Two-dimensional eclipsed arrangement hybrid perovskites for tunable energy level alignments and photovoltaics†

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Excellent long-term durability and moisture tolerance, low cost synthesis routes, and the possibility of flexible tuning of electronic properties have meant that the two-dimensional (2D) hybrid halide perovskites have recently attracted much attention, and have been successfully used as light absorbers in efficient photovoltaic devices. 2D hybrid halide perovskites which feature long chain alkylammonium cations, however, are generally suggested for light emitting diode (LED) applications, due to their strong photoluminescence (PL) but none have been applied thus far for photovoltaic (PV) applications. Additionally, it has been shown that luminescence quenching occurs in the Pb-based analogues, (AEQT)PbX4 (X = Cl, Br, I), however, energy transfer and charge separation between organic and inorganic components of the structures are still not fully understood. Herein, we investigate the geometrical, electronic and optical properties of the semiconducting 2D perovskites (AEQT)BX4 (B = Pb, Sn; X = Cl, Br, I), using relativistic hybrid density functional theory calculations. We demonstrate that unlike the traditional 2D perovskites, the choice of the organic ammonium cation has a considerable effect on the carrier transport properties. Our calculations reveal that optical transitions between the organic and inorganic components is disallowed. The electronic structures of the series are flexibly tailored by different halides and metal cations, with band gaps ranging from 2.06 to 2.68 eV. Energy level alignments greatly hinder the electron–hole recombination in (AEQT)PbCl4, (AEQT)PbBr4, (AEQT)PbI4 and (AEQT)SnBr4, and thereby should enhance their PL efficiencies. With a moderate fundamental band gap (2.06 eV) and strong direct valence band to conduction band transition, (AEQT)SnI4 is the only composition that shows intense and broad optical absorption, and as expected displays a high spectroscopic limited maximum efficiency (SLME) of 20.8%. Our results indicate the (AEQT)SnI4 is a stable and efficient light-absorbing material for application as a top absorber of the tandem solar cell.

Introduction

Organic–inorganic lead halide perovskites have emerged as remarkable photovoltaic absorber materials in recent years.1–6 To date, polycrystalline thin-film perovskite photovoltaic devices have reached power conversion efficiencies of 23.7%,7 largely exceeding most of emerging PV devices, including quantum dot cells, organic tandem cells, dye-sensitized solar cells.8 Although three-dimensional (3D) organic–inorganic halide perovskite solar cells have experienced tremendous development in the past few decades, the involvement of toxic lead and long-term instability are preventing large scale commercialisation.9–13 Two-dimensional (2D) hybrid halide perovskites, a subclass of the organic–inorganic perovskites, were first synthesised by Mitzi et al. in 1994.14 In 2014, Smith et al. reported that 2D perovskites display more resistance to moisture than their 3D counterparts,15 opening a new path in the investigation of solar cell absorbers. One route to addressing the problem of toxicity is to replace lead with the less toxic Sn and Ge cations.16–18 With appealing environmental stability and less toxic components, the Ruddlesden–Popper 2D tin perovskites have been introduced in solar cell devices, however with limited success in terms of efficiencies.15,18–21 So far, general improvements in perovskite...
solar cell efficiency have primarily achieved by better control over thin film morphology, the choice of solvent treatment, and manipulation of the stoichiometry or chemistry of halide precursors (BX₂ or MAX, B = divalent metal, MA = CH₃NH₃⁺, X = Cl, Br, I). In this way, power conversion efficiencies have risen to 15.4% during the past two years. In general, the fundamental band gap is determined mostly by the composition of the inorganic layer, which provides an effective route to tune their electronic properties. With regard to the well-known 3D perovskite, MAPI (CH₃NH₃PbI₃), changing halide composition allows tuning of the band gap from 1.6 to 3.1 eV. Alternatively, replacing metal cation allows tuning from 1.6 to 2.0 eV.

