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Chemical engineering of methylammonium lead iodide/bromide perovskites: tuning of opto-electronic properties and photovoltaic performance†

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Hybrid (organic–inorganic) lead trihalide perovskites have attracted much attention in recent years due to their exceptionally promising potential for application in solar cells. Here a controlled one-step method is presented where PbCl_2 is combined with three equivalents methylammonium halide (MAX , with $\text{X} = \text{I}$ and/or Br) in polar solvents to form $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ perovskite films upon annealing in air at 145°C . The procedure allows for a linear increment of the semiconductor bandgap from 1.60 eV to 2.33 eV by increasing the Br content. A transition from a tetragonal to a cubic structure is found when the Br fraction is larger than 0.3. X-ray photoelectron spectroscopy investigations shows that the increase of Br content is accompanied by a shift of the valence band edge to lower energy. Simultaneously, the conduction band moves to higher energy, but this shift is less pronounced. Time-resolved single-photon counting experiments of the perovskite materials on mesoporous TiO_2 show faster decay kinetics for Br containing perovskites, indicative of improved electron injection into TiO_2 . Interestingly, kinetics of $\text{MAPbI}_{2.7}\text{Br}_{0.3}\text{Cl}_y$ on TiO_2 scaffold became faster after prolonged excitation during the measurement. In solar cell devices, $\text{MAPbI}_{2.7}\text{Br}_{0.3}\text{Cl}_y$ yielded best performance, giving more than 14% power conversion efficiency when used in combination with an n-type contact consisting of fluorine-doped tin oxide glass coated with dense TiO_2 and a mesoporous Al_2O_3 scaffold, and a p-type contact, spiro-MeOTAD/Ag.

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Introduction

Hybrid (organic–inorganic) metal halide perovskite materials are highly interesting for application in very efficient low-cost solar cells.¹ Within a few years of active research of these material for photovoltaic applications, power conversion efficiencies have already reached about 20% for small devices² and may soon approach and surpass the record efficiencies of silicon and thin film technologies, such as $\text{Cu}(\text{In}, \text{Ga})\text{Se}_2$ and CdTe .

Mitzi and co-workers have studied the properties of a large range of hybrid lead halide perovskites in detail.³ These materials were used as the active layer in light emitting diodes and field-effect transistors.³ Hybrid lead halide perovskites have also the potential to be used in photovoltaics, with various device

architectures and efficiencies reported over 20%.^{2,5–12} Hybrid lead halide perovskite materials can be manufactured by simple solution processes, as well as by vacuum evaporation, and their optical, electronic and morphological properties can be tuned by changing the chemical composition, *e.g.* changing the organic cation, the metal atom and/or the halide.^{13–15}

Tunability of the semiconductor bandgap is a very attractive feature for solar cell materials. Specifically, it allows for devices with a specific color, or for semi-transparent solar cells that can be used as top cells in tandem devices. Among the hybrid lead halide perovskites, methylammonium lead triiodide (MAPbI_3) is the most investigated material, exhibiting a bandgap of around 1.5 eV,^{10,11} whereas MAPbBr_3 presents a larger bandgap of 2.2 eV.¹¹ Noh *et al.* were first to demonstrate that the bandgap of these materials can be fine-tuned by mixing iodide and bromide. Interestingly, bromide-containing perovskites were found to display better stability under moist air conditions.¹¹ By comparison, MAPbCl_3 possesses a large bandgap of 3.1 eV.¹⁶ In mixed halide preparations where chloride-based precursors are used, however, no significant inclusion of chloride is observed in the perovskite crystal structure. Instead it appears either as separate MAPbCl_3 crystals,^{17,18} or it disappears upon annealing.¹⁹ Nevertheless, the chloride content in the precursor

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solution plays an important role in the realization of good quality perovskite materials,¹⁸ presumably due to the formation of an intermediate phase.

In this work, we have studied the formation of $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3(\text{Cl})_y$ materials, where x is the fraction of bromide, using PbCl_2 as the lead precursor in a one-step solution-based method. A similar approach was used recently by Suarez *et al.*⁴ We demonstrate the possibility to perform linear bandgap tuning of the hybrid lead halide perovskite, and find an extension of the stability range for the tetragonal crystalline structure. A detailed characterization of the structure and the optoelectric properties of the synthesized materials are presented. Time-resolved single-photon counting experiments suggest improved electron injection from hybrid perovskite into TiO_2 when bromide is included. The kinetics found for bromide containing perovskites on TiO_2 scaffold became faster upon prolonged excitation during the measurement. Best solar cell results were obtained for $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3(\text{Cl})_y$ with $x = 0.1$ on mesoscopic Al_2O_3 scaffold layers.

