Mixed-Organic-Cation Perovskite Photovoltaics for Enhanced Solar-Light Harvesting**

Norman Pellet, Peng Gao, Giuliano Gregori, Tae-Youl Yang, Mohammad K. Nazeeruddin, Joachim Maier, and Michael Grätzel*

Abstract: Hybrid organic–inorganic lead halide perovskite APbX₃ pigments, such as methylammonium lead iodide, have recently emerged as excellent light harvesters in solid-state mesoscopic solar cells. An important target for the further improvement of the performance of perovskite-based photovoltaics is to extend their optical-absorption onset further into the red to enhance solar-light harvesting. Herein, we show that this goal can be reached by using a mixture of formamidinium (HN(CH₂)₂ NH₃⁺, FA) and methylammonium (CH₃NH₃⁺, MA) cations in the A position of the APbI₃ perovskite structure. This combination leads to an enhanced short-circuit current and thus superior devices to those based on only CH₃NH₃⁺. This concept has not been applied previously in perovskite-based solar cells. It shows great potential as a versatile tool to tune the structural, electrical, and optoelectronic properties of the light-harvesting materials.

The large family of inorganic halometallate perovskites has attracted a lot of attention owing to its wide range of outstanding properties, such as antiferromagnetism [1–3], photocconductivity [4,5] ionic conductivity [6] and bipolar semiconductivity [7]. Within this family, the fully organic cesium–metal–trihalide perovskites (CsAX₃, X = Cl, Br, I) have been the subject of intense study for many years. [8–17] In particular, organic–inorganic iodoplumbate and iodostannate perovskites, pioneered by Mitzi et al., have been recognized for their excellent semiconducting properties. However, the extraordinary photovoltaic performance of similar hybrid perovskites only became evident after the demonstration of MAPbI₃ nanoparticles as potent light harvesters in a liquid-electrolyte-based dye-sensitized solar-cell configuration by Miyasaka and co-workers, who observed a power-conversion efficiency (PCE) of 3.9%. A drawback of this system is its poor stability, as the perovskite rapidly degrades owing to its high solubility in the liquid electrolyte. This problem was overcome by replacing the electrolyte with a solid organic hole conductor. Recently, we reported a new record of 15% PCE for a FTO/TiO₂/MAPbI₃/spiro-MeOTAD/Au device in which the perovskite was deposited by a novel sequential deposition technique. By using our two-step deposition technique, we witnessed a significant increase in the open-circuit voltage (Voc) and fill factor (FF) of our devices as compared to devices prepared by the commonly used one-step deposition method from γ-butyrolactone. However, the short-circuit photocurrent density (Jsc) was limited to an average value of 17 mA cm⁻². In theory, a semiconductor with a band gap of 1.5 eV can deliver photocurrents up to 27 mA cm⁻² under standard AM 1.5G illumination. The large difference arises mainly from the lack of light absorption in the 550–800 nm range by the infiltrated perovskite and the parasitic absorption of the conductive oxide glass.

Hybrid organic–inorganic perovskites are synthesized with a variety of organic cations. It has been demonstrated that the size of the organic ammonium cation influences the optical band gap of the perovskite by affecting the M-I-M (M = Sn, Pb) angle or promoting the formation of insulating barriers between semiconducting PbI₂ layers. In the latter case, bigger cations usually lead to two-dimensional perovskite, in which the PbI₂ octahedrons are edge-sharing. Two-dimensional (2D) iodoplumbate and iodostannate perovskites usually show wider band gaps, which make them unsuitable for panchromatic absorption of the visible solar spectrum. A variety of organic cations have been shown to affect the band gap by as much as 1 eV in iodostannate perovskites. Theoretically, methylammonium (CH₃NH₃⁺) and formamidinium (HN(CH₂)₂ NH₃⁺, FA⁴⁺) are sufficiently small cations to form the 3D perovskite, whereas ethylammonium (CH₃CH₂NH₃⁺) is known to already form a 2D perovskite. FASnI₃ has been described by Mitzi and co-workers as early as 1995, whereas its Pb analogue was only recently investigated by Kanatzidis and co-workers, who reported a significant red shift of the optical absorption as compared to that of MAPbI₃. We reasoned that formamidinium offers the potential to lower the band gap of...
the commonly used MAPbI₃ perovskite towards the value of 1.4 eV,[39] which is optimal for the conversion of standard AM1.5 sunlight into electricity. We were able to tune the band gap of MAPbI₃ by the gradual substitution of MA with FA cations, and monitored the shift in the optical response. Earlier studies on mixed-cation perovskites focused on their electronic properties. Thus, Mitzi and co-workers described a semiconductor-to-metal transition within the series (HN=CHNH₃)₂(CH₃NH₃)ₙSnI₃₊₂ as n increased. Three-dimensional perovskites with mixed cations have also been prepared in the form of tin halide perovskites, that is, (HN=CHNH₃)₀.₅(CH₃NH₃)₀.₅SnI₃;[41] however, their optical or photovoltaic properties were not studied. Investigations to tune the band gap of metal halide perovskites have so far focused on the mixing of halide anions, for example, Br/I[37,42] or Cl/I, [3,33] rather than the use of mixed cations.

