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Band Gap and Topology of 1D Perovskite-Derived Hybrid Lead Halide Structures

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Abstract: The unprecedented structural flexibility of hybrid halide perovskites is accompanied by a wide range of useful optoelectronic properties, causing a high interest in this family of materials. However, there are no systematic studies yet on the relationships between the topology of structures derived of chain 1D hybrid halide perovskites and their optoelectronic properties such as the band gap as already reported for 3D and 2D hybrid halide perovskites. In the present work, we introduce a rational classification of hybrid lead iodide 1D structures. We provide a theoretical assessment of the relationship between the topology of 1D hybrid halide perovskite-derived structures with vertex-connected octahedra and show that the distortions of geometry of the chains of PbI 6 octahedra are the main parameters affecting the band gap value while the distance between the chains of vertex-connected octahedra has a minor effect on the band gap.

Keywords: perovskite-derived hybrid structures; structure topology; band gap; perovskite-like; semiconductors

1. Introduction

Hybrid lead halide perovskite-derived materials have been extensively studied recent years due to their potential applications in optics and optoelectronics [1,2], catalysts [3], sensors [4], and ferroelectrics [5,6]. The building blocks in the crystal structures of these materials are PbX 6 octahedra (where X = I −, Br −, Cl −) connected along vertices, edges, or faces, that makes this family of structures to be extremely structurally diverse [7]. It is used to subdivide these materials in different groups based on the dimensionality of their inorganic sublattices: 3D, 2D, 1D and 0D [7], mainly defined by the Goldschmidt tolerance factor [8,9] and the structure of organic counterparts as shown recently [10,11]. However, hybrid halide perovskites with 3D and 2D counterparts are shown to be quite promising for photovoltaic and optoelectronic applications [1,2], the materials with 1D inorganic framework show relatively low carrier mobility and are often used as a auxiliary passivating layers to improve the device stability [12,13] rather than light absorbing/emitting materials.

The relationships between different distortions of the inorganic framework on the band gap for 3D and 2D hybrid halide perovskites have been quantitatively identified previously [14,15]; however, this question remains insufficiently explored for 1D hybrid halide structures composed of the chains of PbI 6 octahedra. Recently, Wong et al. proposed a classification system of hybrid lead halide 1D structures based on notations of PbI 6 octahedra connectivity via three main parameters: the intralayer periodicity, connectivity within the repeating unit and, finally, the connectivity to the next repeating unit [16]. At the same time, the topological description of crystal structures is becoming increasingly popular [17]. In the present work, we show that the application of alternative and more robust classification based on the topology of inorganic sublattice allows us to make
a new classification of hybrid lead halide 1D structures and to subdivide them into the subgroups for the analysis of the influence of various inorganic lattice conformations on their optoelectronic properties such as band gaps. We analyze the influence of arrangements and distortions of 1D perovskite derived structures with PbI\(_6\) chains on their band gaps. Furthermore, we focus on the 1D perovskite-derived compounds (A\(_3\)PbI\(_5\)) exhibiting most interesting optical properties due to highly anisotropic electronic properties and highly tunable band gaps. Particularly, we analyze the influence of arrangements and distortions of vertex-connected octahedra chains on the band gaps.

2. Materials and Methods

2.1. Topological Analysis of Crystal Structures

The TOPOS program package [17,18] was used to analyze Pb-I subnets. Only the inorganic part of the structure was included in the topological analysis. The following topological parameters have been computed for all the studied experimentally refined structures from CSD database [19] (Table A1 in Appendix A). Accordingly to the terminology of nets symbols in TOPOSpro [20], the symbols of net topology ND\(_n\), where N is a sequence of degrees (coordination numbers) of all independent nodes, D is one of the letters C, L, or T designating the dimensionality of the net (C—chain, L—layer, T—three-periodic); \( n \) enumerates non-isomorphic nets with a given ND sequence. For instance, the symbol (2-c)3(6-c) denotes the chain binodal (contains two independent fragments—(2-c) and (6-c)) net with three 2-coordinated and one 6-coordinated independent nodes (Figure 1a). The symbol (1-c)3(2-c)(6-c) denotes the chain three-nodal net with four 1-coordinated, one 2-coordinated and one 6-coordinated independent nodes (Figure 1b).