Results and discussion

Solution-based synthesis of MAPbX_3 and structural characterization

In this study we used PbCl_2 , MAI and MABr as precursors for hybrid lead halide perovskites, in combination with a mixture of polar solvents: dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) in a ratio of 7 : 3. Tetrahydrofuran (THF, 10 vol%) was added to the solvent mixture as it was found to decrease the conversion temperature of the organic-inorganic hybrid perovskites (OIHPs) during in the annealing step. The use of PbCl_2 as precursor for Br-containing hybrid perovskites is inspired by the use of this salt as precursor in the work by Snaith and co-workers, who obtained efficient perovskites with the structure $\text{MAPbI}_{3-x}\text{Cl}_x$.¹⁰ In later studies, it was found that the chloride content of this material was less than 5%.²⁰ In our study, the ratio MAX (where X is I or Br) to PbCl_2 was kept at 3 : 1 in the preparation. We will refer to the formed materials as $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3(\text{Cl})_y$ to indicate that they were made using chloride-containing precursors. The resulting films do, however, not contain substantial amounts of chloride, as discussed elsewhere.¹⁹ The overall reaction for formation of the hybrid perovskite is proposed to be:

where X is I and/or Br. Upon annealing, MACl is decomposed into gas phase components: $\text{MACl}(\text{s}) \rightarrow \text{CH}_3\text{NH}_2(\text{g}) + \text{HCl}(\text{g})$. However, it is expected that to some degree such reactions already occur in the precursor solution.

Fig. 1 presents the X-ray diffractograms of $\text{MAPbI}_3(\text{Cl})_y$ and $\text{MAPbBr}_3(\text{Cl})_y$ materials spin-coated on a mesoscopic $\text{TiO}_2/\text{glass}$ substrate, either dried in ambient environment (25 °C) or annealed at 145 °C for 45 minutes (the substrate temperature increased gradually from 20 to 140 °C in this period, see ESI, Fig. S16†). During the drying process of the OIHP precursor solution, THF, which has a boiling point of 66 °C, is expected to

evaporate readily, while DMF and DMSO may partially remain in the dried OIHP precursor film. This is confirmed by ATR-FTIR, which demonstrates that DMSO is still partially present in the dried precursor films, see Fig. 1c and S1.† The dried precursor films have clear XRD patterns that differ from the XRD patterns of crystalline PbCl_2 , PbI_2 , PbBr_2 or MA salts (see Fig. 1(c) and S3 in ESI†). This is a clear indication that a complexation reaction occurs between PbCl_2 , the halide salts and/or solvents at low temperature. When comparing dried and annealed OIHPs, significant differences are found between $\text{MAPbI}_3(\text{Cl})_y$ and $\text{MAPbBr}_3(\text{Cl})_y$, where $\text{MAPbI}_3(\text{Cl})_y$ is transformed from an intermediate phase at room temperature (see black solid line in Fig. 1(a)) to a tetragonal perovskite structure upon annealing (space group: $I4/mcm$, see blue solid line in Fig. S2(e)†).²¹ The intermediate phase of OIHP does not match with crystalline phases reported in literature, but is similar to the XRD pattern reported for MACl-assisted formation OIHP.²² The $\text{MAPbBr}_3(\text{Cl})_y$ precursor dried at room temperature has a cubic phase (space group: $Pm3m$) and is very similar to the perovskite structure obtained after annealing at 145 °C (see Fig. 1(b)). It has a bright yellow lemon color, which changes to a slightly darker yellow color upon annealing. During this process, the XRD pattern is only slightly shifted to lower angles something that may be attributed to the vaporization of MACl (see red solid line in Fig. 1(b)).^{21–24}

In the preparation method used, it is easy to obtain mixed $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3(\text{Cl})_y$ perovskites, simply by adding the required proportion of MAI and MABr to the PbCl_2 -containing precursor solution. XRD measurements (Fig. 2) show a gradual change from a tetragonal structure, as found for the pure MAPbI_3 phase, to a cubic structure, as found for the pure MAPbBr_3 . The complete XRD patterns for the formed $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3(\text{Cl})_y$ perovskites are shown in ESI (Fig. S2†). Similar observations for mixed I/Br lead perovskite have previously been reported by Noh *et al.* and Eperon *et al.*^{11,25} Fig. 2(a) and (b) shows the (110)t peak that transforms into the (100)c peak, and the (224)t peak that becomes (220)c. The calculated lattice parameters for orientations of all OIHPs are summarized in Fig. 2(c). The crystallinity of (110)t for $\text{MAPbI}_3(\text{Cl})_y$ in this study and in our previous study is observed very much higher than for a standard MAPbI_3 film prepared in the absence of chloride ions.²¹ The lattice constants change gradually with the bromide fraction x , but a clear singularity is found between $x = 0.3$ and 0.4 for all crystal orientations, which we attribute to the transition from a tetragonal to a cubic structure. In the study by Noh *et al.*¹¹ this transition for $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3(\text{Cl})_y$ was found to occur between $x = 0.13$ and 0.20 . This suggests that the synthetic details and the choice of precursors are crucial for the composition of this transition, and that the presence of chloride anions in our preparation and extends the stability range of the tetragonal crystalline structure. Eperon *et al.*²⁵ found for $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ perovskite, where FA is formamidinium, a tetragonal phase for $x = 0$ to 0.2 and a cubic for $x = 0.6$ to 1 , while intermediate preparations did not give crystalline phases.