Herein we report the first use of 3D perovskites of composition (MA)ₓ(FA)₁₋ₓPbI₃ (x = 0–1) as light-harvesting pigments for mesoscopic solar cells. Our previously reported sequential deposition method[23] was used as a powerful and effective tool to generate perovskite crystals containing both methylammonium and formamidinium cations in well-defined proportions. We characterized the perovskite films by powder X-ray diffraction, AC and DC electrical conductivity (using carbon electrodes), absorption and emission spectroscopy, and photoluminescence decay. We tested fully functional photovoltaic (PV) devices with 2,2',7,7'-tetakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobi fluorene (spiro-OMeTAD) as the hole-transporting material (HTM),[43] a mesoscopic TiO₂ scaffold (m-TiO₂) as a host for the nanostructured perovskite, and a compact TiO₂ film (b-TiO₂) as the hole-blocking layer. The results show significant gains in PV performance from the use of lead iodide perovskites with mixed FA/MA cations as light harvesters.

We conducted powder XRD measurements to investigate the simultaneous intercalation of MA and FA cations (Figure 1). Fluorine-doped tin oxide (FTO) glass was covered with a thin compact blocking layer of TiO₂ (b-TiO₂), onto which mesoscopic TiO₂ (m-TiO₂) with a thickness of approximately 300 nm was deposited. The latter layer was infiltrated with PbI₂ by spin coating. Remaining PbI₂ was identified at 12.8°. The morphological feature at 11.8° is assigned to the non-perovskite d-phase of formamidinium. A similar effect is seen in the peaks at 31.8° and 28.4°. D) Summarized peak shift as compared to FAPbI₃. Peaks at 14.0° shifts to lower reflection angles with FAI intercalation. Remaining PbI₂ was identified at 12.8°. The morphological feature at 11.8° is assigned to the non-perovskite d-phase of formamidinium. A similar effect is seen in the peaks at 31.8° and 28.4°. D) Summarized peak shift as compared to FAPbI₃. Peaks at 14, 28.4, and 31.8° are considered. E) Normalized emission of (CH₃NH₃)ₓ(HN=CHNH₃)₁₋ₓPbI₃ (x = 0, 0.2, 0.4, 0.6, 0.8, 1). The emission is shifted further into the red and broadened as x is decreased. F) Light-harvesting spectra of the different perovskite films recorded in an integrating sphere. Note the 20 nm red shift of the absorbance onset for (CH₃NH₃)₀.₅(HN=CHNH₃)₀.₅PbI₃ as compared to (CH₃NH₃)PbI₃. As the formamidinium concentration was increased, the absorbance of the film decreased, while no change in the band gap was discernable.
Structural changes were observed for the peaks at 14.1 (Figure 1A), 20.0, 24.4, 28.4 (Figure 1B), 31.8 (Figure 1C), 40.6, and 43°, whereby the diffraction angle decreases with increasing formamidinium content, in keeping with the bigger size of the formamidinium cation, which expands the crystal lattice (see Figure S16 in the Supporting Information for full XRD spectra). Figure 1D shows the peak shift with respect to the reference α-FAPbI3 peak at 13.8°. The gradual shift in the diffraction angle (that is, rather than the appearance of two separate peaks of variable intensities) is a strong indication that a mixed phase of (MA)0.6(FA)0.4PbI3 is formed in which the two cations are both inserted in the same lattice frame. Additional diffractions specific to FAPbI3 appeared at 11.8, 16.25, 30.54, 32.8, and 41.63° and were assigned by measuring spin-coated reference samples produced by the one-step deposition of (MA)0.6(FA)0.4PbI3 from N,N-dimethylformamide (see Figures S14 and S15). All of these features were also present in pure FAPbI3 deposited in this way, and are assigned to the yellow δ-phase of FAPbI3.[38] However, the perovskite α-FAPbI3 phase was not produced in this manner, as is evident from the lack of a peak at 14°, and even subsequent annealing failed to induce any δ→α phase transition. The δ-FAPbI3 diffraction peaks gradually disappeared as the MAI concentration was increased. In contrast, the desired black α-FAPbI3 perovskite phase was formed immediately in substantial proportion relative to δ-FAPbI3 when the sequential deposition method was applied. Furthermore, the α-phase was formed quantitatively already at a MAI molar ratio as low as 0.2 in the 2-propanol dipping solution, as confirmed by the lack of a diffraction peak at 11.8°. Yet another key advantage of the two-step over the single-step perovskite deposition method is that it directs perovskite crystallization in the desired α-phase upon exposure of the PbI2 to the MAI/FAI mixture in 2-propanol.