![Figure 1](image1.png)

**Figure 1.** Scheme of net topology definition for binodal (a) and three-nodal (b) nets.

2.2. DFT Calculations

Electronic band structure calculations were obtained with the density functional theory (DFT) implemented with the Quantum ESPRESSO (version 6.1) freeware in combination with the BURAI (version 1.3.1) GUI [21–23]. The electronic exchange-correlations were treated by the Perdew–Burke–Ernzerhof (PBE) under a generalized gradient approximation (GGA) [24], and the OTFG Ultrasoft pseudo-potential was used to describe the interaction between electrons and ions [25]. Geometry optimization of the model structures was not carried out. The integration calculation of the system in Brillouin region uses the monkhorst-pack scheme, the k grid point is \(2 \times 2 \times 2\) and the cut-off energy of plane wave of the system is set at 435 eV to ensure the convergence of energy and configuration of the system at the level of quasi-complete plane wave base. In the self-consistent field operation, Pulay density mixing method is adopted, and the self-consistent field is set as \(5 \times 10^{-6}\) eV/atom. The valence electrons involved in the calculation are Pb-6s\(^2\)6p\(^2\) and I-5s\(^2\)5p\(^3\). The calculations did not include spin–orbit coupling. A visualization of crystal structures was performed using the VESTA program [26].
2.3. Analysis of the Distortions of Structures

To identify the relationships between the distortions of the inorganic framework, the band gaps and the sizes of the A-site organic cations, we analyzed the Pearson correlation coefficients of the sizes of A-site cations with the geometric parameters of inorganic framework and calculated band gaps for the experimentally known phases with [PbI$_5$]$^{3-}$ chains (see Table A2). Pearson correlation coefficient is a statistical measure of the linear relationship between two variables. Pearson correlation coefficient between two variables $x$ and $y$ can be calculated using the following formula:

$$ \rho = \frac{\sum(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum(x_i - \bar{x})^2 \sum(y_i - \bar{y})^2}} $$

where $\bar{x}$ is the mean value of $x$ and $\bar{y}$ is the mean value of $y$. $x_i$ and $y_i$ represent different values of $x$ and $y$. The Pearson correlation coefficient can range from $-1$ to $1$.

To calculate the distortion of the inorganic framework, we used the following geometrical descriptors: the distortions of PbI$_6$ octahedra ($\Delta d$), distance between adjacent chains of PbI$_6$ octahedra (I-I distance between adjacent chains), Pb-Pb-Pb angle in a chain (Figure A2), and shortest I-I distance in a chain (Figure A2).

To determine the degree of distortion of PbI$_6$ octahedra, we used the equation than commonly used for evaluation of the distortion degree of perovskite-derived structures:

$$ \Delta d = \frac{1}{5} \sum \left( \frac{d_n - \bar{d}}{\bar{d}} \right)^2, $$

where $d_n$ is the individual Pb-I distances and $\bar{d}$ is the arithmetic mean values of the individual Pb-I distances.

3. Results

To reveal the topological features of 1D hybrid lead halides crystal structure, we analyzed the inorganic Pb-I subnets for 182 refined structures from the Cambridge Structural Database (CSD) [19], separated and identified nets of crystal structures and their relations using topological method that implemented in the TOPOSpro program package [17]. The structures of 1D hybrid lead halides can be distinguished in four main types according to the stoichiometry of a chain of connected octahedra and its topology notations (Figure A1, details are in Table A1 in Appendix A). The most common stoichiometry is A(PbI$_3$) (where A is organic cations) (about 160 structures from 182) represented by two types of topology: face-connected PbI$_6$ octahedra formed of 2-nodal net (contains two topologically inequivalent nodes) (Figure 2a) [18] with the topology (2-c)3(6-c) and edge-connected PbI$_6$ octahedra with 4-nodal net topology (1-c)(2-c)(3-c)(6-c) (Figure 2b); however, there is only one experimentally refined structure with the latter chains up to now. The structures A$_4$(Pb$_3$I$_{10}$) consisting of chains of octahedra [Pb$_3$I$_{10}$]$^{4-}$ connected along edges and faces have a 5-nodal net with topology (1-c)(2-c)(2-c)(6-c)(2(c)6-c) (Figure 2c). The structures A$_2$(PbI$_4$) consisting of chains of octahedra [PbI$_4$]$^{2-}$ connected along edges have a 3-nodal net with topology (1-c)(2-c)(2-c)(6-c) (Figure 2d). The structures A$_3$(PbI$_5$) with vertex-connected octahedra [PbI$_5$]$^{3-}$ chains are represented by a 3-nodal net with stoichiometry (1-c)(2-c)(6-c) (Figure 2e).

