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## ARTICLE

## “Breathing” organic cation to stabilize multiple structures in low-dimensional Ge-, Sn-, and Pb-based hybrid iodide perovskites

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Low-dimensional hybrid inorganic–organic perovskites are candidates for stable optoelectronic devices. The dimensionality of these perovskites depends largely on the organic and inorganic compositions, as well as the synthetic conditions. Here, we report five new hybrid iodides, (ETU)<sub>4</sub>Ge<sub>5</sub>I<sub>18</sub>, (ETU)GeI<sub>4</sub>, (ETU)SnI<sub>4</sub>, (ETU)PbI<sub>4</sub>, and (ETU)<sub>3</sub>Pb<sub>2</sub>I<sub>10</sub> using only one type of organic cation, namely, S-(2-Aminoethyl)isothiuronium (ETU). (ETU)GeI<sub>4</sub> and (ETU)SnI<sub>4</sub> belong to the (110)-oriented structure-type with “3 × 3” sawtooth corrugated layers and crystallize in a structure with the orthorhombic space group *Pbca*. (ETU)<sub>4</sub>Ge<sub>5</sub>I<sub>18</sub> crystallizes in a structure with the triclinic space group *P-1*, featuring a 2D layered structure with combinations of corner, edge, and face-sharing [GeI<sub>6</sub>] octahedra. For the Pb-based series, (ETU)PbI<sub>4</sub> has the conventional (100)-oriented 2D type whereas (ETU)<sub>3</sub>Pb<sub>2</sub>I<sub>10</sub> has a unique 0D structure. Remarkably, the unstable 2D orange-phase (ETU)PbI<sub>4</sub> transforms to a stable 0D yellow phase (ETU)<sub>3</sub>Pb<sub>2</sub>I<sub>10</sub>, accompanied by the reduction of the C-S-C angle of the organic cation ETU. The optical band gaps are largely regulated by the diverse types of structure and are in the range of 1.8 eV to 2.8 eV. (ETU)SnI<sub>4</sub> is the only material showing notable photoluminescence at room-temperature. Our work showcases the flexibility of the organic cation in determining the structural dimensionality and provides a new strategy in generating new hybrid materials.

### Introduction

Hybrid halide perovskite materials with small exciton binding energy, high carrier lifetime, high absorption coefficient and other favorable properties have been extensively studied for optoelectronic applications.<sup>1–6</sup> Three-dimensional (3D) halide perovskites have a general formula of  $AMX_3$  ( $A = Cs^+$ ,  $CH_3NH_3^+$ ,  $HC(NH_2)_2^+$ ;  $M = Pb, Sn$  or  $Ge$ ;  $X = \text{halide}$ ),<sup>4,7,8</sup> for a limited set of A-site cations. In contrast, low-dimensional perovskites enjoy tremendous chemical flexibility as well as structural diversity, offering the opportunity to use a large variety of functional organic molecules as cations.<sup>9–12</sup> 2D perovskites can be obtained via chemically sectioning the 3D perovskite lattice along different planes, resulting in (100)-, (110)- and (111)-oriented perovskites, which have layered or corrugated sheets that are sandwiched between large organic cations.<sup>9,13,14</sup> Other derivatives with lower dimensionality such as 1D or 0D structures often consist of edge-shared or face-shared octahedra.<sup>15,16</sup> The reduction of dimensionality in these materials has an enormous influence on their physical and optoelectronic properties, leading to other specific applications.<sup>17,18</sup>