The degree of crystallinity of the different films is shown in Fig. 2(d), which displays the integrated intensity of the crystalline populations. This value is rather constant value for Br

Fig. 1 XRD patterns of room temperature-dried hybrid perovskite precursors and hybrid perovskite thin films. (a) Comparison between dried and annealed OIHP samples of $\text{MAPbI}_3\text{Cl}_y$. (b) Comparison of dried and annealed $\text{MAPbI}_3(\text{Cl})_y$. (c) ATR-FTIR spectra of dried and annealed $\text{MAPbI}_3(\text{Cl})_y$.

fractions from $x = 0.0$ to 0.3 in $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3(\text{Cl})_y$. From $x = 0.4$ to 1 an increase in crystallinity is found. The boundary between decreasing and increasing crystallinity at $x = 0.3$ – 0.4 lies at the same position as the transition from tetragonal to cubic phase.

The surface morphologies of the different perovskite samples on mesoporous (ms) TiO_2 were investigated using scanning electron microscopy (SEM), see Fig. 3. In all samples part of the underlying ms- TiO_2 is visible; there is thus no complete over-standing layer of perovskite. The coverage was best (ca. 80%) for samples with $x = 0.3$ to 0.7 . Clear differences in the perovskite morphology are observed depending on its composition. In $\text{MAPbI}_3(\text{Cl})_y$ many morphological defects are found, while in the case of $\text{MAPbI}_{2.7}\text{Br}_{0.3}(\text{Cl})_y$ the surface appears to be much denser (Fig. 3(a) and (b)). Jeon *et al.* reported rather similar observations of morphological differences between FAPbI_3 and $(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$, namely, that Br improves the formation of dense, defect free perovskite films.²

Optical absorption and emission

Thin films of mixed $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ perovskites on ms- $\text{TiO}_2/\text{glass}$ substrates display a gradual change of color when the fraction Br is increased, from dark brown ($x = 0$) to yellow ($x = 1$), see the pictures in Fig. 4. The corresponding shifts in optical spectra are

shown in Fig. 4(a). The absorption onset of $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3(\text{Cl})_y$ changed systematically from 780 nm to 540 nm with increasing Br fraction, consistent with observations in recent studies.^{4,11,25} Notably, crystalline bulk MAPbI_3 is also reported to have a higher absorption onset of about 820 nm .²² The optical band gaps were extracted from a Tauc plots, presented in Fig. S8 in ESI.† Based on this procedure optical bandgaps of 1.60 eV and 2.33 eV in were determined for $\text{MAPbI}_3(\text{Cl})_y$ and $\text{MAPbBr}_3(\text{Cl})_y$, respectively, and the bandgaps of the intermediate compositions $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3(\text{Cl})_y$ vary rather linearly between these numbers (see Fig. 4(b)). The values found here are slightly larger than those reported by Noh *et al.* and Suarez *et al.* in similar studies.^{4,11}

An interesting observation is that the gradual increase in absorbance at wavelengths below 650 nm for $x = 0.0$ to 0.2 , a feature which is frequently found in MAPbI_3 thin films, is absent for $x = 0.3$ to 0.5 . The origin of this absorption is not well understood, but it is possibly due to the presence of amorphous OIHP, left after incomplete reaction.²⁶ Absence of this absorbance can then be attributed to formation of more crystalline OIHPs for films with Br fraction $x = 0.3$ to 0.5 (although it is noted that the integrated XRD intensities do not show significant changes in this range (Fig. 2(d))). For $x = 0.6$ to 1.0 , the onset wavelength of the gradual increase in absorbance changes from 550 to 480 nm .

Photoluminescence (PL) spectra were measured on aged $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3(\text{Cl})_y$ samples at around 30°C for 20 days,

Fig. 2 Transition of the tetragonal to the cubic phase in XRD diffractograms of $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3(\text{Cl})_y$, for $x = 0\%$ Br to 100% Br in 10% steps (from left to right), shown for (a) the (110)t peak to (100)c peak and (b) (224)t to (220)c. (c) Calculated lattice constants and (d) calculated crystalline population for variable ratio of Br substitution of OIHPs.