Since MAPbI3 displays mixed electronic–ionic conduction,[39] we performed impedance analysis and DC polarization to probe electrical transport in the single- and mixed-crystallization perovskites. AC impedance data acquired for all compositions considered in this study are characterized by a single semicircle (Figure 2A), whereby the capacitance corresponds to the bulk properties (relative dielectric constant ε, ≈ 30). AC measurements performed between 30 and 70°C yielded the activation energy E of the different samples. Remarkably, as shown in Figure 2B, the value of E of the two-phase mixtures (e.g. 0.53 eV for MAI:FAI 2:3 as well as MAI:FAI 3:2) is very close to the activation energy of the FAI single phase (0.55 eV) rather than the MAI single phase (0.40 eV), thus suggesting that the electrical conduction properties are dominated by the FAI phase. DC polarization measurements with carbon electrodes revealed a minor but substantial ionic contribution.

Figure 1F shows UV/Vis absorption spectra of the mixed-crystallization lead iodide perovskites (MA)x(FA)1−xPbI3 for various compositions. The addition of only 20 mol% FAI to the dipping solution caused the absorption onset of the perovskite to red shift by 20 nm, whereas the desired steepness of the absorption edge characteristic of MAI was maintained. As the FAI concentration was further increased, the absorption onset was shifted to longer wavelengths, while the absorbance of the film was reduced. A MAI:FAI ratio of 4:1 or 3:2 in the 2-propanol bath solution proved to be optimal for the extension of the light absorption of the perovskite into the red with retention of the high absorption coefficient of MAPbI3. MAPbI3 scatters light more strongly than FAPbI3, as is apparent from the tailing of the absorbance beyond the band gap. This difference probably arises from the smaller size of FAPbI3 crystals as compared to their methylammonium counterparts.

The normalized near-infrared photoluminescence (PL) of the (MA)x(FA)1−xPbI3 (x = 0–1) films is shown in Figure 1E. A significant 27 nm red shift in the emission peak from MAPbI3 (λmax = 776 nm) to FAPbI3 (λmax = 803 nm) was observed—consistent with the absorption spectrum—along with a noticeable broadening of the emission profile. The gradual shift in emission indicates the formation of a solid solution of MA and FA in the perovskite lattice. The shifts in emission of samples prepared by sequential deposition or by single-step deposition are plotted in Figure S12 of the Supporting Information. The similarity of the observed trends suggests that the ratio of intercalated cations is similar to that of the dissolved cations in the precursor solution. The nonlinearity of the emission shift reflects interactions between methylammonium and formamidinium cations. PL measurements of films prepared by the one-step deposition method were complicated by the appearance of the yellow δ-phase of the formamidinium iodide[38] which optically manifests itself only weakly in the FAPbI3 samples prepared...
by sequential deposition. The absence of the α-phase explains the blue-shifted emission in FAPbI$_3$ prepared by the one-step deposition method (see Figure SI1).

We measured the current ($J$)–voltage ($V$) characteristics of the solar cells in the dark and under simulated air mass 1.5 global standard sunlight (AM1.5 G). To avoid batch-to-batch variations in the photocurrent, cells from the same batch were compared, and the PbI$_2$-coated TiO$_2$ films were selected at random before dipping in the solutions of RNH$_3$ (R: CH$_3$– and/or NH=CH–). In this manner, clear trends in the short-circuit current densities were established reproducibly. The pure formamidinium lead iodide (FAPbI$_3$) with variations in the photocurrent, cells from the same batch were global standard sunlight (AM1.5G). To avoid batch-to-batch of the solar cells in the dark and under simulated air mass 1.5 and/or NH$_x$=CH$_x$.

