Structure–Electronic Property Relationships of 2D Ruddlesden-Popper Tin- and Lead-based Iodide Perovskites

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Abstract

Two-dimensional (2D) halide perovskites are receiving considerable attention for applications in photovoltaics, largely due to their versatile composition and superior environmental stability over 3D perovskites, but show much lower power conversion efficiencies. Hence, further understanding of the structure-property relationships of these 2D materials is crucial for improving their photovoltaic performance. Here, we investigate by means of first-principles calculations the structural and electronic properties of 2D lead and tin Ruddlesden–Popper perovskites with general formula (BA)$_2$A$_{n-1}$B$_n$I$_{3n+1}$, where BA is the butylammonium organic spacer, A is either methylammonium (MA) or formamidinium (FA) cations, B represents Sn or Pb atoms, and n is the number of layers (n = 1, 2, 3, and 4). We show that the band gap progressively increases as the number of layers decreases in both Sn- and Pb-based materials. Through substituting MA by FA cations, the band gap slightly opens in the Sn systems and narrows in the Pb systems. The electron and hole carriers show small effective masses, which are lower than those of the corresponding 3D perovskites, suggesting high carrier mobilities. The structural distortion associated with the orientation of the MA or FA cations in the inorganic layers is found to be the driving force for the induced Rashba spin-splitting bands in the systems with more than one layer. From band alignment diagrams, the transfer process of the charge carriers in the 2D perovskites is found to be from smaller to higher number of layers n for electrons and oppositely for holes, in excellent agreement with experimental studies. We also find that when interfaced with 3D analogues, the 2D perovskites could function as hole transport materials.

Keywords

Halide Perovskites, Tin, Lead, Ruddlesden-Popper, DFT, band alignment

1 Introduction

Halide perovskites have recently gained considerable interest for applications in photovoltaics and solar cells owing to their exceptional physical and chemical properties. In particular, Pb-based halide perovskites have attained power conversion efficiencies (PCEs) exceeding 25%. However, these materials have stability problems, resulting in impaired long-term performance of perovskite solar cells, as well as the toxicity issue of Pb, which may hinder practical applications. Sn-based perovskite materials seem to be amongst the most...
promising Pb-free alternatives,\textsuperscript{12-22} although they also suffer from oxidation of Sn$^{2+}$ to Sn$^{4+}$, resulting in poor stability.\textsuperscript{18,23,24}

Recent studies showed that the incorporation of 2D layered halide perovskites alongside the 3D perovskites effectively enhanced the performance of the perovskite solar cell devices.\textsuperscript{25-30} The most well-known 2D perovskites are the so-called Ruddlesden-Popper compounds with general formula $A_n^+B_{n-1}X_{3n+1}$, where $A^+$ are organic cations, such as phenylethylammonium (PEA) or butylammonium (BA) used as spacing layers for separating the perovskite units, $A^-$ are methylammonium (MA) or formamidinium (FA) cations within the perovskites units, $B^-$ refers to the metal cations such as Pb, Sn or Ge, $X^-$ are the halide anions (Cl, Br, or I), and $n$ corresponds to the number of the inorganic layers formed by the BX$_6$ octahedra. These 2D perovskites show a wide range of appealing properties,\textsuperscript{31-39} including tunable band gaps with the number of layers, small charge-carrier effective masses, and good stability when exposed to moisture and radiation.\textsuperscript{40-47} The crystal structures of these materials consist of stacks formed by alternating 2D strongly bonded inorganic layers, resembling the structure of the 3D halide perovskites, such as MAPbI$_3$, and weakly bonded organic layers.

Within solar cells, 2D perovskites can be used as light absorbers or can be integrated for the reinforcement of the photoactive 3D perovskites. Smith et al.\textsuperscript{48} reported the first perovskite solar cell device fabricated using exclusively a 2D perovskite, displaying a PCE of 4.73% and an open-circuit voltage ($V_{oc}$) of 1.18 V.\textsuperscript{48} Tsai et al.\textsuperscript{49} recorded a PCE of 12.52% using $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ ($n = 3, 4$), and showed enhanced environmental stability compared to their 3D counterparts.\textsuperscript{49}