see Fig. 4(c) and S5.† Sadhanala *et al.* found that fresh $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films and 21 days aged films have significantly different PL spectra, suggesting stabilization of the structure upon aging.²⁷ We find a systematic change of the emission peak with the fraction of Br, as has been demonstrated previously,^{25,27,28} ranging from 535 nm for $\text{MAPbI}_3(\text{Cl})_y$ to 775 nm for $\text{MAPbBr}_3(\text{Cl})_y$, see Fig. 4(e). In the range $x = 0.4$ to 0.9 in $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3(\text{Cl})_y$, however, rather different PL spectra are found: these spectra show a weak emission peak in the expected range between 535 and 700 nm, but a much larger peak at lower wavelength, see Fig. 4(d) (PL spectra without normalization are shown in ESI, Fig. S5†). We attribute this to energy transfer from the mixed $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3(\text{Cl})_y$ phase to a small fraction of MAPbI_3 nanocrystals, which subsequently emits. The emission is blue shifted compared to that found for the $\text{MAPbI}_3(\text{Cl})_y$ sample, which is due to either a small fraction of Br in the nanocrystals or the small size of the MAPbI_3 nanocrystals, so small that the bandgap is increased due to quantum-size effects (quantum confinement effects).²⁹

X-ray photoelectron spectroscopy (XPS) studies

Valence band (VB) spectra of the series of $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3(\text{Cl})_y$ materials deposited on ms-TiO_2 are presented in Fig. 5(a). A close-up of the upper valence band (+3.5 to −2 eV energy range) is shown in the insert and includes a linear extrapolation and an indication of the experimental spectral edge as described in the

Experimental section. We can observe that the valence band for the present set of samples shift to higher binding energy *versus* the Fermi level when the amount of bromine increases in the material. In such comparisons, it is important to remember that the observed Fermi level might be sensitive to subtle variations such as bulk doping and surface states. A difference in valence band edge of about 0.5 eV between $\text{MAPbI}_3(\text{Cl})_y$ and $\text{MAPbBr}_3(\text{Cl})_y$ is observed.

Using the valence band data from XPS and the bandgap determined from optical absorption, we can construct the energy diagrams presented in Fig. 5(b). Increase of Br content in $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3(\text{Cl})_y$ leads to a decrease in the VB energy and an increase in the conduction band (CB) level. The procedure used here indicates that the shift in VB is slightly more pronounced than the shift in CB.

Time-correlated single photon counting (TCSPC)

To gain further insight into the luminescence properties, we measured time-resolved emission of $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3(\text{Cl})_y$ samples. The main results are summarised in Fig. 6. For samples on mesoporous TiO_2 with different fractions of Br ($x = 0, 0.1, 0.4, 0.7$ and 1), the decay traces are given in Fig. 6(a). Clearly, the observed decays are not single exponential, but are well-fitted using a bi-exponential function. The obtained lifetimes and amplitudes are shown in Fig. 6(b) and (c), respectively. As a general trend, increasing the Br fraction leads to

Fig. 3 Top view SEM images (4 μm scales, horizontal bars) of the different $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3(\text{Cl})_y$ perovskite deposited on a mesoscopic $\text{TiO}_2/\text{glass}$ substrate.

significantly faster luminescence decay. A very long-lived component (25% amplitude, $\tau_2 = 3.5 \mu\text{s}$) is found for perovskite with a Br mole fraction of 0.1. The longer of the fitted lifetimes components τ_2 changes from 1.0 *via* 3.5, 0.9, 0.5 to 0.1 μs when increasing x from 0 to 1, while the corresponding decreases for the faster component τ_1 is from 0.18 μs to 0.01 μs . A possible explanation for the bi-exponential decay is that part of the perovskite material is in direct contact with mesoscopic TiO_2 , and shows a short lifetime due to electron injection,³¹ while the over-standing layer of perovskite is not able to inject directly and gives longer PL lifetimes.³² This idea is strengthened by measurements of perovskite films on glass substrates. As can be seen in Fig. 6(g) and (h) for $\text{MAPbI}_3(\text{Cl})_y$ and $\text{MAPbI}_{2.7}\text{Br}_{0.3}(\text{Cl})_y$ respectively, both perovskite samples on glass substrates, show very long lifetimes ($\tau_2 = 1.2 \mu\text{s}$), which is indicative of high-quality photovoltaic material.³³ These films are presumably structurally similar to the overstanding layers of perovskite films deposited on mesoscopic scaffold layers. Surprisingly, perovskites on Al_2O_3 scaffold layers shows a significant part of rapid luminescence quenching. In this case electron injection cannot take place. Rapid quenching must be induced by the mesoscopic structure, or by interface states at the Al_2O_3 . Aristidou *et al.*³⁴ found a fast quenching process for MAPbI_3 on mesoscopic Al_2O_3 that is related to the generation of superoxide

(O_2^-) on the perovskite surface formed in a photoinduced reduction process of oxygen. Further detailed studies are, however, needed to resolve the precise origin of rapid emission quenching in our case.

