectively. At high and intermediate frequency, both HTL-free device and the sample
39 containing Spiro-OMeTAD (Fig. 2f) show the same behavior of the crystalline system
40 in the intermediate frequency range, corresponding to the Warburg diffusion behavior
41 truncated to a vertical rise, see inset of Fig. 2f. However, a very different scenario is
42 obtained at low frequencies comparing the two samples. For the HTL-free
43 polycrystalline device a vertical line similar to that of the monocrystalline device and
44 typical for reflective electrodes is observed. In contrast, for the Spiro-OMeTAD
45 containing sample the low frequency line bends down as a characteristic mark of the
46 absorbing boundary, see Fig. 1d. The fact that devices free of Spiro-OMeTAD show a
47 reflecting boundary behavior and devices containing this HTL show a partially
48 absorptive boundary behavior is a clear indication that Br⁻ diffuses into the Spiro-
49 OMeTAD. These inserted ions can react with the oxidized HTL needed to obtain
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adequate conductivity, as previously reported by us and more recently confirmed by SIMS-TOF.^{5,12} We note that in many cases this type of reactivity leads to noisy signals in the frequency domain as it can take up to 16 min to measure one data point in the lowest frequency limit (1 mHz). Therefore, we can conclude that not only ions in the perovskite layer are being monitored in the transport regime but ion diffusion and reactivity with the external contacts can be monitored in real time.

In conclusion we showed that impedance spectroscopy measured in the dark provides access to the transport response of ions at intermediate frequencies providing detailed information on the diffusion coefficients. The capacitive response in the low frequency region reveals the response of ion accumulation for ion-reflective contacts, while the presence of an arc for ion-absorptive contacts supports the hypothesis for ion diffusion into the contact and/or chemical reactivity with the external interfaces. The advanced understanding presented in this study of the ionic conduction properties of this exciting type of materials open a new avenue for solving some of the main degradation and performance issues hampering perovskite optoelectronics.

Experimental Section

Monocrystalline MAPbBr₃ device fabrication

Monocrystalline MAPbBr₃ on TiO₂ (~60 nm)/FTO glass were grown using the cavitation-triggered asymmetric crystallization method, as previously reported.²⁷ 100 nm thick Au electrodes of full coverage on as-grown monocrystalline film were deposited through a metal shadow mask by thermal evaporation.

Polycrystalline MAPbBr₃ devices fabrication

MAPbBr₃ film was deposited on TiO₂ by spin coating at 4000 rpm for 40s, using toluene as anti-solvent. This was followed by annealing at 100 °C for 3 min to obtain a shiny and homogenous film. When required, a solution of Spiro-OMeTAD is deposited as HTL in chlorobenzene by spin coating at 4000 rpm. Finally, 60 nm of gold was thermally evaporated on top of the device as a back contact.

Film and Device characterization

Photovoltaic devices were characterized using an Abett Solar simulator equipped with 1.5 AM filter. The light intensity was adjusted to 100 mWcm⁻² using a calibrated Si solar cell. Devices were measured using a mask to define an active area of 0.11 cm². Impedance spectroscopy measurements were performed using an Autolab PGSTAT-30 equipped with a frequency analyzer module in the dark. The DC bias was selected at 0 V with the AC perturbation to cover the frequency range of 1 mHz to 1 MHz.

Supporting Information. Mott-Schottky analysis, Device performance characteristics, Impedance spectroscopy data, anomalous diffusion.

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