A promising strategy for novel functional hybrid materials is to combine the properties of the inorganic frameworks with the functionality and flexibility of the organic component. Especially for 2D perovskites, the selection of cations has a great influence on the formation of different types of layers such as (110)-oriented layered types. These “sawtooth” (110)-oriented 2D perovskites are named “n × n”, where n represents the number of octahedra that form half of the sawtooth, thus these structures can be regarded as “2 × 2”, “3 × 3”, “4 × 4”, etc.<sup>19</sup> Previously, the “2 × 2” structural type has been extensively studied.<sup>20–22</sup> In the case of the “3 × 3” type,  $\alpha$ -(DMEN)PbBr<sub>4</sub> (DMEN = 2-(dimethylamino)ethylamine) was the first example, and was constituted of alternating rows of *cis* and *trans* octahedra.<sup>19</sup> Recently, Tremblay *et al.* have reported a new “3 × 3” corrugated 2D hybrid perovskite, (4NPEA)<sub>2</sub>PbI<sub>4</sub> (4NPEA = 4-nitrophenylethylammonium), demonstrating that the optical property is similar to other 2D perovskites with distorted [PbI<sub>6</sub>] octahedra.<sup>23</sup> Guo *et al.* have further reported that [ImH][TzH]PbBr<sub>4</sub>, ([ImH<sup>+</sup>] = imidazolium, [TzH<sup>+</sup>] = 1,2,4-triazolium), adopting a “3 × 3” structural type, is the first example of a bromide perovskite incorporating two types of ordered organic cations.<sup>24</sup> Other similar “3 × 3” corrugated 2D Pb-based perovskites have also been reported and employed in solar cell devices.<sup>25</sup> In contrast, the Sn-based “3 × 3” corrugated 2D perovskites are much rarer, with the only example being (ImEA)[SnI<sub>4</sub>] (ImEA<sup>2+</sup> = 1-(2-ammonioethyl)-1H-imidazol-3-ium).<sup>26</sup> For the “4 × 4” corrugated structures,  $\alpha$ -[NH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>NH<sub>3</sub>][SnI<sub>4</sub>]<sup>27</sup> and  $\alpha$ -(HA)SnI<sub>4</sub><sup>28</sup> are the only two examples reported. An additional consideration in our work is that most reports on hybrid halide perovskites have mainly

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focused on Pb- and Sn-based phases. Within the same group,  $\text{Ge}^{2+}$  has a similar electron configuration of  $\text{Sn}^{2+}$  and  $\text{Pb}^{2+}$ , and significant effect of its lone pair.<sup>29</sup> However, Ge-based phases are much less explored.<sup>30,31</sup>

Here, by using S-(2-aminoethyl)isothiuronium (ETU) as the organic templating cation, five new hybrid iodides, namely  $(\text{ETU})_4\text{Ge}_5\text{I}_{18}$ ,  $(\text{ETU})\text{GeI}_4$ ,  $(\text{ETU})\text{SnI}_4$ ,  $(\text{ETU})\text{PbI}_4$  and  $(\text{ETU})_3\text{Pb}_2\text{I}_{10}$ , are reported.  $(\text{ETU})\text{GeI}_4$  and  $(\text{ETU})\text{SnI}_4$  are structurally analogous, featuring interesting corrugated “3 × 3” layered structures which belong to the (110)-oriented 2D perovskite family.  $(\text{ETU})\text{GeI}_4$  represents the first Ge-based example of the “3 × 3” type of corrugated sawtooth 2D perovskite. A different structure,  $(\text{ETU})_4\text{Ge}_5\text{I}_{18}$ , is also obtained by controlling the reaction ratio of the precursor organic cation and the inorganic precursors. Interestingly, an orange phase 2D perovskite  $(\text{ETU})\text{PbI}_4$  can be further converted to the yellow phase 0D structure  $(\text{ETU})_3\text{Pb}_2\text{I}_{10}$ , with the reduction of the C-S-C angle of the sulfur-containing ammonium cation ETU. The above compounds have optical band gaps in the range of 1.8–2.8 eV, which can be tuned with varying structural types and octahedral connectivity. At room-temperature, only  $(\text{ETU})\text{SnI}_4$  exhibits photoluminescence (PL), which could be due to the relatively stable configuration since it is the only material with just one structure (Ge and Pb each have two). This work demonstrates the utility of flexible organic cations in dictating a range of hybrid structures that are significant in the development of materials for advanced optoelectronic applications.

## Experimental

### Synthesis

All chemicals were purchased from Sigma-Aldrich and used without further purification or modification.

**$(\text{ETU})_4\text{Ge}_5\text{I}_{18}$  and  $(\text{ETU})\text{GeI}_4$ .**  $\text{GeO}_2$  (0.1 g, 1 mmol) powder was dissolved in 47% hydriodic acid (8.0 mL) and 50% aqueous  $\text{H}_3\text{PO}_2$  (1.5 mL) by heating under stirring for 30 min at 127 °C until the solution clarified. Then, S-(2-aminoethyl)isothiuronium bromide hydrobromide (0.168 g, 0.8 mmol) was added to the above solution under heating and stirring for an additional 5 min. Yellow needle crystals of  $(\text{ETU})_4\text{Ge}_5\text{I}_{18}$  precipitated during slow cooling. Orange plate crystals of  $(\text{ETU})\text{GeI}_4$  were formed in the same fashion except the ratio of S-(2-aminoethyl)isothiuronium bromide hydrobromide (0.281 g, 1 mmol) to  $\text{GeO}_2$  (0.1 g, 1 mmol) was enlarged to 1:1.