When conducting the TCSPC measurement of mixed I/Br perovskites on TiO_2 , the kinetics was observed to change during the course of the data acquisition. Early, quick measurements showed very long lifetimes, which became faster with increasing measurement times. For samples with Al_2O_3 and glass as substrate, however, no such trend was observed. This is illustrated in Fig. 6(d)–(f), where the fitted lifetimes are plotted against the irradiation time during the measurement (given as accumulated counts in the maximum channel). A light-induced modification of mixed-halide perovskites has recently been reported by Hoke *et al.*³⁵ They reported that observed fluorescence changes are accompanied by changes in the XRD pattern and are thus assumed to involve structural modifications and segregation into two crystalline phases, including an iodide-rich (I-rich) one acting as quencher for the high-energy states. An important observation in our work is that light-induced changes were only visible on ms-TiO_2 as a substrate, not on glass or $\text{ms-Al}_2\text{O}_3$ under the given illumination conditions. This may hint at the role of charges that are required for the formation of I-rich OIHP centers.

Fig. 4 Top: Optical photographs of MAPb(I_{1-x}Br_x)₃(Cl)_y films. (a) UV-vis absorption spectra of these samples. (b) Optical bandgap as function of Br-fraction in MAPb(I_{1-x}Br_x)₃(Cl)_y. (c) Photoluminescence spectra for the same films (normalized at maximum emission peak). (d) PL spectra of MAPb(I_{1-x}Br_x)₃(Cl)_y films scaled for bandgap emission. (e) PL emission peak energy as function of Br-fraction in MAPb(I_{1-x}Br_x)₃(Cl)_y.

Toluene addition to OIHP precursor was found to improve crystallinity, coverage area and density of the films for solar cell application. This effect was investigated by UV-vis spectra, XRD,

SEM images and solar cell performances, reported in ESI, Fig. S9 to S11.† Toluene addition in OIHP precursor also gave slightly better PL lifetimes (MAPbI₃(Cl)_y/Al₂O₃/glass: around 1.4

Fig. 5 (a) Valence levels spectra of the $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3(\text{Cl})_y$ series measured by XPS with a photon energy of 1486.6 eV. Inset: zoom of the upper valence band (+3.5 to -2 eV energy range) including a linear extrapolation and an indication of the experimental spectral edge for the MAPbI_3 and MAPbBr_3 samples. (b) Schematic drawing of the $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3(\text{Cl})_y$ energy levels determined from (a) and Fig. 4(b). The energy level scale is set versus the Fermi level using the experimental spectral edge (full arrows), i.e. 0.4 eV were removed from the linear extrapolation energies (dashed arrows).

μs (τ_2) and $\text{MAPbI}_{2.7}\text{Br}_{0.3}(\text{Cl})_y/\text{Al}_2\text{O}_3/\text{glass}$: around 0.8 μs (τ_2)). The fitting values are shown in Fig. S7(c) and (d).†

Solar cell performance

The solar cell performance of $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3(\text{Cl})_y$ with a low fraction of Br (0 to 10%) was tested. In this regime, the differences in light harvesting efficiency due to the change in bandgap were not significant. In Fig. 7, J - V and IPCE curves of

solar cells using ms-TiO_2 scaffold layer are summarized. Short-circuit current densities calculated by integration of IPCE results are in good accordance with experimental J_{sc} data under simulated sunlight. The open-circuit potential (V_{oc}) and the short-circuit photocurrent density (J_{sc}) increased from 0.68 to 0.82 V and from 13.7 to 21.6 mA cm^{-2} , respectively, with an increase of Br content from 0 to 10%. The effect of Br content from 0 to 10% is also clearly seen in IPCE curves in the plateau values that increase, and in the slight blue shift

Fig. 6 Time-Correlated Single Photon Counting (TCSPC) results at 2500 counts of $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3(\text{Cl})_y$ films. (a) TCSPC results for variation of fraction of Br on OIHPs/ TiO_2 ($x = 0.0, 0.1, 0.4, 0.7$ and 1.0) (b) PL decay time constants τ_1 and τ_2 obtained from biexponential fits of data shown in (a). (c) Fitted amplitudes A1 and A2 from the same, (d) effect of illumination time on PL decay time constants for $\text{MAPbI}_3(\text{Cl})_y/\text{TiO}_2$ (the amplitudes are constant at A1 79% and A2 21%), (e) effect of illumination time on PL decay time constants for $\text{MAPbI}_{2.7}\text{Br}_{0.3}(\text{Cl})_y/\text{TiO}_2$ (the amplitudes are constant at A1 25% and A2 75%). (f) Effect of illumination time on PL decay time constants for $\text{MAPbI}_{2.7}\text{Br}_{0.3}(\text{Cl})_y/\text{Al}_2\text{O}_3$ (the amplitudes are constant at A1 50% and A2 50%). TCSPC results at 20 000 counts on (g) $\text{MAPbI}_3(\text{Cl})_y$ and (h) $\text{MAPbI}_{2.7}\text{Br}_{0.3}(\text{Cl})_y$ with different substrates as indicated.

of the photocurrent onset edges from 800 nm to 778 nm in Fig. 7(b). We believe that these enhancements are related to the denser perovskite structure with lower amount of defects found for the 10% Br substituted OIHP. These results may also be correlated with TCSPC experiments that show faster initial decay for the 10% Br perovskite, which may be indicative of more efficient electron injection in the mesoporous TiO_2 , as well as a longer lived photoluminescence tail, which may indicate better perovskite quality in the overstanding layer.³²