Using quasi-2D perovskites based on Pb, Zheng et al.\textsuperscript{50} demonstrated an efficiency of 17.40% with high quality films and excellent resistance to moisture.\textsuperscript{50} Wang et al.\textsuperscript{51} intercalated butylammonium (BA) cations as a spacing layer in a 3D Pb-based perovskite to form a mixed 2D/3D heterostructure, and achieved a record PCE of 20.6%.\textsuperscript{51}

However, these 2D perovskites have not yet achieved the efficiencies of their 3D counterparts. It is, therefore, necessary to further explore the structure-property relationships of these 2D materials to understand the changes in their electronic properties with layer thickness, the role of the organic cations in the perovskite-like units, and to identify the features that can improve their use in photovoltaic applications as the main light absorbing materials or in combination with 3D parent perovskites.

In this work, density functional theory methods are used to investigate the 2D Ruddlesden–Popper perovskites based on lead and tin with the general formula of $(BA)_2A_{n-1}B_nI_{3n+1}$, where BA is the butylammonium (CH$_3$(CH$_2$)$_2$NH)$^+$ cation, $A$ refers to MA (CH$_3$NH)$_2$ or FA (CH(NH$_2$)$_2$) cations, B is Pb or Sn, and $n$ varies from 1 to 4, which extends our recent studies on 3D halide perovskites.\textsuperscript{52-55} We examine the structural and electronic properties of these Sn- and Pb-based systems by varying the number of layers $n$. We also examine the effect of the organic A cation in the perovskite units by substituting MA with FA cations, since it has been shown recently that mixed A cations results in better stability and efficiency of solar cell devices.\textsuperscript{56,57}

We show that the band gaps typically decrease with increasing layer thickness $n$ and converge towards those of the 3D perovskites, as well as exhibiting low charge-carrier effective masses. The structural arrangement of MA or FA cations in the perovskite cages are found to induce Rashba splitting in the band structures for systems with $n > 1$. The band level alignment provides the transport mechanism of photogenerated charge carriers within the 2D materials and the type of charge extraction from their 3D counterparts.

## 2 Methods

Calculations were carried out using density functional theory (DFT)\textsuperscript{58} as implemented in the Quantum Espresso simulation package.\textsuperscript{59,60} The Kohn-Sham wave-functions and energies were calculated using the PBEsol exchange-correlation functional,\textsuperscript{61} and a plane-wave basis
with energy and charge density cutoffs of 40 and 400 Ry, respectively. Ultra-soft pseudopotentials were used to describe the core-valence interactions. The structural relaxation is performed until the force on each atom is smaller than 0.01 eV/Å. The Brillouin Zone integration was sampled following the Monkhorst-Pack scheme, using $4 \times 4 \times 2$ ($4 \times 2 \times 4$ for $n = 1$) and $6 \times 6 \times 1$ ($6 \times 1 \times 6$ for $n = 1$) $k$-point grids for the ionic optimization and the electronic structure calculations, respectively. Full relativistic calculations were accounted by the inclusion of spin-orbit coupling (SOC). We have also examined the effect of van der Waals (vdW) corrections in simulating these halide perovskites (details in the SI, section S1). We found that the geometries and the electronic structure remain unaffected, and therefore, in the following work, vdW corrections are not included.

For the calculation of the work-function and a better description of the energy level alignment between the 2D and 3D perovskites, we performed hybrid functional calculations at the PBE0 level, which has been shown to provide reliable values for the ionization and affinity potentials. The crystal structures of these 2D perovskites include several hundreds of atoms and work-function calculations with plane-wave methods would require prohibitive computational resources. To reduce the computational cost, we used the Crystal17 code, which employs localized basis functions and does not require artificial periodicity along the out-of-plane direction to the slab. The work-function is then calculated following the method proposed by Doll. For comparison, we have also calculated the band gaps, work-functions and energy band alignment diagram using HSE for Pb-based systems with MA cations. Details on the calculation of the work-functions and the energy band alignment are given in section S2 of the supporting information.