Classified by the position of metal atoms (B) from one inorganic layer over those in the adjacent ones, the 2D hybrid perovskites are generally sorted into “staggered” ([R-NH₃]BX₄) and “eclipsed” arrangement ([H₃N-R-NH₃]BX₄) (Fig. S1, ESI†), where R-NH₃ is an aliphatic or single ring aromatic ammine cation, B is a divalent metal, and X is a halogen. They both have multi-quantum-well structures of which semi-conducting inorganic perovskite-like sheets are alternatively arranged with dye organic layers. Due to the large exciton binding energies and excitonic oscillator strengths of the materials, both types of layered systems have efficient photoluminescence and electroluminescence. Additionally, the perovskite-like framework in the alternating structure will reduce the quenching interactions between dye molecules, and therefore further improve the luminescence efficiency. To our knowledge, “staggered” arrangement perovskites and their analogues generally consist of small organic moieties, and the corresponding conduction band maximum (CBM) valence band minimum (VBM) are derived from the inorganic component. Recent evidence suggests that most of “staggered” arrangement perovskites have strong absorption in the visible light region and can be applied in visible light harvesting applications. However, the studies of the “eclipsed” arrangement perovskites are limited to the Pb- or Ge-based systems and the majority concentrate on the luminescence properties instead of their photovoltaic capabilities.

In 1999, Mitzi and co-workers synthesised a series of “eclipsed” arrangement layered materials, (AEQT)PbX₄ (AEQT = H₃NC₂H₄C₁₆H₈S₄C₂H₄NH₃⁺; X = Cl, Br, I), and found the offsets between the energy levels of organic and inorganic components from distinct layers, of which the organic cation could play a role in the determination of band gaps and carrier mobility. Recent theoretical research into the electronic structure of the analogues of (AEQT)PbX₄ (AEQT = AE4TPbX₄) has revealed that due to the quantum-well-like behaviour of layered perovskites, the states associated with inorganic and organic components are possibly spatially well-separated, thereby allowing for an additional degree of electronic structure tuning and effectively impeding the electron-hole recombination.

To date, an understanding of the Sn-based analogues is missing, and a non-toxic 2D hybrid halide would be of huge interest to the materials community and PV industry which deserves further study. Flexibly tunable energy level alignments and restricted energy loss from electron–hole recombination could enable these materials to be solar absorbers with the potential for high PV efficiencies. Studying electron transfer between different components during the photovoltaic effect would be of great significance to understand whether the unique behaviour will enhance the PV or carrier transport performance. With these in mind, in this study, we report the crystal structures, electronic properties and optical properties of three Pb-based and three Sn-based layered perovskites, (AEQT)BX₄ (B = Pb, Sn; X = Cl, Br, I), using relativistic hybrid density functional theory. We provide an insight into the band offset of these series, shed light on the transition possibility between the inorganic framework and organic components, and how the selection of organic molecules affects the PV performance. With the evaluation of the thin-film PV ability, we demonstrate that (AEQT)SnI₄ holds promise for PV applications.

Computational details

First-principles calculations were carried out using the Vienna ab initio simulation package (VASP), with the scalar relativistic projector augmented-wave (PAW) pseudopotentials applied to describe the interactions between core and valence electrons. The plane wave cutoff energy was set to 580 eV, and k-point meshes of 1 × 1 × 2 were employed for the geometry optimisation, electronic structure and optical property calculations. These parameters enable the total energy of each system converge within 10 meV per atom.

Lattice relaxations were tested via using the Perdew–Burke–Ernzerhof functional (PBE), with dispersion interactions included via Grimme’s D3 dispersion correction (PBE-D3), and the PBEsol functional, a version of PBE revised for solids. Both functionals are generally able to accurately reproduce the structural parameters of layered materials and containing weak long-range forces. During geometry optimisation, the atomic positions, lattice shape and cell volume were allowed to relax, and were considered converged when all forces totalled less than 0.02 eV Å⁻¹.