**$(\text{ETU})\text{SnI}_4$ .**  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (0.225 g, 1 mmol) powder was dissolved in 47% hydriodic acid (8.0 mL) and 50% aqueous  $\text{H}_3\text{PO}_2$  (1.5 mL) by heating under stirring for 10 min at 127 °C until the solution turned light yellow. Then S-(2-aminoethyl)isothiuronium bromide hydrobromide (0.281 g, 1 mmol) was added to the above solution, and the resultant mixture was stirred and heated for 5 min. Dark red plate-like crystals precipitated during slow cooling.

**$(\text{ETU})\text{PbI}_4$  and  $(\text{ETU})_3\text{Pb}_2\text{I}_{10}$ .**  $\text{PbO}$  (0.223 g, 1 mmol) powder was dissolved in 47% hydriodic acid (4.0 mL) and 50% aqueous  $\text{H}_3\text{PO}_2$  (1.0 mL) by heating under stirring for 5 min at 127 °C until the solution turned bright yellow. Then S-(2-aminoethyl)isothiuronium bromide hydrobromide (0.281 g, 1 mmol) was added to the above solution, and the resultant mixture was evaporated to approximately at half its original volume by stirring and heating. The solution was then left to stand overnight and allowed to crystallize into orange block crystals  $(\text{ETU})\text{PbI}_4$  at room temperature. However, the orange phase  $(\text{ETU})\text{PbI}_4$  is unstable. After removing a part of the crystals in the mother liquid, all of the orange block crystals in contact with the mother liquid quickly changed to yellow block crystals. Similarly, orange block crystals placed in the air also turned to yellow block crystals about one hour. Similar synthetic approaches were used to directly synthesize the yellow block crystals  $(\text{ETU})_3\text{Pb}_2\text{I}_{10}$  except S-(2-aminoethyl)isothiuronium bromide hydrobromide (0.562 g, 2 mmol) to  $\text{PbO}$  (0.223 g, 1 mmol) ratio was doubled to 2:1.

### Single Crystal X-ray Diffraction

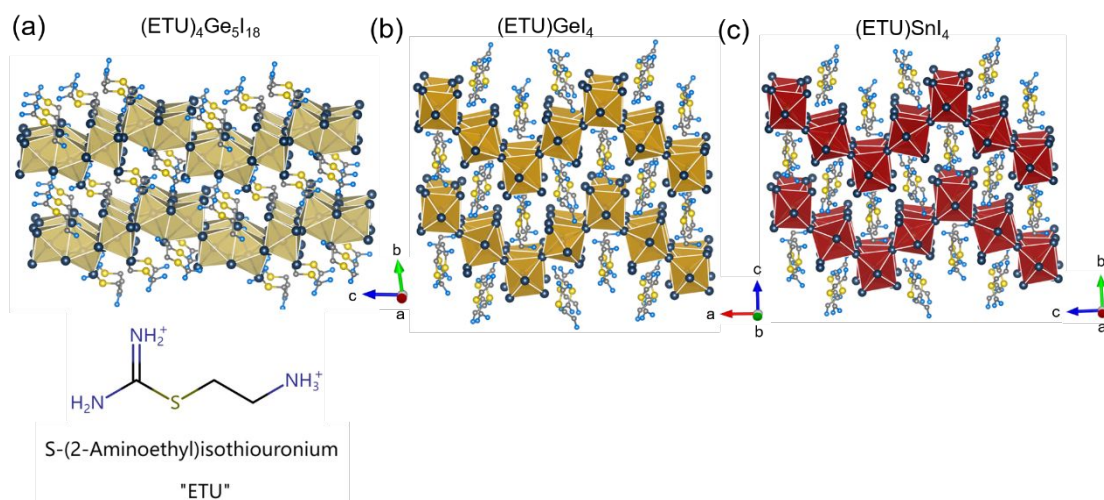
The single-crystal diffraction data was collected on a Bruker APEX-II CCD diffractometer for  $(\text{ETU})\text{SnI}_4$  and  $(\text{ETU})_3\text{Pb}_2\text{I}_{10}$  at 298 K, as well as on a Bruker D8 Venture diffractometer for  $(\text{ETU})\text{GeI}_4$ ,  $(\text{ETU})_4\text{Ge}_5\text{I}_{18}$  at 298 K and  $(\text{ETU})\text{PbI}_4$  at 100 K using  $\text{Mo-K}\alpha$  ( $\lambda=0.71073$  Å) radiation. The data collection and reduction were carried out using the Bruker APEX3 program for all compounds.<sup>32</sup> The crystal structures were solved by direct method and refined using the OLEX2 program package based on  $F^2$  with refinements of full-matrix least-squares.<sup>33,34</sup> All the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms attached to C and N atoms of organic molecules were positioned geometrically and refined isotropically. The data has been deposited in the CCDC database under 2169490–2169494.