## 3 Results & discussion

### 3.1 Structural properties

Sn- and Pb-based 2D perovskites ($[(BA)_{2n-1}B_nI_{3n+1}]$) with butylammonium (BA) as the organic separating layers have been characterized by single crystal X-ray diffraction and are found to adopt orthorhombic systems with space groups $Pbca$ and $C2cm$. The inorganic layers of these 2D perovskites resemble the parent 3D perovskite structures, such as MAPbI$_3$ and MASnI$_3$. They are mainly synthesized with the MA cation occupying the cages between the PbI$_6$ or SnI$_6$ octahedra for different numbers of layers $n$ ranging from 1 to 4, as shown in Figure 1. In this study, the initial MA-based structures are taken from diffraction experiments. We also investigate 2D perovskites with the FA cation substituting the MA cation, as this was shown to affect the optoelectronic properties of the 3D halide perovskites.

The lattice parameters of the fully optimized Sn– and Pb–based structures are shown in Table 1 for systems with MA cations and in Table S1 for Sn/Pb systems with FA cations. Our calculated results agree well with the available experimental and theoretical data for both Pb– and Sn–based structures with MA cations. For systems with FA cations, no experimental data are available for direct comparison. In the case of Pb- and Sn-based 2D perovskites with MA cations, the average lattice constants in the in-plane directions of the layers ($a + b$)/2 for $n = 1$, and $(a + c)$/2 for $n = 2 - 4$) are slightly smaller than those corresponding experimental structures, whereas the out-of-plane lattice constants are relatively larger, for even number ($n = 2$ and 4) and shorter for odd numbers ($n = 1$ and 3) compared to the experimental results. By replacing MA with FA cations in the Pb and Sn systems with $n > 1$, the average lattice constants become larger, while the out-of-plane lattice constants are reduced for $n = 2$ and 4 and enlarged for $n = 3$. For the Pb and Sn structures with an even number of layers ($n = 2, 4$), the angles between the lattice vectors deviate from $90^\circ$.
Figure 1: Crystal structures of a typical 3D perovskite and 2D Ruddlesden-Popper perovskites \((BA)_{2n-1}B_nI_{3n+1}\), for \(n = 1-4\). BA denotes the organic alkylammonium spacer, MA and FA are, respectively, the organic methylammonium and formamidinium cations in the perovskite units, Pb and Sn are the metal cations, and I represents the iodine anions.

Table 1: Comparison of experimental\(^{32,70}\) and computed structural parameters of \((BA)_{2}SnI_{4}\) and \((BA)_{2}MA_{n-1}Pb_nI_{3n+1}\) and \((BA)_{2}MA_nSnI_{3n+1}\) and \((BA)_{2}MA_{n-1}Pb_nI_{3n+1}\)

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by up to 1.87%. Hence, these systems prefer lower symmetry structures and adopt triclinic instead of orthorhombic crystals as compared to experimental structures.\(^{32,70}\) This is probably because such systems are non-centrosymmetric compared to the systems with an odd number of layers. We note that the randomly oriented MA or FA cations in the cages of the inorganic PbI\(_6\)/SnI\(_6\) octahedra exhibit lower formation energies than highly ordered cations with a difference of ~10 meV/atom.
Table 2: Calculated band gaps and charge–carrier effective masses of \((BA)_{2n-1}B_{n}I_{3n+1}\) materials, where \(A = \text{MA or FA}, \ B = \text{Sn or Pb}, \) and \(n = 1-4\). The available experimental data are taken from Ref.\(^{41}\) and Ref.\(^{70}\) for Sn– and Pb–based systems, respectively.

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<th>System</th>
<th>(n)</th>
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<th>(m_{h}^{*}/m_{0})</th>
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<td>1.50</td>
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<td>0.57</td>
<td>0.35</td>
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<td>((BA)<em>{2}(FA)</em>{2}Pb_{3}I_{10})</td>
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<td>4</td>
<td>1.52</td>
<td>0.62</td>
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### 3.2 Band gaps, effective masses, and Rashba effects

The 2D Pb– and Sn–based perovskites are all found to be semiconducting with a direct band gap character around the \(\Gamma\) point, independent of the number of layers \(n\) or the organic cation \(A\) (MA or FA). The band gap values, with and without SOC, are reported in Table 2, which indicate that the band gap decreases with increasing \(n\) and are consistent with the trends reported experimentally.\(^{32,41,70}\) The calculated values are smaller than those obtained from experiment (see Table 2), as DFT is well-known to systematically underestimate band gaps, especially with the inclusion of spin-orbit interactions. In terms of trends, we find that for 2D Sn–based perovskites, the systems with FA cations exhibit slightly larger band gaps than their corresponding systems with MA cations. In contrast, for 2D Pb-based perovskites the opposite trend is observed, where the systems with FA cations have slightly smaller band gaps than those with MA cations with the same layer thickness \(n\).