The fill factors (FF) of the perovskite solar cells using ms- TiO_2 scaffold layer are poor, ranging from 0.35 for $\text{MAPbI}_3(\text{Cl})_y$ to 0.48 (5% Br sample). We attribute the low FF to the poor overstanding OIHP layer that covers only part of the ms- TiO_2 scaffold (see Fig. 3 and S10(a,b,e and f)†). This implies that there is much contact between the spiro-OMeTAD hole conducting material (HTM) and the ms- TiO_2 , giving rise to significant electron/hole recombination.

The use of an ms- Al_2O_3 scaffold layer has been reported to enhance V_{oc} and PCE of hybrid perovskite solar cells.¹⁰ Recombination between ms- TiO_2 to HTM is prevented in this device structure. Using Al_2O_3 scaffold layer in combination with $\text{MAPbI}_3(\text{Cl})_y$ and $\text{MAPbI}_{2.7}\text{Br}_{0.3}(\text{Cl})_y$, we obtained much improved PCE values of 8.0% and 14.2%, respectively. A possible explanation is that rapid trapping of one charge carrier occurs in case of the presence of an Al_2O_3 scaffold layer, as may be deduced from TCSPC results. This can be beneficial charge separation.³⁴ There is a significant hysteresis in the $J-V$ curves for forward and reverse scan these devices. Interestingly, the composition of the perovskite had a large effect on the degree of hysteresis. For $\text{MAPbI}_3(\text{Cl})_y$, 30% difference in the calculated PCE value was found (forward (short circuit current to open circuit voltage): 5.6% and backward (open circuit voltage to short circuit current): 8.0%), while for $\text{MAPbI}_{2.7}\text{Br}_{0.3}(\text{Cl})_y$ it was less than 10% (PCE forward: 14.2% and backward: 12.8%). This different $J-V$

Fig. 7 Solar cell performances for different ratio of Br substituted OIHPs; (a) J–V curve (TiO₂ scaffold layer), (b) IPCE curves (TiO₂ scaffold layer), (c) J–V curves of MAPbI₃(Cl)_y and MAPbI_{2.7}Br_{0.3}Cl_y (Al₂O₃ scaffold layer), (d) summary of PCE values obtained for perovskite solar cells with TiO₂ or Al₂O₃ scaffold layer with different fractions of Br.

hysteresis can be attributed to the improved quality of OIHP film that contains a fraction of Br.

Conclusion

A convenient 1-step synthesis method for the mixed hybrid perovskite MAPb(I_{1-x}Br_x)₃(Cl)_y, using PbCl₂ as lead source, was investigated. The boundary between tetragonal and cubic crystalline phase was found to occur between $x = 0.3$ and 0.4 . The optical bandgap varied linearly with the bromide fraction x from 1.60 to 2.33 eV. PL spectra showed the same gradual change, however, at intermediate x -values additional and stronger emission was found at lower energy, attributed to energy transfer of a small fraction of I-rich OIHP quantum dots.

Time-resolved single-photon counting investigations suggest that inclusion of bromide leads to improved electron injection from hybrid perovskite into mesoporous TiO₂. Prolonged excitation during this measurement led to faster decay kinetics of bromide containing perovskites on TiO₂ scaffold, while they were unchanged on mesoscopic Al₂O₃. Best solar cell results

were obtained for MAPb(I_{1-x}Br_x)₃(Cl)_y with $x = 0.1$ on mesoscopic Al₂O₃ scaffold layers, yielding 14% efficiency.

Methods

Materials and sample fabrication for characterization

MAI was synthesized by reacting 360 mL methylamine (40% in water, Sigma Aldrich), 280 mL methylamine (40% in methanol, TCI) and 40 mL of hydroiodic acid (without stabilizer, distilled 57 wt% in water, Aldrich) in a 1000 mL round bottom flask at around 0 °C for 5–7 h with stirring. The precipitate was recovered by evaporation at 70 °C for 3 h. The MAI was washed with diethyl ether by stirring the solution for 30 min, which was repeated three times then finally dried at 70 °C in a vacuum oven for 24 h. The yellowish colored MAI (MW 158.96) product was obtained. MABr (MW 111.97) was synthesized as described elsewhere.¹¹ Precursor solutions MAPbI₃(Cl)_y, MAPb(I_{1-x}Br_x)₃(Cl)_y and MAPbBr₃(Cl)_y were formed by mixing a ratio of three to one of MAI (0.9 to 0.0 M) and MABr (0.0 to 0.9 M) with PbCl₂ (0.3 M) in dimethylformamide (DMF)/dimethyl sulfoxide (DMSO) (7/3 = v/v). PbCl₂ was first completely dissolved by stirring on a hot-plate