Strictly speaking, first four types of structures are not perovskite-derived since their structures are not the derivatives of the perovskite structure type. Only the latter type of the structures with vertex-connected octahedra [PbI$_5$]$^{3-}$ chains preserve the fragment of perovskite structure in the form of vertex-connected 1D chains and can therefore be called a “perovskite-derived”. Such structures retain, in one of the dimensions, a high dispersion of the band characteristics of 3D halide perovskites and, accordingly, a sufficiently high mobility of charge carriers along the chains, while in the other two dimensions, a low dispersion is observed and the carriers are actually localized. Thus, the structure of 1D A$_3$PbI$_5$ perovskites determines the unique anisotropy of the electronic and optical
properties of these materials. The vertex connection of octahedra corresponds to the maximum number of degrees of freedom for various distortions of the 1D chain and makes it possible to vary the band gap over a wide range. Therefore, understanding of the influence of \([\text{PbI}_5]^3^-\) chain conformations on the band gap is important for the design of new low-dimensional hybrid halide materials.

![Figure 2](image-url)

**Figure 2.** 1D lead-halide hybrid Pb-I subnets with different type of topology: (a,b) \([\text{PbI}_3]^-$, (c) \([\text{Pb}_3\text{I}_{10}]^{4-}\), (d) \([\text{PbI}_4]^{2-}\), (e) \([\text{PbI}_5]^3-\).

The relationships between the structural geometrical descriptors and the band gap for corresponding compounds with \([\text{PbI}_5]^3-\) chain topology were estimated using DFT calculations of the band gap of modeled structures. The following parameters were considered as relevant structural descriptors: axial and equatorial Pb–I distances, equatorial Pb–I–Pb, and tilting angles, and the distance between the \([\text{PbI}_5]^3-\) chains. We found that for hypothetical structures with the same Pb-I distance (3.16 Å) and without tilting of octahedra an increase in the distance between neighboring \([\text{PbI}_5]^3-\) chains from 4.45 Å to 7.5 Å leads to the band gap increase by 0.1 eV only (Figure 3). Thus, the geometric descriptor of the distances between the chains does not affect strongly the change in the band gap for the considered 1D structures with \([\text{PbI}_5]^3-\) chains since the overlap of halogen–halogen orbitals becomes insignificant at distances of 5.5 Å, similar with 2D hybrid compounds reported before [14,15,27]. It should be noted that among the experimentally known 1D hybrid halide structures with \([\text{PbI}_5]^3-\) chains, the minimum distance between chains is 5.14 Å (CSD ID 1048274). Thus, the main geometric factors affecting the band gap in this type of structures will be the Pb-I angles in the octahedra, the Pb-I bond lengths, and tilting of octahedra in a chain.

Figure 4 shows the calculated band structures for two hypothetical 1D perovskite-derived structures with \([\text{PbI}_5]^3-\) chains of vertex-connected octahedra spaced by 5.5 Å and a Pb-I bond length of 3.16 Å. The first one, featured by undistorted chains of octahedra (Figure 4a) and Pb-I-Pb angle of 180 degrees, has the band gap of 2.1 eV. In contrast, the second structure with strongly distorted chains of octahedra (Figure 4b) (the distance between the adjacent chains of 5.04 and 5.69 Å, Pb-I bond lengths in the PbI₆ octahedra...
3.16 Å, 3.22 Å, 3.22 Å, 3.3 Å, 3.2 Å, 3.3 Å, the Pb-I-Pb angle between the octahedra (145 degrees) has the band gap is 2.55 eV.