In order to obtain an accurate description of the electronic structure of our systems, hybrid density functional theory was employed. Herein, we used the Heyd–Scuseria–Ernzerhof (HSE) functional incorporating 43% HF exact exchange and 100% of the correlation energy from PBE. This has been shown to reproduce the band gap of MAPI and BaSnI₄ ([CH₃(CH₂)₃NH₃]SnI₄) and we expect that it will perform well here. Explicit treatment of spin–orbit coupling (SOC) effects is considered in all electronic structure calculations, due to the relativistic effects present on the heavy elements Pb, Sn and I. This combination of HSE43 + SOC was used for all band structure, density of states, optical absorption and charge density calculations. The high-frequency dielectric response was calculated from the optical transition matrix elements within the transversal approximation. The ionic dielectric contribution was calculated using density functional perturbation theory (DFPT), using the PBE-D3 functional. Atom-projected band structure diagrams were plotted used the sumo package.
Discussion and results

Crystal structure

Fig. 1 displays the crystal structures of the series, where each of the inorganic layers consists of sheets of corner-sharing metal halide octahedra ([BX₆]⁴⁻). The site cation (Pb²⁺ or Sn²⁺) is generally a divalent metal that can adopt an octahedral coordination. The inorganic layers are separated by a long-chain bipolar AEQT²⁺ dye molecule cation, where the cation spans the distance between adjacent inorganic layers, with both sides of ammonium head ionically bonding to the halogens in the inorganic layers.

All geometry relaxations were started from the experimental structures or from modifying the existing structures by swapping elements in the same group of the periodic table. Although (AEQT)PbCl₄, (AEQT)PbBr₄ and (AEQT)PbI₄ have been synthesized, only (AEQT)PbBr₄ has been structurally characterized.³⁴ Additionally, none of the Sn-based analogues have been reported thus far. Thus, only (AEQT)PbBr₄ is optimized from its experimental structure,³⁴ while the rest of the series [(AEQT)PbCl₄, (AEQT)PbBr₄, (AEQT)PbI₄, (AEQT)SnCl₄, (AEQT)SnBr₄ and (AEQT)SnI₄] were created based on the structure of (AEQT)PbBr₄ via replacing Pb with Sn, and Br with Cl or I. Both PBE-D3 and PBEsol were tested for the geometry relaxations. The optimized lattice constants and available experimental data on the (AEQT)BX₄ structures are given in Table 1. The results indicated PBE-D3 gives better agreement with experiment for (AEQT)PbBr₄, and therefore PBE-D3 has been used for all of the structural analysis employed for the rest of the calculations. As a general trend, the metal–halogen bond lengths increase down Group VIIA, as is expected.⁶¹ As shown in Table 1, we also see an enlargement of lattice parameters a and b, going from chloride to bromide and then to iodide, which is in agreement with the variation of the halogen ionic radii.

It is worthwhile mentioning that we obtained a different symmetry of 2D perovskites (Cc) to those in a recent computational study (P₂₁/c).³⁷ As compared with the recent study in the Table S1 (ESI†),³⁷ we found our structures showed slightly contracted lattice parameters and were lower in energy, indicating they are the ground state structures at the level of theory used in this study. These differences could result from the different methodology for the relaxation. Although both studies used the PBE functional with dispersion corrections, in our work we have employed Grimme's corrections, whereas in the work by Blum and co-workers, the Tkatchenko–Scheffler.³⁷

To test the stability of (AEQT)BX₄ (B = Pb, Sn; X = Cl, Br, I) in respect of stable compounds, we have tested two decomposition routes:

\[
\text{(AEQT)BX}_4 \rightarrow \text{(AEQT)X}_2 + \text{BX}_2, \quad (1)
\]

\[
\text{(AEQT)BX}_4 \rightarrow \text{(AEQT–2H) + BX}_2 + 2\text{HX}, \quad (2)
\]

where AEQT–2H stands for the neutral molecule by removing two H atoms from the AEQT²⁺ cation. The similar reaction pathways have been applied for estimation of the thermal stability of other hybrid perovskites, such as MAPbI₃ and its analogues.³⁰,⁶²

The enthalpies of decomposition for the pathways shown in eqn (1) and (2) are given as ΔH₁ and ΔH₂, respectively, and are provided in Table 1. Across all decomposition routes, all series showed positive enthalpies of decomposition, indicating that spontaneous decomposition is unfavourable.