### Powder X-ray Diffraction (PXRD)

The powder X-ray diffraction (PXRD) data were collected on SmartLab X-ray Diffractometer ( $\text{Cu-K}\alpha$ ,  $\lambda = 1.54056$  Å) at a voltage of 45 kV and a current of 200 mA in the range of 5–50° with the step size of  $10^\circ \cdot \text{min}^{-1}$  to confirm the purity of each sample at room temperature. By using the crystallographic file from the single-crystal X-ray diffraction experiment, the simulated powder pattern was calculated via Mercury software.

### Optical Absorption Spectroscopy

The solid UV-Vis absorbance spectra were recorded at room temperature on a Shimadzu UV-3600i Plus spectrophotometer with  $\text{BaSO}_4$  as the reference substance with the wavelength range at 200 nm to 900 nm. The reflectance spectra were converted to absorption spectra according to the Kubelka-Munk function:  $\alpha/S = F(R) = (1-R)^2/2R$ , where S is the scattering coefficient,  $\alpha$  is the absorption coefficient, and R is the reflectance.<sup>35</sup>



**Fig. 1** Crystal structures of (a)  $(\text{ETU})_4\text{Ge}_5\text{I}_{18}$ , (b)  $(\text{ETU})\text{GeI}_4$ , and (c)  $(\text{ETU})\text{SnI}_4$  and structure of the organic cation used here. Elements indicated by: dark blue (I), yellow (S), blue (N), dark gray (C). All hydrogen atoms are omitted for clarity.

### Steady-State Photoluminescence (PL)

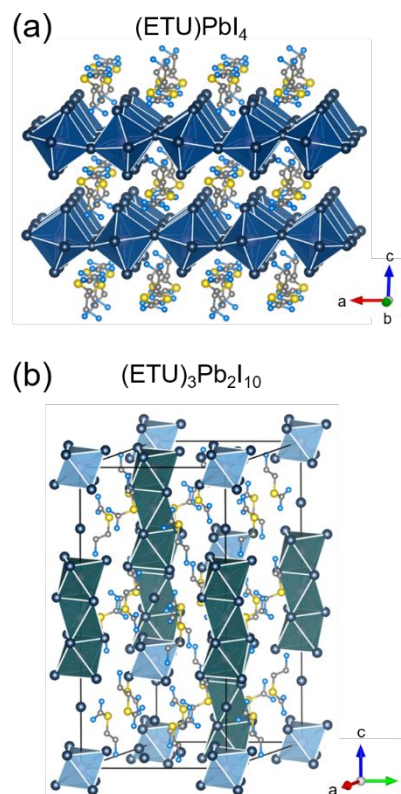
Steady-state PL spectra were conducted on LabRAM HR Evolution Laser Confocal Micro-Raman Spectroscopy at room temperature with 532 nm laser.

### Computational Details.

Density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package<sup>36-38</sup> (VASP), version 5.4.4. The Perdew-Burke-Ernzerhof<sup>39</sup> (PBE) functional and projector-augmented wave<sup>40,41</sup> (PAW) pseudopotentials were used with a plane-wave cut-off energy of 700 eV and energy convergence of  $10^{-5}$  eV or better. PAW potentials were chosen following the version 5.2 guidelines. Automatic k-mesh generation<sup>42</sup> was used with a length parameter ( $R_k$ ) of 40 or better. Spin-orbit coupling corrections were included for the Pb-based structures. For band-structure calculations, an appropriate k-path was generated using SeeK-path.<sup>43,44</sup> Density of states were plotted and analysed using Sumo.<sup>45,46</sup>