Figure 3. Calculated band structures for hypothetical 1D perovskite-derived structures with different distances between the \([\text{PbI}_5]^3-\) chains.

Figure 4 shows the calculated band structures for two hypothetical 1D perovskite-derived structures with \([\text{PbI}_5]^3-\) chains of vertex-connected octahedra spaced by 5.5 Å and a Pb-I bond length of 3.16 Å. The first one, featured by undistorted chains of octahedra (Figure 4a) and Pb-I-Pb angle of 180 degrees, has the band gap of 2.1 eV. In contrast, the second structure with strongly distorted chains of octahedra (the distance between the adjacent chains of 5.04 and 5.69 Å, Pb-I bond lengths in the PbI\(_6\) octahedra 3.16 Å, 3.22 Å, 3.22 Å, 3.3 Å, 3.2 Å, 3.3 Å, the Pb-I-Pb angle between the octahedra 145 degrees) has the band gap is 2.55 eV.

These results clearly illustrate that the distortions of geometry of the chains of PbI\(_6\) octahedra are the main parameters affecting the band gap value, while the distance between the chains of vertex-connected octahedra has minor effect on the band gap in these materials. Therefore, while band structure of 1D hybrid halide perovskite-derived compounds is mainly defined by the size and geometry of organic cations, occupying the interchain space, the band gap of such compounds can be tuned in range from 1.98 eV to 2.55 eV by choosing an appropriate organic counterpart.

To confirm our conclusions, we considered the experimental crystal structures of perovskite-derived compounds with vertex-connected octahedra \([\text{PbI}_5]^3-\) chains (see...
These results clearly illustrate that the distortions of the Pb-I bond length in PbI$_6$ octahedra ($\Delta d$), the distance between adjacent chains of vertex-connected octahedra, Pb-Pb-Pb angles in a chain (see Figure A2), and shortest I-I distance in a chain (see Figure A2). The heatmap of Pearson correlation coefficients clearly illustrates that the descriptors of shortest I-I distance in a chain of octahedra and Pb-Pb-Pb angle in a chain (Figure A2) are responsible for rotations and tilts of octahedra in chains relative to each other. Interestingly, that the Pearson correlation coefficient between shortest I-I distance in a chain of octahedra (Figure A2) and $\Delta d$ is strongly negative ($−0.95$), while the correlation coefficient between shortest I-I distance in a chain of octahedra and Pb-Pb-Pb angle in a chain is positive ($0.72$). Thus, the distortions of octahedra chains affect the Pb-I distance in the octahedra ($\Delta d$), and hence the band gap. The Pearson correlation coefficient between the $\Delta d$ and the band gap is strongly positive ($0.82$) for the considered experimental compounds. To summarize, an increase of the distortions of the Pb-I distances in octahedra ($\Delta d$) lead to an increase in the band gap, and a decrease in the shortest I-I distances in octahedra chains also leads to an increase in the $\Delta d$ and to an increase in a chain tilting. It is worth noting that for the experimentally known 1D perovskite-derived structures with vertex-connected chains of PbI$_6$ octahedra and various organic cations, the Pearson correlations of the “A-site” cation sizes with the band gap and geometrical distortions in octahedra are weakly positive ($0.5$ and $0.46$, respectively) (Figure 5).

**Figure 5.** Heatmap of Pearson correlation coefficient matrix for geometrical descriptors and the band gaps of 1D perovskite-derived experimental structures with vertex-connected chains of PbI$_6$ octahedra.

4. Conclusions

To summarize, we introduce a topological classification of 1D hybrid lead halide structures with chains of lead halide octahedra revealing five different types of such structures. We estimated an influence of the distortions in inorganic frameworks of 1D hybrid halide perovskite-derived structures with vertex-connected octahedra and [PbI$_3$]$^3$–stoichiometry on their band gaps. It was shown that the distortions of geometry of the chains of PbI$_6$ octahedra are the main parameters affecting the band gap value and turning them in range from $2.10$ eV to $2.55$ eV, whereas a shortening of the distance ($d$) leads to...
a decrease in the band gap to 1.98 eV, and in the case of d greater than 5.5 Å, it actually does not affect the $E_g$.