The charge-carrier effective masses along the in-plane directions of the 2D perovskites are almost isotropic and the averaged values are given in Table 2. Overall, the electron and hole effective masses of these 2D perovskites are comparable to the experimental reduced effective masses \((0.10–0.12m_{e})\) of MAPbI\(_{3}\)\(^{73,74}\) and smaller than those calculated for 3D MAPbI\(_{3}\) and MASnI\(_{3}\), which are typically larger than 0.14\(m_{e}\)\(^{75,76}\), where \(m_{e}\) is the electron mass. These results suggest that 2D perovskites could exhibit higher charge-carrier mobilities. However, experimental measurements indicate that 2D perovskites displayed lower charge-carrier transport than the 3D perovskites.\(^{77–79}\) This is likely due to the strong dielectric confinements associated with the small dielectric constants of the organic spacing layers, such as BA or PEA whose dielectric constants are 2.2\(^{80}\) and 3.3,\(^{81}\) respectively. This results in large exciton binding energies compared to 3D counterparts. Such binding energies hinder the dissociation of the excitons to form free charge-carriers via thermal excitation, which, in addition to quantum confinement effects, leads to
the observed low charge-carrier conduction.\textsuperscript{77,82} Subsequently, it was suggested that a preferential vertical growth of the 2D perovskite crystals with respect to the substrate\textsuperscript{49} or reducing the distance between the inorganic perovskite layers by using small alkylammonium cations\textsuperscript{82,83} would lead to higher charge-carrier mobilities.\textsuperscript{84} Table 2 shows that electron and hole effective masses are similar and vary only slightly with \( n \) for both Pb and Sn systems. For 2D Pb-based perovskites with \( n > 1 \), both electron and hole effective masses decrease slightly with the increase of the layer thickness \( n \). For 2D Sn-based perovskites, no trend is observed for the systems containing the MA cations, whereas the effective masses of the systems with FA cations and \( n > 1 \) increase when the layer thickness \( n \) is increased. Our calculated effective masses corroborate a recent study, where they measured a hole mobility of 34 cm\(^2\text{V}^{-1}\text{s}^{-1}\) in a 2D Sn-based perovskite.\textsuperscript{84}

The band structures of 2D Sn-based perovskites with MA and FA are plotted in Figures S1 and S2, respectively, with and without SOC for comparison. We find that the inclusion of SOC is important for obtaining accurate band dispersions as it has been shown that SOC associated with the symmetry properties and the orbital character of the bands have a significant effect on the band splittings, especially around the conduction band minimum (CBM) and the valence band maximum (VBM) at the \( \Gamma \) point.\textsuperscript{85}

From the band structures with only SOC for 2D Sn-based perovskites shown in Figure 2, the systems with \( n = 2, 3, \) and \( 4 \) containing the MA cations display band splittings due to the Rashba effect in both conduction and valence band extrema. These Rashba band splittings are caused by the symmetry breaking in these distorted crystal structures. Yin et al.\textsuperscript{86} investigated 2D Pb-based perovskites with phenethylammonium (PEA) as a spacing layer and \( n = 1, 2, \) and 3. They found that the Rashba splitting occurs only in the system with even number of layers \( (n = 2) \), whereas, the systems with odd number of layers \( (n = 1 \text{ and } 3) \) show no band splitting since the centrosymmetry of the crystal structures is preserved. In our case, \((\text{BA})_2\text{SnI}_4\) and \((\text{BA})_2\text{PbI}_4\) have centrosymmetric crystal structures and, therefore, no Rashba band splitting is found. However, for \( n > 1 \), we believe that the interplay between the organic spacing molecules (BA) and the different orientations of the organic cations (MA or FA) in the perovskite layers induces a symmetry breaking in the Sn- and Pb-based structures.