The most efficient FAPbI$_3$-based device gave a PCE of 16.6 mA cm$^{-2}$, 1046 mV, 0.655, and 12.5%, respectively. On average, the devices showed a short-circuit current density ($J_{sc}$), open-circuit potential ($V_{oc}$), fill factor (FF), and power-conversion efficiency (PCE) were determined to be 17.83 mA cm$^{-2}$, 1046 mV, 0.655, and 12.5%, respectively. On average, the devices showed a short-circuit current density of 17.3 mA cm$^{-2}$ and a PCE of 12.0%, in excellent agreement with our previously reported results.$^{[23]}$ The solid trace in Figure 3A shows a $J$–$V$ curve obtained from pure MAPbI$_3$, from which the short-circuit current density ($J_{sc}$), open-circuit potential ($V_{oc}$), fill factor (FF), and power-conversion efficiency (PCE) were determined to be 17.83 mA cm$^{-2}$, 1046 mV, 0.655, and 12.5%, respectively. On average, the devices showed a short-circuit current density of 17.3 mA cm$^{-2}$ and a PCE of 12.0%, in excellent agreement with our previously reported results.$^{[23]}$ The solid trace in Figure 3A shows a $J$–$V$ curve obtained from pure formamidinium lead iodide (FAPbI$_3$) with $J_{sc}$ = 16.6 mA cm$^{-2}$, $V_{oc}$ = 928 mV, FF = 0.66, and PCE = 10.5%. The most efficient FAPbI$_3$-based device gave a PCE of 11.0%, clearly below the average PCE obtained with MAPbI$_3$.

Table 1: Photovoltaic properties of eight devices sensitized by MA$_x$FAP$_{1-x}$PbI$_3$ with I$_2$ in a concentration of either 0.062 M (first four devices) or 0.050 M (last three devices) in the dipping bath.

<table>
<thead>
<tr>
<th>$J_{sc}$ [mA cm$^{-2}$]</th>
<th>$V_{oc}$ [V]</th>
<th>FF</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.860</td>
<td>1025</td>
<td>0.692</td>
<td>13.71</td>
</tr>
<tr>
<td>18.893</td>
<td>1033</td>
<td>0.722</td>
<td>14.52</td>
</tr>
<tr>
<td>17.820</td>
<td>1033</td>
<td>0.673</td>
<td>12.93</td>
</tr>
<tr>
<td>18.340</td>
<td>1039</td>
<td>0.697</td>
<td>13.57</td>
</tr>
<tr>
<td>19.865</td>
<td>931</td>
<td>0.660</td>
<td>12.45</td>
</tr>
<tr>
<td>19.617</td>
<td>936</td>
<td>0.696</td>
<td>13.19</td>
</tr>
<tr>
<td>19.305</td>
<td>951</td>
<td>0.707</td>
<td>13.39</td>
</tr>
<tr>
<td>18.957 ± 0.66</td>
<td>992 ± 46</td>
<td>0.692 ± 0.019</td>
<td>13.4 ± 0.6</td>
</tr>
</tbody>
</table>

To rationalize the substantial gains in photocurrent observed for the mesoscopic cells based on mixed-cation perovskite light harvesters, we measured their incident-photon-to-current conversion efficiency (IPCE), or external quantum efficiency (EQE), across the visible spectrum. Figure 4B shows that the photocurrent onset is shifted by 20 nm to the red from 780 to 800 nm for FAPbI$_3$ and MA$_0.6$FAP$_{0.4}$PbI$_3$ in accordance with the absorbance spectra shown in Figure 1F. The IPCE spectrum of MA$_0.6$FAP$_{0.4}$PbI$_3$ is most impressive, as it combines the advantage of the redshifted onset observed for FAPbI$_3$ with the steep increase in the IPCE at the band gap characteristic for MAPbI$_3$. The IPCE values attained with MA$_0.6$FAP$_{0.4}$PbI$_3$ exceeded the levels of the two single-cation perovskites across the whole visible range and reached close to 90% at 500 nm. Integration of the IPCE spectra (340–850 nm) over the air mass 1.5 global (AM1.5 G) solar emission spectrum yielded short-circuit photocurrent densities of 17.0, 16, and 20.2 mA cm$^{-2}$ for MAPbI$_3$, FAPbI$_3$, and MA$_0.6$FAP$_{0.4}$PbI$_3$, respectively.