## Results and discussion

Unlike the relatively common perovskite-like organic-inorganic hybrids formed by rigid cations, a flexible organic cation can lead to richer and more diverse structures. The flexible cation ETU used here forms two different compounds with Ge and Pb, respectively, and one layered compound with Sn. The crystal structures of all five compounds are shown in Fig. 1 and 2, and crystallographic data are tabulated in Table S1 and S2.  $(\text{ETU})_4\text{Ge}_5\text{I}_{18}$  crystallizes in the triclinic space group  $P-1$ , and the inorganic sheets consist of mixed corner-sharing, edge-sharing and face-sharing  $[\text{GeI}_6]$  octahedra (Fig. 1a and S2).  $(\text{ETU})\text{GeI}_4$  crystallizes in a structure with the orthorhombic space group  $Pbca$ . It adopts a layered structure templated by the divalent organic cation, where each layer is formed with corner-sharing of  $[\text{GeI}_6]$  octahedra resulting in a “3 × 3” type of sawtooth corrugated structure (Fig. 1b). This is the first example of “3 × 3” corrugated 2D Ge-based perovskite.  $(\text{ETU})\text{SnI}_4$  is structurally analogous to  $(\text{ETU})\text{GeI}_4$  (Fig. 1c). We



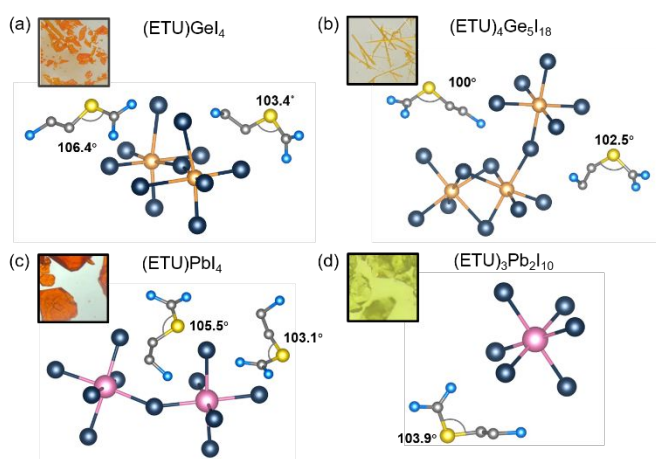
**Fig. 2** Crystal structures of (a)  $(\text{ETU})\text{PbI}_4$  and (b)  $(\text{ETU})_3\text{Pb}_2\text{I}_{10}$ . Elements indicated by: dark blue (I), yellow (S), blue (N), dark grey (C). Shown also are the metal halide units including distorted octahedra (light blue) and trimer octahedra (dark green) for  $(\text{ETU})_3\text{Pb}_2\text{I}_{10}$ . All H atoms are omitted for clarity.

further quantified the individual distortion of the octahedra for  $[\text{GeI}_6]$  and  $[\text{SnI}_6]$  by determining the bond length distortion ( $\Delta d$ ) and octahedral angle variance ( $\sigma^2$ ) listed in Table S3 (calculated using VESTA software). We note that the average  $\Delta d$  ( $3.18 \times 10^{-2}$ ) and average  $\sigma^2$  (12.76) for  $(\text{ETU})\text{SnI}_4$  is less than the value of  $(\text{ETU})\text{GeI}_4$ , where the larger radius of Sn compared to that of Ge accounts for

the smaller distortion in the Sn analogue. The octahedral distortion index  $\Delta d$  for all three individual  $[\text{PbI}_6]$  in  $(\text{ETU})_3\text{Pb}_2\text{I}_{10}$  is either zero or close to zero, which indicates the stable nature of the compound and the higher tolerance for the OD structure.