set at 70–80 °C for few hours, after then they reacted with MAI or MABr (mixed MAX: X = Br and I) for 2 hours. Finally, tetrahydrofuran (THF, 10 vol%) was added. TiO₂ nanoparticles were deposited on microscope glass by spin coating method at 3000 rpm for 30 s. The TiO₂ suspension was Dyesol paste (DSL 30 NR-D) diluted with terpinol 25 wt% in ethanol (1 : 4 = g/g). The TiO₂ nanoparticle coated microscope glass was annealed onto hot plate at 550 °C for 30 min. The film thickness was approximately 300 nm (± 50 nm) as determined by a Dektak3 profiler. Unless stated otherwise, OIHP precursors are coated onto TiO₂/glass substrate by spin-coating method at 1500 rpm for 30 s. These are annealed onto hot plate at 145 °C for 30–45 min in a dry box (humidity $\leq 20\%$), see Fig. S16.†

ATR FT-IR spectra

ATR FT-IR spectra were obtained from the powders of MAcl, MABr, MAI, dried MAPbBr₃(Cl)_y and MAPbI₃(Cl)_y which were carried on a Nicolet Avatar 370 DTGS spectrophotometer (Thermo Co. LTD., resolution is 0.964 cm⁻¹, scan counting has 300 times per a sample). Background signal was subtracted.

UV-vis-NIR spectra

To measure UV-visible-NIR absorption spectra, organic–inorganic perovskite coated TiO₂ electrodes deposited on working electrode were prepared according to the mention above and the measurements were carried on a Varian Cary 5000 UV-vis-NIR spectrophotometer. The FTO glass substrate signal was used as calibration background.

Steady-state emission measurements

Standard steady-state emission spectra were obtained on a Fluorolog-3 instrument (Horiba Jobin Yvon) equipped with double-grating excitation and emission monochromators and a 450 W Xe lamp as a light source. The emission spectra were corrected for the spectral sensitivity of the detection system by using a calibration file of the detector response. Front-face illumination (30° with respect to the incident beam) was used to minimize inner-filter effects. The pump laser had setup at relevant wavelength to the valence band of OIHPs. The filters has been setup front of detectors.

Time-correlated single photon counting (TCSPC)

A detailed description of the experimental setup has been given recently.³⁶ Briefly, the sample was excited on the perovskite side with 77.1 ps pulses of 404.6 nm from a picosecond diode laser (Edinburgh Instruments, EPL-405). Certain measurements were done with 470 nm excitation (EPL-470). As practically the same results were obtained, we used 404.6 nm excitation because of the shorter instrument response function due to shorter excitation pulses. The laser pulse energy was very low, *ca.* 15 pJ and was attenuated even further to reach the desired count rate of *ca.* 1%. This ensures low enough excitation to avoid Auger recombination³⁷ in OIHPs and that the results are free from pulse pile-up.^{38,39} Measurements were done in reverse mode at 5–10 MHz and under magic angle polarization. A cutoff filter

(OG590) was used to block stray excitation light. A dilute solution of Ludox was used to record the instrument response function without any filter. No monochromator was used, *i.e.* all wavelengths transmitted by the cutoff filter were collected, increasing the instrumental sensitivity.

Crystallographic properties

The OIHP deposited on TiO₂/glass substrate were investigated for crystallographic properties using X-ray diffraction (XRD) with a Siemens diffraktometer D5000 apparatus at room temperature using CuK α radiation in time period. Diffrac plus XRD commander program was used to control the instrument. The instrument was set in “detector scan” mode, and the acquisition was done in θ –2 θ mode for every 0.02° increment over the Bragg angle range of 10–60°.

Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) was performed on a Zeiss (Gemini 1550) microscope having a field emission (FE) electron source and an in-lens detector for secondary electrons. Top view images were recorded using a high tension of 10 kV.

X-ray photoelectron spectroscopy (XPS)

XPS measurements were performed with a Scienta ESCA 300 instrument, using monochromatized AlK α radiation $h\nu = 1486.7$ eV with an overall instrumental resolution of 0.6 eV. The pressure in the analysis chamber was around 1×10^{-8} mbar and the electron take off angle was 90°. The valence spectra presented were binding energy calibrated using the Ti 2p core level signal from the TiO₂ substrate which in this study was set to 459.45 eV. This value was obtained by measuring the energy difference between the Ti 2p core level of pure TiO₂ and the Fermi level on an Au sample with the same instrument. This calibration was crosschecked with the position of the metallic lead sometimes observed and found at 137.0 eV *versus* the Fermi level of the Au sample. Charging and radiation effects were checked for by measuring the specific core level repetitively and was found negligible for all spectra reported in the present investigation. The shape of the VB will depend on the photon energy used.⁴⁰ To evaluate the relative changes in the upper energies of the valence band, we used a linear extrapolation. The *linear extrapolation energy* is defined as the intersection of a linear extrapolation of outermost experimental valence levels with the baseline. Moreover, in the spectra of MAPbI₃ and MAPbBr₃ we indicate an *experimental spectral edge* where the amount of counts above the baseline is less than about one percent of the maximum value at about 4.0 eV. For both MAPbI₃ and MAPbBr₃ we note that the difference between the *experimental spectral edge* and *linear extrapolation energy* is close to 0.4 eV. In the present paper, we therefore remove 0.4 eV to the linear extrapolation energy as an estimation of the valence band edge when compared to the Fermi level.³⁰ This procedure gives values that relate to literature values of the difference between a Fermi level of TiO₂ pinned to the conduction band edge and an anatase bandgap of 3.2 eV.