Figure 4A shows the absorbance spectra measured with an integrating sphere for the three devices. For this analysis, we removed the gold back contact and cut the films to preserve the active area alone. For wavelengths between 320 and 520 nm, the films harvested more than 93% of the incident photons. The remaining few percent are transmitted or lost either by specular reflectance or parasitic absorbance by the FTO. Above 520 nm, the light-harvesting efficiency of the films decreases gradually and then dropped sharply to zero near the band gap of the perovskite. FAPbI$_3$ showed the fastest drop in absorbance with increasing wavelength, and MAPbI$_3$ the slowest, while the mixed-cation perovskite lay in-between. A slight red shift in the band gap was observed
from the onset of the absorption, that is, 787 nm (1.575 eV) for MAPbI₃ and 810 nm (1.530 eV) for FAPbI₃. Interestingly, MA₀.₆FA₀.₄PbI₃ showed the same band gap as FAPbI₃, contrary to expectations.

To account for the reflection of the gold counter-electrode, we corrected the absorptance of the films on the basis of the following assumptions: a) the counter-electrode is described by the optical parameters \( n \) and \( k \) of gold, \[44\], whereby transmission is neglected and a flat interface is assumed; b) the perovskite film behaves as a Beer–Lambert medium; c) the parasitic absorptions from oxidized spiro-OMeTAD, TiO₂ and FTO are negligible; d) there is no light-scattering perovskite capping layer; and e) spiro-OMeTAD has a refraction index of 1.5 with a negligible imaginary part.

By using these approximations, we derived the absorbed-photon-to-current conversion efficiency (APCE) or internal quantum efficiency (IQE) from dividing the IPCE by the absorptance values. Figure 4c shows that for MA₀.₆FA₀.₄PbI₃, high APCE values of 80–85% were maintained throughout the visible spectrum. These values attest the very high quantum efficiency of carrier generation and collection by the device, in contrast to MAPbI₃ and FAPbI₃, which seem to collect less charges produced by red than by blue photons, thus indicating a shorter carrier-diffusion length for the single-cation perovskite phases.

To further substantiate this interpretation, we measured the photoluminescence lifetime of the perovskite deposited on nonconductive glass from solutions of MAI/FAI and PbI₂ in N,N-dimethylformamide (20% wt). The samples were excited by a 406 nm laser diode and their emission recorded at a right angle through a double monochromator. All films were measured over a 200 ns window divided into 1024 channels. Fluorescence lifetimes are displayed in Figure 5 for (MA)ₓ(FA)₁₋ₓPbI₃ \((x = 0, 0.2, 0.4, 0.6, 0.8, 1)\). The time decay of the fluorescence signals was fit to two or three exponentials; the lifetimes for the three components were in the range of 1–10, 20–70, and 100–300 ns (Table 2). Strikingly, about 85% of the emission of MA₀.₆FA₀.₄PbI₃ decayed with a long lifetime of 130 ns; thus, the emission persisted much longer than for the pure-phase perovskites. It also appears that for the mixed cations, a double exponential is sufficient to fit the decay kinetics well, since the fast decay observed for the single cations is absent. The prolongation of the lifetime in the mixed-cation perovskite most likely contributes to the better carrier-collection efficiency observed.
Table 2: Fluorescence lifetime and corresponding intensities for MAPbI$_3$, FAPbI$_3$, and MA$_x$FA$_{1-x}$PbI$_3$ fitted with three exponentials (extracted from the traces in Figure 5).

<table>
<thead>
<tr>
<th>Lifetime</th>
<th>MAPbI$_3$</th>
<th>MA$<em>x$FA$</em>{1-x}$PbI$_3$</th>
<th>FAPbI$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>2.58 ns</td>
<td>–</td>
<td>17.3 ns</td>
</tr>
<tr>
<td>intensity</td>
<td>11%</td>
<td>–</td>
<td>14%</td>
</tr>
<tr>
<td>2nd</td>
<td>17.3 ns</td>
<td>27.6 ns</td>
<td>76.4 ns</td>
</tr>
<tr>
<td>intensity</td>
<td>46%</td>
<td>14%</td>
<td>51%</td>
</tr>
<tr>
<td>3rd</td>
<td>103 ns</td>
<td>135 ns</td>
<td>173 ns</td>
</tr>
<tr>
<td>intensity</td>
<td>43%</td>
<td>86%</td>
<td>35%</td>
</tr>
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with MA$_x$FA$_{1-x}$PbI$_3$, as it enhances the diffusion length of the material.