We have assessed the effect of different orientations of the MA/FA cations in the inorganic layers, and find that when these cations are perfectly aligned (as shown in Figure 3-a), the systems do not exhibit any Rashba splitting. In contrast, when the FA cations are randomly oriented (shown in Figure 3-b), the systems display lower symmetry caused by the SnI\(_6\)/PbI\(_6\) octahedra tilting, which yields the Rashba-type effect. The band splittings and the values of the Rashba parameters \( (\alpha_R) \) are found to be dependent on the in-plane directions, in which the symmetry is broken. For example, the \((\text{BA})_2\text{MASnI}_4\) system has a \( \alpha_R \) of 0.30 eV\(\cdot\)Å and a splitting energy of 7 meV along the \( \Gamma-Z \) direction and \( \alpha_R \) of 0.18 eV\(\cdot\)Å and a splitting energy of 3 meV along the \( \Gamma-X \) direction in the conduction band. As the content of the heavy elements (Sn, Pb, and I) increase with the thickness of the perovskite units, the splittings also become larger. For example, the system \((\text{BA})_2\text{MA}_3\text{SnI}_{13}\) exhibits a Rashba parameter \( \alpha_R \) of 0.65 eV\(\cdot\)Å with a splitting energy of 16 meV along the \( \Gamma-Z \) direction. These values indicate that 2D perovskites display significant Rashba band splittings, which is in accord with experimental measurements on PEA\(_2\)PI\(_4\) for which a Rashba parameter \( (\alpha_R) \) of 1.6 eV\(\cdot\)Å and an energy splitting of 40 meV have been reported.\textsuperscript{87} For \((\text{BA})_2(\text{MA})_2\text{Sn}_3\text{I}_{10}\) and \((\text{BA})_2(\text{FA})_2\text{Sn}_3\text{I}_{10}\) systems, we find that the splittings are only along the \( \Gamma-Z \) direction and are more significant in the conduction band than in the valence band.

One key finding induced by the Rashba effect in these 2D materials is that the splittings of the bands slightly shift the valence and conduction band extrema from the \( \Gamma \) point in the in-plane \( k \)-space and, therefore, the band gap adopts an indirect character. This, of course, could play
an important role in the dynamics and the lifetimes of photo-generated carriers, for which the recombination process may be delayed by forbidden indirect transitions.

3.3 Interfaces and band alignment

The properties of interfaces in solar cells are crucial for their performance. Therefore, optimizing the energy level alignment between device components is one of the key factors for reducing non-radiative recombination and for efficient charge-carrier extraction and transfer, which would lead to improved photovoltages and power conversion efficiencies. However, the fundamental band alignment between 3D and 2D perovskites is not fully characterized.

We provide in Figure 4 the band alignment between the 3D perovskites (namely MAPbI$_3$, FAPbI$_3$, MASnI$_3$, and FASnI$_3$) and the 2D Sn– and Pb-based perovskites considered in this study. The level aligned is constructed based on the calculated work-functions (W) and band gaps using the PBE0 hybrid functional. It is noted that W coincides with the valence band maximum (VBM) of each material. We find that the VBMs and CBMs in the 2D perovskites increase with increasing $n$, ultimately converging to those of the 3D parent perovskites. This means that the transfer of photogenerated charge-carriers would go from $n = 1$ to
$n = 4$ for electrons, but conversely from $n = 4$ to $n = 1$ for holes for both Sn and Pb materials with either MA or FA cations. These results are consistent with ultrafast transient absorption and photoluminescence measurements by Liu et al. on (BA)$_2$(MA)$_{n-1}$Pb$_n$I$_{3n+1}$, where they showed that the electron transfer proceeds from systems with smaller $n$ to larger $n$ and hole transfer in the opposite way.\cite{88}

Figure 4 shows that the CBMs of the 2D perovskites are higher in energy than those of the 3D parents, whereas the VBMs of the 2D perovskites are located mainly between the band edges of the corresponding 3D perovskites. This suggests that the 2D perovskites would form staggered (type-II) heterojunctions with their 3D counterparts. Hence, when 2D perovskites are used alongside the 3D perovskites, they are prone to promote the hole extraction from the 3D materials and block the transfer of electrons.\cite{89} These findings are in good agreement with ultraviolet photoelectron spectroscopy results on (BA)$_2$(MA)$_{n-1}$Pb$_n$I$_{3n+1}$ reported by Kanatzidis and co-workers,\cite{40} in which the VBM