Electronic properties

To assess the nature of the band gap in (AEQT)BX₄ (B = Pb, Sn; X = Cl, Br, I) series, and better understand the effects of the AEQT²⁺ cation on the electronic structure of the layered perovskite, the band structures and the density of states (DOS) were calculated by HSE43 + SOC shown in Fig. S2 of the ESI. The orbital-projected band structures are displayed in Fig. 2, and the fundamental band gaps and in-plane effective masses are listed in Table 2.

The fundamental band gaps of the Pb-based series increase from 2.06 eV (X = I) to 2.20 eV (X = Br), then to 2.45 eV (X = Cl), which shows the same trend in 3D lead halide perovskites.²⁵,²⁶ Unlike the work by Blum and co-workers,³⁷ the Pb-based series we calculated were all indirect in nature, of which average energy difference between the direct and indirect band gaps is 0.04 eV across the series. In addition, the calculated band gaps were slightly larger by an average of 0.29 eV, though similar functionals were applied for geometry optimization and electronic property calculations. It is expected that these differences result from the different relaxed structures obtained by the different methodologies.³⁷ Both studies, however, found that the CBM of Pb-based series were composed of the p orbital of Pb and halogens, and their VBM originated from the AEQT²⁺ cations. This induces the small electron effective mass (<0.5 m₀) and heavy hole effective mass (>27 m₀).

In terms of the Sn-based systems, the fundamental band gaps increase from 2.06 (X = I) to 2.67 (X = Cl) eV, and although indirect, they are only slightly indirect, with the direct band gaps only a maximum of 0.1 eV higher in energy across all cases. The frontier orbitals of the Sn-based series are derived from different components. The CBMs in (AEQT)SnCl₄ and (AEQT)SnBr₄
are determined by the molecular cation and inorganic framework, respectively, whereas their VBMs are both composed of the orbitals of AEQT cation. Particularly, the conduction band edges of (AEQT)SnBr4 nearly consists solely of AEQT cation, because the energy difference between its CBM and lowest unoccupied molecular orbital (LUMO) of AEQT cation is less than 20 meV. In contrast, like the majority of 3D perovskites, the frontier orbitals of (AEQT)SnI4 are composed of the inorganic components, of which CBM are derived from the Sn’s p orbital, and VBM from Sn’s s and I’s p orbitals. For these reasons, (AEQT)SnI4 exhibits dispersive CBM and VBM and relatively light effective masses ($\approx 0.6 m_0$). (AEQT)SnCI4 and (AEQT)SnBr4 share large hole effective mass ($> 15 m_0$), while (AEQT)SnBr4 possess a much smaller electron effective mass than (AEQT)SnCI4. The atomic orbital contributions of the series at the VBM and CBM are further characterised by the electron density isosurfaces in Fig. S3 (ESI†).

As shown in Fig. 2, the highest occupied molecular orbital (HOMO) of AEQT cation exhibits a very small variation amongst the series ($<0.2$ eV), and the maximum energy differences of their LUMO are 0.4 eV. Across the series, the organic HOMO–LUMO gaps exhibit a narrow range (2.66 to 2.80 eV), which is in agreement with 2.7 eV measured by the singlet transition of the organic chromophore in (AEQT)PbCl4 via a photoluminescence measurement.33 The minor variation of HOMO–LUMO gap is also confirmed by the recent theoretical study with energy of 2.2 to 2.4 eV.37