In summary, we have demonstrated for the first time a perovskite-sensitized photovoltaic device based on the mixed-cation 3D perovskite (MA)$_x$(FA)$_{1-x}$PbI$_3$ ($x = 0–1$). The formamidinium cation is presented as a potential replacement for methylammonium in lead iodide perovskites, owing to the red-shifted absorption onset of FAPbI$_3$ as compared to that of MAPbI$_3$. Devices based on FAPbI$_3$ were made by sequential deposition and gave a PCE of 11.0% (a lower value than that of MAPbI$_3$ owing to the presence of the yellow δ-phase). The sequential deposition method and the addition of 20% MA to the FA dipping bath completely avoided the undesirable formation of the δ-phase while maintaining the red-shifted band gap of FAPbI$_3$. The mixed-cation perovskite MA$_x$FA$_{1-x}$PbI$_3$ exhibited superior PV performance to that of the single-cation analogues owing to a greater harvesting and collection of red photons, which resulted in higher short-circuit photocurrents without sacrificing photovoltage. The superior carrier-collection efficiency is probably related to the longer excited lifetime of more than 130 ns in the MA$_x$FA$_{1-x}$PbI$_3$ material. By using this technique, we were able to fabricate devices yielding up to 14.9% photon-to-current conversion efficiency under the AM1.5G simulated solar spectrum. The strategy of mixing organic ammonium compounds opens up new prospects for the further improvement of the photovoltaic efficiency of perovskite-sensitized solar cells by tuning the optical, electrical, and morphological properties of the semiconducting sensitizer. It is believed that if the formation of the yellow δ-FAPbI$_3$ component could be fully avoided, the performance of pure FAPbI$_3$ would most likely surpass that of MAPbI$_3$-based mesoscopic solar devices. We are currently carrying out studies with this aim.

Keywords: energy conversion - light harvesting - organic cations - perovskite solar cells - photovoltaics

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Experimental Section

Chemicals and Reagents.

Unless otherwise specified, all chemicals and reagents were purchased from Sigma-Aldrich and solvents from Acros Organics and used without further purification. Spiro-MeOTAD was purchased from Merck KGaA. CH3NH3I was synthesized using a reported procedure\textsuperscript{[45]}. NH=CHNH3I was synthesized by dropping slowly 15 ml of hydroiodic acid (45 % wt. in water) (in excess) to a solution of 5 g formamidine acetate in methanol cooled at 0°C. The solution was further stirred for 5 h at room temperature. The light yellow solution was concentrated by rotary evaporation at 50°C for 30 min until no obvious liquid remained. Then the crude solid was dissolved by a minimum amount of methanol and reprecipitated in diethyl ether and filtered. The procedure was repeated three times and the resulting white solid was collected and dried at room temperature under vacuum for 2 days.

Device Fabrication.

Laser-etched FTO glass substrates (NSG10, Nippon Sheet Glass) were cleaned by ultrasonication in an alkaline, aqueous washing solution for 30 min followed by rinsing with deionized water and isopropanol and then UV/O3 treatment for 30 min. A blocking TiO\textsubscript{2} layer was deposited by spin-coating at room-temperature TiCl\textsubscript{4} (2 mol L\textsuperscript{-1}) solution over the conductive glass (speed: 5’000 r.p.m., acceleration: 2’000 r.p.m. sec\textsuperscript{-1}, time: 20 sec) followed by drying at 70°C for approximatively 10 min. The mesoporous TiO\textsubscript{2} layer consisted of commercially available 20 nm-sized TiO\textsubscript{2} nanoparticles (Dyesol 18NRT paste) in a colloidal suspension. The paste was diluted in ethanol (2:7, mass ratio) and stirred continuously. The film was spin-coated over the blocking layer (speed: 4’000 r.p.m., acceleration: 2’000 r.p.m. sec\textsuperscript{-1}, time: 20 sec) followed by drying at 80°C
and 125°C, sequentially. The films were then baked by gradual heating to 500°C for 15 min under dry air flow. Upon cooling, the films were transferred to a dry-atmosphere glove box (< 1% relative humidity) for further manipulations.