Fabrication and measurement of solar cell devices

Fabrication of solar cell device. All experiments are carried out in 30%–45% humidity. The OIHP precursors were prepared as follow as in the section of material and sample fabrication for characterization. $\text{MAPbI}_3\text{Cl}_y$, $\text{MAPbI}_{3-x}\text{Br}_x\text{Cl}_y$ and $\text{MAPbBr}_3\text{Cl}_y$ were formed by mixing a ratio of three to one of MAI (3.60 M (100%)–3.24 M (90%)) and MABr (0.00 M (0%)–0.36 M (10%)) with PbCl_2 (1.2 M) in DMF/DMSO (7/3 = v/v) on a hot plate of 70–80 °C for 90 min. For the solar cell devices, tetrahydrofuran (THF)/toluene (1/2 = v/v) mixed solvent was added to the OIHP precursor and it is consisted of 85% precursor and 15% THF/toluene solvent (v/v). The effect of toluene on morphology of OIHP has well been investigated in previous report.⁴² All OIHP precursors are kept on 70 °C on a hot plate during fabrication processes. TiO_2 precursor was prepared as follow as in the section of Materials and sample fabrication for characterization. Al_2O_3 precursor purchased from Sigma Aldrich which is size of ~50 nm in isopropanol and diluted with isopropanol as 1 : 2 (v/v). Fluorine-doped tin oxide (FTO) coated glass (Pilkington TEC 15) $15 \Omega \square^{-1}$ was patterned according to etching processes with Zn powder and 2 M HCl diluted in water. TiO_2 compact layer as electron extracting layer was deposited the film thickness of 40–70 nm onto the etched FTO substrate and temperature of hot plate was kepted at 400–450 °C during spray pyrolysis deposition process. The prepared TiO_2 and Al_2O_3 precursors were spincoated for 20 s at 4000 and 2750 rpm, respectively, and dried on a hot plate at 450 °C (TiO_2) or 150 °C (Al_2O_3) for 30 min. The prepared OIHP precursor was spin coated at 1250 rpm for 20 s and annealed at 145 °C for 30–45 min. The hole transporter was deposited by spin-coating at 1250 rpm for 20 s using an 8 wt% 2,20,7,70-tetrakis-(*N,N*-di-*p*-methoxyphenyl-amine)9,9-spirobifluorene (spiro-OMeTAD) in chlorobenzene with added *tert*-butylpyridine (TBP) and lithium bis(tri-fluoromethanesulfonyl)imide (Li-TFSI) of 80 and 30 mol%, with respect to spiro-OMeTAD. The final producing spiro-OMeTAD was oxygen doped.⁴¹ Finally, 150 nm thick silver electrodes were deposited on top of devices by thermal evaporation at $\sim 10^{-6}$ bar, through a shadow mask.

Power conversion efficiency (PCE). The light source of a solar simulator for measuring the current–voltage (*J*–*V*) characteristics was a 300 W solar simulator (Newport) calibrated to a 1000 W m^{-2} light intensity at the 1.5 AM Global condition (1 sun AM 1.5 G illumination) by a certified silicon solar cell (Fraunhofer ISE). The electrical data were recorded with a computer controlled digital source-meter (Keithley Model 2401) with the scan direction from the open-circuit to the short-circuit at a scan rate of 800–1250 mV s^{-1} .^{42,43} TiO_2 scaffold based solar cells were masked during the measurement with an metal mask with a square aperture of 0.2 cm^2 (0.10 cm^2 for Al_2O_3 scaffold based solar cells).

Incident photon to current conversion efficiency (IPCE). The IPCE spectra were recorded with a computer-controlled setup comprised of a xenon lamp (Spectral Products, ASB-XE-175), a monochromator (Spectral Products, CM110), chopped at 30 Hz, a potentiostat (PINE instrument Company, Model AFRDE5) and a lock-in amplifier (SRS830), using white LED bias light. The

setup was calibrated with a certified silicon solar cell (Fraunhofer ISE) prior to the measurements. TiO_2 scaffold based solar cells were illuminated from the WE side using a black mask with an rectangular aperture of 0.20 cm^2 (0.10 cm^2 for Al_2O_3 scaffold based solar cells). The white LED bias light was approx. 0.08 sun in intensity.

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