To illustrate the relative positions of band edges of organic and inorganic components from each series, each of their energy level is calculated with respect to the HOMO of AEQT cations, respectively. It is found that their HOMO–LUMO gaps of AEQT cation are similar, and thus their energy level schemes could be aligned together. To simplify the whole diagram, all separate schemes are merged relative to the same schemes could be aligned together. To simplify the whole diagram, all separate schemes are merged relative to the same

### Table 1

| Compounds | Functional | $a$ | $b$ | $c$ | $x$ | $\beta$ | $\gamma$ | $\Delta_{BH}$ | $\Delta_{BH}$ |
|-----------|------------|----|----|----|-----|--------|--------|-------------|-------------|
| (AEQT)PbCl4 | PBE-D3 | 5.596 | 11.346 | 39.976 | 92.5 | 90.0 | 90.0 | 3.82 | 6.90 |
| (AEQT)PbBr4 | PBE-D3 | 5.762 | 11.824 | 39.037 | 91.9 | 90.0 | 90.0 | 4.26 | 7.38 |
| PBEsol | 5.751 | 11.864 | 40.104 | 93.2 | 90.0 | 90.0 | 4.20 | 7.30 |
| Ref. 34 | 5.842 | 11.573 | 39.741 | 92.4 | 90.0 | 90.0 | 4.36 | 7.46 |
| (AEQT)PbI4 | PBE-D3 | 6.054 | 12.589 | 38.072 | 92.2 | 90.0 | 90.0 | 3.81 | 7.19 |
| (AEQT)SnCl4 | PBE-D3 | 5.677 | 11.175 | 39.803 | 92.8 | 90.0 | 90.0 | 4.34 | 6.93 |
| (AEQT)SnBr4 | PBE-D3 | 5.847 | 11.608 | 38.989 | 91.9 | 90.0 | 90.0 | 4.28 | 7.40 |
| (AEQT)SnI4 | PBE-D3 | 6.087 | 12.335 | 38.018 | 91.9 | 90.0 | 90.0 | 4.05 | 7.43 |

Optical properties

Fig. 4 shows the HSE43 + SOC calculated absorption spectra for (AEQT)BX4 (B = Pb, Sn; X = Cl, Br, I). In the optical absorption spectra, there are large differences between the fundamental direct band gaps and the adsorption edges in both the Pb-based and Sn-based series. We note large difference between the fundamental direct band gaps and the absorption edges in the Type IIb series, indicating the direct VB–CB optical transition from organic to inorganic component may be unfavourable. The optical transition matrix elements were calculated using the transversal approximation including explicit treatment of SOC effects.63 Allowed and disallowed transitions were judged by the square of magnitude of matrix element, $|M|^2$.64

In all cases, the $|M|^2$ of the transition between the AEQT cation and the perovskite-like framework is less than 10$^{-2}$ eV$^{-2}$ Å$^{-2}$, revealing this transition is unfavourable. This likely results from the limited orbital overlap of the organic and inorganic wavefunctions. In other words, only the transition from inorganic to organic components or from organic to inorganic components are allowed. Since the electrons and the holes are located separately across the alternative layers in the inorganic and organic hybrid components, in addition to the unfavourable transition between the two components, such unique energy level alignments therefore enable the electron–hole recombination to be suppressed among (AEQT)PbCl4.
(AEQT)PbBr₄, (AEQT)PbI₄ and (AEQT)SnBr₄, and find broad applications in the LED industry.

To evaluate the hypothetical photovoltaic performance of the series, a metric proposed by Yu and Zunger,⁶⁵ the spectroscopic limited maximum efficiency (SLME) with a thin film thickness of 0.5 μm, has been calculated and shown in Table 2. As (AEQT)SnI₄ exhibits strong and broad absorption in the visible light region, it possesses the highest SLME (20.8%). This is comparable to other Sn-based layered perovskites, such as (BA)₂(MA)Sn₂I₇ (BA = (CH₃(CH₂)₃NH₂)²⁺) (22.6%).¹⁸ For the rest of the series, the unfavourable inorganic–organic optical transition, coupled with large optical band gaps (> 2.4 eV), results in very poor optical absorption in the visible light region and corresponding low SLMEs.