PbI₂ was dissolved in N,N-dimethylformamide at a concentration between 554 mg ml⁻¹ and 623 mg ml⁻¹ (~1.2 to 1.35 mmol ml⁻¹ DMF) under continuous stirring at 75°C and kept at this temperature during the whole procedure. The mesoporous TiO₂ films were infiltrated by the PbI₂ solution prior to spin-coating (speed: 6’500 r.p.m., acceleration: 5’000 r.p.m. sec⁻¹, time: 10 sec) and then dried at 75°C for approximately 10 min. The films were dipped in a solution of CH₃NH₃I, HN=CHNH₃I or a mixture thereof for 30 seconds prior to rinsing with pure isopropanol and spin coating to uniformly dry the films (speed: 2’000 r.p.m., acceleration: 1’200 r.p.m sec⁻¹, time: 30 sec). In the solution, the total iodide concentration was kept constant at 0.062 mol g⁻¹ iPrOH. After spin-coating, the films were dried at 75°C for 10 min before cooling down to room temperature (~25°C) for further manipulation.

The hole-transporting-material layer was deposited by spin coating (speed: 2’000 r.p.m., acceleration: 1’200 r.p.m. sec⁻¹, time: 20 sec) from a solution containing 72.3 mg of (2,2’,7,7’-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene) (spiro-OMeTAD), 28.8 µg of 4-tert-butylpyridine, 17.5 µl of a stock solution 520 mg ml⁻¹ lithium bis(trifluoromethylsulphonyl)imide in acetonitrile and 29 µl of a stock solution of 300 mg ml⁻¹ tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) bis(trifluoromethylsulpho- nyl)imide in acetonitrile in 1 ml chlorobenzene.

Finally, about 100 nm of gold was thermally evaporated on top of the device to form the counter-electrode.
Device characterization.

The J-V characteristics were recorded by biasing an external potential bias to the cell while recording the current output using a digital source meter (Keithley Model 2400). The light source was a 450 W Xenon lamp (Oriel) equipped with a Schott K113 Tempax sunlight filter (Praezisions Glas & Optik GmbH) to match the emission spectra of the lamp to the AM1.5G standard. Before each measurement, the exact solar intensity was determined using a calibrated Si diode equipped with a color filter (KG-3, Schott). IPCE spectra were recorded as a function of wavelength under a constant light bias of approximately 5 mW cm\(^{-2}\) supplied by an array of white light-emitting diodes. The excitation beam coming from a 300 W xenon lamp (ILC Technology) was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd) and chopped at approximately 2 Hz. The signal was recorded using a Model SR830 DSP Lock-In Amplifier (Stanford Research Systems).

All measurements were conducted using a non-reflective metal aperture of 0.285 cm\(^{-1}\) or larger to define the active area of the device and avoid waveguide effects. Each point was measured every 5 or 10 nm with 2 mm slit width.

Single optical path spectrophotometry.
Figure SI 1. Normalized emission of MA$_x$FA$_{1-x}$PbI$_3$ (x = 0 to 1) spin coated over non-conductive glass from a $N,N$-dimethylformamide solution of 20% wt. PbI$_2$ and MAI/FAI in the right stoichiometry.

Figure SI 2. Emission maximum for the two different deposition processes as a function of MAI molar ratio in the precursor solution. The films formed by sequential deposition show similar emission shifts as the films spin-coated from the common precursors in $N,N$-dimethylformamide.
Figure SI 3. Absorbance spectra of the different films in transmission mode. The scale is extended to demonstrate the tailing scattering absorption of the films up to 1000 nm. Note that the both samples using either pure MAPbI$_3$ and MA$_{0.8}$FA$_{0.2}$PbI$_3$ show significant scattering that is not present in other samples. This scattering is attributed to the formation of a perovskite capping layer which is supported by SEM pictures shown in SI 7.

Single-pass absorbance measurements were conducted in transmission mode using a custom-made setup equipped with a commercial halogen lamp (20 W) chopped by a rotating wheel at about 36 Hz. The incident beam was restricted to an aperture of approximately 0.05 cm$^2$. The signal was dispersed through a Gemini-180 double monochromator (Jobin Yvon Ltd) with 1.6 mm slit width and recorded by a UVS/IGA 2-color photodiode. The signal was processed by a Model SR830 DSP Lock-In Amplifier (Stanford Research Systems). Each point was recorded for 0.5 s each nanometer. Blank acquisitions were measured with FTO-coated glass covered by a blocking TiO$_2$ layer and mesoporous TiO$_2$ film deposited in the same conditions as the measured samples. Photoluminescence were recorded using the same setup operated without bias light. A blue diode (460 nm) was flashed at 9 Hz by the Lock-In Amplifier. The light was filtered through a K-45 interference filter (Balzers) and focused onto an aperture of 0.05 cm$^2$. The sample was installed at 30$^\circ$ from the incoming light source.
The photoluminescence signal was dispersed through the monochromator (0.8 mm slit width) and recorded by the Lock-In Amplifier (8 seconds per point, 1 nm steps).