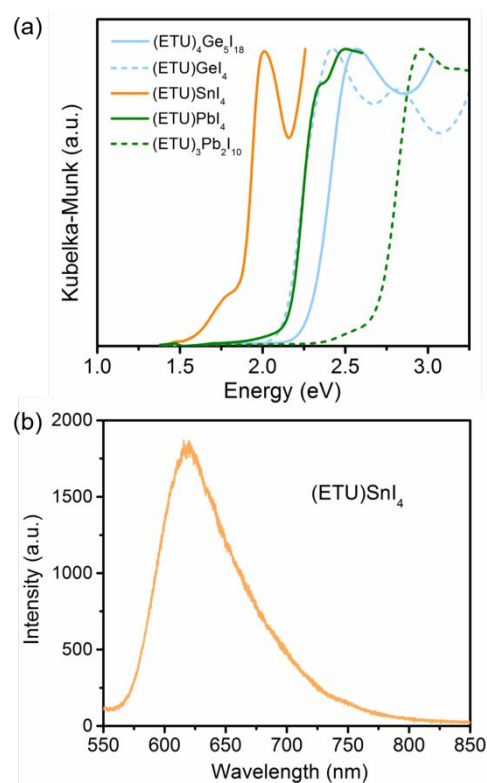
For the Pb-based materials,  $(\text{ETU})\text{PbI}_4$  crystallizes in a structure with the monoclinic space group  $P2_1/c$ , featuring the conventional (100)-oriented 2D structure with corner-sharing  $[\text{PbI}_6]$  octahedra (Fig. 2a). The Br analogue  $(\text{ETU})\text{PbBr}_4$  has been previously reported by Kundu *et al* and belongs to the (110)-oriented type.<sup>47</sup>  $(\text{ETU})_3\text{Pb}_2\text{I}_{10}$  crystallizes in the trigonal space group  $R\bar{3}$ , where the isolated  $[\text{PbI}_6]$  octahedra and  $[\text{Pb}_3\text{I}_{12}]^{6-}$  trimer are surrounded by ETU cations and iodide anions, giving rise to an OD structure (Fig. 2b and S3). Interestingly, the 2D orange phase  $(\text{ETU})\text{PbI}_4$  can be transformed to the stable OD yellow phase  $(\text{ETU})_3\text{Pb}_2\text{I}_{10}$  when the concentration of the mother liquor is low or exposed in air. This conversion is irreversible.

More interestingly, the degree of cations torsion angle (C-S-C angle) also varies in different structures. One can easily see from Fig. 3a and 3b that degree of cation distortion is changed in the two distinct 2D Ge-based structures. The torsion angles of the C-S-C in  $(\text{ETU})_4\text{Ge}_5\text{I}_{18}$  structure are  $100^\circ$  and  $102.5^\circ$  (Fig 3b), respectively, whereas the torsion angles of the C-S-C are  $106.4^\circ$  and  $103.4^\circ$  in the  $(\text{ETU})\text{GeI}_4$  structure (Fig 3a). In Pb-based series, there are two different conformational cations with the C-S-C torsion angles of  $105.5^\circ$  and  $103.1^\circ$  within the 2D orange phase  $(\text{ETU})\text{PbI}_4$  (Fig. 3c). Owing to the inherent flexibility of the cations in the crystal structure, the cation has only one configuration in the OD phase, with the C-S-C torsion angle of  $103.9^\circ$  (Fig. 3d). Generally speaking, the yellow phases  $(\text{ETU})_4\text{Ge}_5\text{I}_{18}$  and  $(\text{ETU})_3\text{Pb}_2\text{I}_{10}$  with smaller C-S-C angles are more stable than the orange phases  $(\text{ETU})\text{GeI}_4$  and  $(\text{ETU})\text{PbI}_4$ . The dynamic movement of ETU cations reaches a final state, where the yellow phases are stabilized.



**Fig. 3** The layout of cationic entities in the structures of (a)  $(\text{ETU})\text{GeI}_4$ , (b)  $(\text{ETU})_4\text{Ge}_5\text{I}_{18}$ , (c)  $(\text{ETU})\text{PbI}_4$ , (d) and  $(\text{ETU})_3\text{Pb}_2\text{I}_{10}$ . Elements indicated by: orange (Ge), pink (Pb), dark blue (I), yellow (S), blue (N), dark gray (C), and all H atoms are omitted here for clarity. Inserted: optical microscope picture of corresponding single crystals.