One of the distinct features of the 2D perovskites is their quantum-well-like structure, in which dielectric constant varies across the inorganic sheets (“wells”) to the organic layers (“barriers”) due to their different polarizability.⁶⁶,⁶⁷ The dielectric constants for the full range of analogues are provided in Table 2. The dielectric constants in the direction parallel to the series.
Table 2 | Indirect ($E_\text{g}^{\text{ind}}$) and direct ($E_\text{g}^{\text{dir}}$) fundamental band gaps, dielectric constants ($\varepsilon_r$), and SLMEs of the series (AEQT)BX$_4$ (B = Pb, Sn; X = Cl, Br, I). Superscripts $|$ and $\perp$ indicate properties parallel (in-plane) and perpendicular (out-of-plane) to the 2D perovskite sheets, respectively. Band gaps given in eV, effective masses given in units of electron rest mass ($m_0$), and SLMEs in %.

| Compounds      | $E_\text{g}^{\text{ind}}$ | $E_\text{g}^{\text{dir}}$ | $m_0^\parallel$ | $m_0^\perp$ | $\varepsilon_r^\parallel$ | $\varepsilon_r^\perp$ | SLME$^a$ |
|----------------|---------------------------|---------------------------|-----------------|--------------|---------------------------|-------------------|----------|
| (AEQT)PbCl$_4$ | 2.45                      | 2.50                      | 27.30           | 0.47         | 4.84                      | 3.34              | 9.5      |
| (AEQT)PbBr$_4$| 2.20                      | 2.24                      | 46.60           | 0.47         | 4.79                      | 3.13              | 12.5     |
| (AEQT)PbI$_4$ | 2.06                      | 2.07                      | 105.21          | 0.43         | 4.92                      | 3.08              | 7.7      |
| (AEQT)SnCl$_4$| 2.67                      | 2.77                      | 15.45           | 1.38         | 10.29                     | 4.37              | 7.9      |
| (AEQT)SnBr$_4$| 2.68                      | 2.73                      | 19.34           | 0.80         | 12.04                     | 3.64              | 7.8      |
| (AEQT)SnI$_4$ | 2.06                      | 2.07                      | 0.63            | 0.50         | 12.37                     | 5.09              | 20.8     |

$^a$ Thickness: 0.5 µm.

Conclusions

In conclusion, we have demonstrated that the electronic properties of (AEQT)BX$_4$ (B = Pb, Sn; X = Cl, Br, I) can be tuned through incorporation of different halides and metal cations, with band gaps varying from 2.06–2.68 eV. The location of frontier orbitals varies according to the halide and metal. Such tunability of electronic properties, especially the energy level alignments of organic and inorganic components, opens up the possibility to theoretically tailor charge separation or recombination, which is important to suppress the PL quenching caused by electron–hole recombination. The unique energy alignments of (AEQT)PbCl$_4$, (AEQT)PbBr$_4$, (AEQT)PbI$_4$ and (AEQT)SnBr$_4$ may make them of use in the LED industry. The transition between the organic and inorganic components is confirmed to be unfavourable, resulting in poor absorption of light in the visible spectrum for most of the series. However, we identify a novel 2D perovskite material, (AEQT)SnI$_4$, in which the VBM and CBM are composed of contributions from the inorganic sheets. Due to its broad absorption in the visible light region, reasonably large dielectric constants and SLME of 20.8%, (AEQT)SnI$_4$ shows a promise as a potential solar absorber. (AEQT)SnI$_4$ thus presents an exciting prospect because of its earth abundance, and possible enhanced moisture stability and defect tolerance. Experimental verification of our computational predictions are welcomed.

Conflicts of interest

There are no conflicts to declare.

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