**Absorptance spectra.**

To measure the absorptance spectra, the films were cut to the dimension of a custom-made sample holder (13 x 12 mm) and placed in a 102 mm diameter integration sphere (Horiba F-3018). The measurements were conducted in a Fluorolog 322 (Horiba Jobin Yvon Ltd Spectrofluorometer). Samples were illuminated with a 450 W Xe lamp filtered through a double monochromator (slit with 0.5 mm) directed into the sphere. The samples were measured successively at 90° and 0° from the incoming beam and subtracted. The outgoing beam was filtered through a 0.5% grey filter (Horiba). All the spectra were photometrically corrected. The emission monochromator was scanned synchronously with the excitation monochromator and was calibrated before the measurement.

**Fluorescence lifetime measurements.**

Photoluminescence measurements were conducted on a Fluorolog 322 (Horiba Jobin Yvon Ltd) spectrofluorometer equipped with a NanoLED-405LH (Horiba) laser diode (406 nm) pulsed at 1 MHz (Pulse duration < 200 ps). The output aperture was covered by a 520 nm cut-off filter (Schott Glass) and additional grey filters if required. The emission monochromator was set at 750 nm with 10 mm slit width. Photoluminescence was recorded using a picosecond photodetection module (TBX-04, Horiba Scientific). The samples were mounted at 60° and the emission recorded at 90° from the incident beam path.
XRD measurements.

For X-Ray diffractograms measurements, films of mesoporous TiO2 were spincoated onto FTO glass using the previously mentioned procedure. X-ray powder diagrams were recorded on an X’Pert MPD PRO (Panalytical) equipped with a ceramic tube (Cu anode, \( \lambda = 1.54060 \) Å), a secondary graphite (002) monochromator and a RTMS X’Celerator (Panalytical). The measurements were done in the Bragg-Brentano geometry. The samples were mounted without further modification and the automatic divergence slit and beam mask were adjusted to the dimension of the films. A step size of 0.008° was chosen for an acquisition time of 7.5 min deg\(^{-1}\). A baseline correction was applied to all X-Ray powder diffractograms to compensate for the broad feature arising from the glass substrate.

Figure SI 4. X-Ray diffraction spectra of mesoporous TiO\(_2\) films infiltrated with MA\(_x\)FA\(_{1-x}\)PbI\(_3\) (x = 0 to 1). The precursors were mixed together in a 20% wt. N,N-dimethylformamide solution and spin-coated over the film before annealing at 120°C for 10 minutes.
Figure SI 5. Zoom of Figure SI 5 over the 11-14° region.

Figure SI 6. X-Ray diffraction spectra of mesoporous TiO$_2$ films infiltrated with MA$_x$FA$_{1-x}$PbI$_3$ (x = 0 to 1). PbI$_2$ was deposited from a 1.2M solution in N,N-dimethylformamide for 10 seconds at 6’500 r.p.m. After drying at 80°C for about one hour, the samples were cooled down to room temperature (about 25°C) and dipped into a dilute solution of MAI/FAI or a mixture thereof in isopropanol where the iodide concentration was 0.062 mol g$^{-1}$ iPrOH. The films were then dried at 80°C for one hour before the measurement.
Electrical measurements

For the electrical transport properties, polycrystalline samples of the different compositions were obtained by uniaxially pressing (150 MPa) the starting powders. Electrochemical a.c. impedance spectroscopy were carried out using a high resolution dielectric analyzer (Novocontrol GmbH) at frequencies ranging between 10 MHz and 1 Hz (applied a.c. voltage = 0.1 V, carbon electrodes). The impedance spectra were analyzed using the commercial software Z-View by Scribner Ass. For galvanostatic d.c. measurements, currents ranging between 1 and 10 nA were applied with a Keithley 220 programmable current source and the corresponding voltage response was measured with a Keithley 6514 system electrometer. For the d.c. tests, the same electrodes as for the impedance spectroscopy were used. Note that all electrical measurements were carried out in Argon atmosphere and temperatures ranging between 30 and 70°C.
Figure SI 7. (a) Top view SEM of a full FAPbI₃ device showing small crystals in the capping layer. (b) Top view SEM of a full MAPbI₃ device showing massive perovskite crystals in the capping layer.