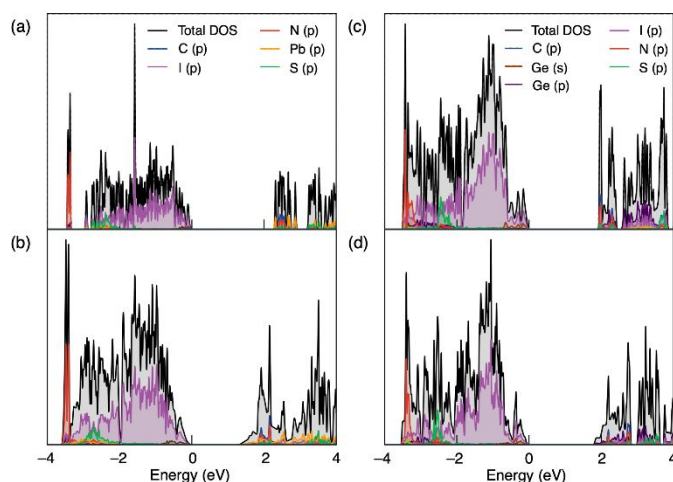
Differences in the structure remarkably affect the photophysical properties of these materials. The optical band gaps of the five compounds reported here were determined by diffuse reflectance UV-vis spectroscopy measurements (Fig. 4a). These materials all show clear excitonic features close to the band edges.  $(\text{ETU})_4\text{Ge}_5\text{I}_{18}$  has a band gap of 2.30 eV, with an average Ge-I-Ge angle of  $111.2^\circ$ , while  $(\text{ETU})\text{GeI}_4$  has a slightly smaller band gap (2.14 eV), due to a larger averaged angle of  $162.3^\circ$ . These hybrid germanium iodides, reasonably have narrower band gaps compared with reported 2D Ge-Br perovskites.<sup>31</sup>  $(\text{ETU})\text{SnI}_4$  has the narrowest band gap of the series (1.87 eV), which is consistent with band gap value of  $\alpha\text{-(HA)SnI}_4$  with “4 × 4” corrugated structure.<sup>28</sup> Within the Pb series,  $(\text{ETU})\text{PbI}_4$  with the 2D structure has the lower band gap of 2.17 eV while  $(\text{ETU})_3\text{Pb}_2\text{I}_{10}$  with the OD structure has higher band gap (2.71 eV) because the later has lower dimensionality. These two phases are easily distinguishable by color, which are consistent with previously reported.<sup>16,48</sup>



**Fig. 4** (a) UV-vis absorption spectra of  $(\text{ETU})_4\text{Ge}_5\text{I}_{18}$ ,  $(\text{ETU})\text{GeI}_4$ ,  $(\text{ETU})\text{SnI}_4$ ,  $(\text{ETU})\text{PbI}_4$  and  $(\text{ETU})_3\text{Pb}_2\text{I}_{10}$  at room temperature. (b) Steady-state photoluminescence (PL) spectra (excited at 532 nm) for  $(\text{ETU})\text{SnI}_4$  at room temperature.

To further evaluate the optical properties of these materials, we performed photoluminescence (PL) measurements on single crystals at room temperature. Unfortunately, no significant emission peaks were observed in Ge- and Pb-based materials, which may be related to structural parameter variations as reported previously.<sup>49,50</sup> Under other stimuli such as low-temperature or with extra pressure, PL may be able to be observed. The PL spectrum for  $(\text{ETU})\text{SnI}_4$  is presented in Fig. 4b and has a significantly emission peak at 620 nm under excitation at 532 nm with a wide

full width at half maximum (FWHM) of 74 nm, as well as an Stokes shift of 88 nm. This PL band is closely overlapped with the absorption profile and appears to be due to band edge recombination process, in which the photogenerated free excitons (FE) relax back to the valence band. The PL emission energy is generally consistent with the previously reported band edge emission of many 2D tin-iodine perovskites.<sup>28</sup> It is intriguing that (ETU)SnI<sub>4</sub> is the only compound here found to have PL at room temperature, and also the only compound that is composed of ETU with metal iodide with just one composition (Ge and Pb each have two). This may be due to that the dynamics of the organic cations suppress radiative recombination processes in the Ge- and Pb-based phases, whereas the Sn analogue has higher rigidity to maintain the FE emission.



**Fig.5** DFT-calculated DOS for (a) (ETU)<sub>3</sub>Pb<sub>2</sub>I<sub>10</sub>, (b) (ETU)PbI<sub>4</sub>, (c) (ETU)<sub>4</sub>Ge<sub>5</sub>I<sub>18</sub>, and (d) (ETU)GeI<sub>4</sub>.