$\Gamma$ point of the (BA)$_2$FASn$_2$I$_7$ structure with different FA orientations within the cages formed by the SnI$_6$ octahedra. a) Highly ordered FA cations show no splitting, b) randomly oriented FA cations show band splittings in both VBM and CBM.
level of the 2D compounds goes upward with decreasing $n$ in comparison to the VBM of MAPbI$_3$. Our calculated band gaps using the PBE0 functional for the Pb-based systems also agree well with their measured optical band gaps. Similar observations are also reported by the same group on the 2D Sn-based perovskites. The only exception is the system with a single layer ($n = 1$) that do not contain either MA or FA cations, namely BASnI$_4$ and BAPbI$_4$, for which the VBM levels are higher in energy than those of the 3D analogues. Accordingly, they would form a type-III heterojunction with a broken gap alongside the 3D perovskites. Hence, no charge extraction would be permitted from these 3D to the 2D single-layer systems.

Overall, the band alignment profiles indicate that these 2D perovskites can be used as hole transport layers (HTL) for the charge carrier extraction from the 3D analogues toward the contacts. However, reducing the nonradiative recombination and minimizing the photovoltage losses would depend on the number of layers $n$. It was shown that the open-circuit voltage ($V_{oc}$) depends highly on the energy difference between the CBM of the light absorber and the VBM of the HTL and the larger this difference the higher the $V_{oc}$. Other effects, such as interfacial recombination, trap states, and interface defects, which play a role in the charge-carrier extraction would be similar in these materials. Consequently, our band level diagrams suggest that the 2D perovskites with larger number of layers $n$ would result in higher $V_{oc}$ than smaller $n$; for example, a 2D system with $n = 4$ would provide higher $V_{oc}$ than 2D systems with $n = 2$ or $n = 1$. Therefore, efficient control of the material dimensionality with desirable thickness and adequate design of the device architecture would lead to improved photovoltaic performance of the mixed 3D/2D perovskite solar cells.

### 3.4 Conclusions

We have investigated the structural and electronic properties of 2D Sn– and Pb-based Ruddlesden–Popper perovskites with butylammonium (BA) as a spacer and the number of layers ($n$) from 1 to 4, using density functional theory techniques. We have also examined the effect of substituting the MA with FA cations at the A site in the perovskite-like units.
First, the simulated crystal structures agree well with the available experimental parameters; the systems with even number of layers prefer low symmetry structures for both Sn and Pb materials with MA or FA cations. The calculated band gap progressively decreases with increasing layer thickness \(n\) for both Sn- and Pb-based materials, which is consistent with experimental trends. By replacing MA with FA cations in the perovskite units, the band gap slightly increases in the Sn systems, but decreases in the Pb systems. The electron and hole effective masses of these 2D perovskites are very light and smaller than those of the corresponding 3D perovskites, which suggest that these 2D compounds could exhibit high charge carrier mobilities.

Second, our band structure analysis indicates Rashba band splitting in the systems of \(n > 1\) due to symmetry breaking in the distorted structures. However, the splitting magnitude is strongly associated with the orientation of the MA or FA cations and the degree of octahedra tilting in the perovskite units. For highly ordered MA or FA cations no band splitting is observed.

Finally, our band alignment diagrams indicate that the possible transfer process of photogenerated carriers in the 2D Ruddlesden–Popper perovskites goes from smaller to higher number of layers \((n = 1 \text{ to } 4)\) for electrons and in the opposite way for holes, which is in excellent accord with absorption and photoluminescence experiments. When 2D perovskites with \(n > 1\) are used alongside 3D perovskites, they are expected to form staggered type-II heterojunctions that would promote hole charge extraction and transfer. In addition, 2D perovskites with a large number of layers are expected to deliver high open-circuit voltages in 2D/3D heterostructures. Hence, these 2D materials could be employed as efficient intrinsic hole transport layers.

Our findings provide new insights into understanding the structural and optoelectronic properties of both Sn- and Pb-based 2D perovskites and offer a possible route towards their integration into perovskite solar cell devices.

4 Notes

The authors declare no competing financial interest.

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5 Supporting Information

Structural parameters of 2D Sn and Pb perovskites with FA cations, band structures of 2D Sn Perovskites with and without SOC, van der Waals corrections, computational details for computing the work-function and the energy level alignment, HSE energy band alignment between MAPbI\(_3\) and (BA)\(_2\)MA\(_{n-1}\)Pb\(_n\)I\(_{n+1}\), crystal structures used in this work.

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