Density functional theory (DFT) calculations were performed in order to gain a better understanding of how the various structure-types presented here affect the electronic structures of these compounds. Fig 5 displays the calculated density of states (DOS) for (ETU)<sub>3</sub>Pb<sub>2</sub>I<sub>10</sub>, (ETU)PbI<sub>4</sub>, (ETU)<sub>4</sub>Ge<sub>5</sub>I<sub>18</sub>, and (ETU)GeI<sub>4</sub>, which allow us to estimate the band gaps of these materials and understand the contribution of different orbitals to the valence and conduction bands. First, considering the Pb series of compounds, we find that the trend in the band gaps is qualitatively similar to what was observed experimentally, with (ETU)PbI<sub>4</sub> having a significantly smaller bandgap than (ETU)<sub>3</sub>Pb<sub>2</sub>I<sub>10</sub> (1.22 eV versus 2.22 eV, respectively.) Both band gaps are underestimated compared to experiment, which is typical of DFT calculations using the PBE functional. However, the band gap for (ETU)PbI<sub>4</sub> is underestimated by almost 1 eV, compared with approximately 0.5 eV for (ETU)<sub>3</sub>Pb<sub>2</sub>I<sub>10</sub>. This discrepancy may be due to the fact that (ETU)PbI<sub>4</sub> is inherently unstable, and the crystal structure used for the calculations needed to be collected at 100 K, versus 298 K for the (ETU)<sub>3</sub>Pb<sub>2</sub>I<sub>10</sub> structure. Examining the orbital contributions to the DOS, the valence band edges for both compounds are dominated by the I 5p orbitals with a small contribution from the Pb 6s orbitals. In the case of the conduction band, both compounds show a contribution from the Pb 6p states at the band edges, with a

contribution from the ETU orbitals (N 2p, C 2p, and S 3p) slightly higher in energy. The dimensionality of these two compounds manifests itself very clearly in the DOS, where the 0D (ETU)<sub>3</sub>Pb<sub>2</sub>I<sub>10</sub> shows a very “spiky” DOS due to the molecular-like nature of its structure, while the 2D (ETU)PbI<sub>4</sub> shows a more continuous curve. In the Ge-based compounds, the band gap trends are again reproduced, where (ETU)<sub>4</sub>Ge<sub>5</sub>I<sub>18</sub> has a calculated gap of 1.94 eV and (ETU)GeI<sub>4</sub> has a gap of 1.71 eV. In this case, both band gaps are underestimated by approximately 0.4 eV. The orbital-projected DOS for these compounds shows that, similarly to the lead compounds, the valence band edge is predominately made up of the I 5p orbitals with a small contribution from the Ge 4s orbitals. Interestingly, for (ETU)<sub>4</sub>Ge<sub>5</sub>I<sub>18</sub>, the edge of the conduction band is dominated by states originating from the ETU cation. These states may be lower in energy compared to those in the other compounds due to the lower C-S-C angle in the ETU cation, which, as previously noted, appears to enhance stability. The DOS for (ETU)GeI<sub>4</sub> shows similar features, but the conduction band edge appears to be primarily comprised of the Ge 4p states and the contributions from the ETU cation are shifted to slightly higher energies. In summary, the DOS for both (ETU)PbI<sub>4</sub> and (ETU)GeI<sub>4</sub> is similar to that of other 2D halide perovskite materials. Additionally, the DOS for (ETU)<sub>4</sub>Ge<sub>5</sub>I<sub>18</sub> illustrates how conformational changes in the organic cation can potentially influence the makeup of the band edges in these materials.

## Conclusions

In summary, we have synthesized and characterized the structure, optical and electronic properties of five new hybrid iodides by selecting flexible organic species as the stabilizing cations. Among them, two intriguing new “3 × 3” corrugated (110)-oriented type 2D perovskites (ETU)GeI<sub>4</sub> and (ETU)SnI<sub>4</sub> are reported, where (ETU)GeI<sub>4</sub> is the first Ge-based example of the “3×3” type 2D structure. Due to the flexibility of the bond angle of the organic cation, (ETU)PbI<sub>4</sub>, featuring conventional (100)-oriented type 2D structure, can be readily transformed into a new yellow-phase 0D structure (ETU)<sub>3</sub>Pb<sub>2</sub>I<sub>10</sub>. The materials with larger band gaps and lower dimensionality show smaller torsion angles of the organic cations, hinting the movement of the cations are stabilized. Our work highlights the importance of properly manipulate the interactions between the organic and inorganic counterparts, suggesting new design principles for inorganic-organic hybrid halides.

## Conflicts of interest

There are no conflicts to declare.

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