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**Data Availability Statement:** Data available on request.

**Conflicts of Interest:** The authors declare that they have no conflict of interest.

### Appendix A

**Table A1.** Net topology of 1D hybrid lead halide structures from CSD database using TOPOSpro program package.

| CSD Ref Code | Type of Chain | Topology of the Net * |
|--------------|---------------|----------------------|
| 214790       | chains [0 1 0] with [Pb$_3$I$_{10}$]$^{4-}$ | 1,2,2,6,6-c net with stoichiometry (1-c)(2-c)(6-c)(2-c)(6-c)(6-c); 5-nodal net |
| 104219       | chains [1 0 1] with [Pb$_3$I$_{10}$]$^{4-}$ | 1,2,2,6,6-c net with stoichiometry (1-c)(2-c)(6-c)(2-c)(6-c)(6-c); 5-nodal net |
| 82074        | chains [0 0 1] with [Pb$_3$I$_{10}$]$^{4-}$ | 1,2,2,6,6-c net with stoichiometry (1-c)(2-c)(6-c)(2-c)(6-c)(6-c); 5-nodal net |
| 836347       | chains [0 1 –1] with [Pb$_3$I$_{10}$]$^{4-}$ | 1,2,2,6,6-c net with stoichiometry (1-c)(2-c)(6-c)(2-c)(6-c)(6-c); 5-nodal net |
| 1119690      | chains [1 0 0] with [Pb$_3$I$_{10}$]$^{4-}$ | 1,2,2,6,6-c net with stoichiometry (1-c)(2-c)(6-c)(2-c)(6-c)(6-c); 5-nodal net |
| 1515524-957318 | chains [1 0 1] with [Pb$_3$I$_{10}$]$^{4-}$ | 1,2,2,6,6-c net with stoichiometry (1-c)(2-c)(6-c)(2-c)(6-c)(6-c); 5-nodal net |
| 1515524-957318 | chains [1 0 1] with [Pb$_3$I$_{10}$]$^{4-}$ | 1,2,2,6,6-c net with stoichiometry (1-c)(2-c)(6-c)(2-c)(6-c)(6-c); 5-nodal net |
| 1945576      | chains [1 0 1] with [Pb$_3$I$_{10}$]$^{4-}$ | 1,2,2,6,6-c net with stoichiometry (1-c)(2-c)(6-c)(2-c)(6-c)(6-c); 5-nodal net |
| 160842       | chains [0 0 1] with [PbI$_3$]$^-^$ | 2,6-c net with stoichiometry (2-c)(3-c)(6-c); 2-nodal net |
| 210812       | chains [0 0 1] with [PbI$_3$]$^-^$ | 2,6-c net with stoichiometry (2-c)(3-c)(6-c); 2-nodal net |
| 254879       | chains [0 0 1] with [PbI$_3$]$^-^$ | 2,6-c net with stoichiometry (2-c)(3-c)(6-c); 2-nodal net |
| 277224       | chains [0 0 1] with [PbI$_3$]$^-^$ | 2,6-c net with stoichiometry (2-c)(3-c)(6-c); 2-nodal net |
| 790923       | chains [0 0 1] with [PbI$_3$]$^-^$ | 2,6-c net with stoichiometry (2-c)(3-c)(6-c); 2-nodal net |
| 291886       | chains [0 0 1] with [PbI$_3$]$^-^$ | 2,6-c net with stoichiometry (2-c)(3-c)(6-c); 2-nodal net |
| 298933       | chains [0 0 1] with [PbI$_3$]$^-^$ | 2,6-c net with stoichiometry (2-c)(3-c)(6-c); 2-nodal net |
| 604996       | chains [0 0 1] with [PbI$_3$]$^-^$ | 2,6-c net with stoichiometry (2-c)(3-c)(6-c); 2-nodal net |
| 609997       | chains [0 0 1] with [PbI$_3$]$^-^$ | 2,6-c net with stoichiometry (2-c)(3-c)(6-c); 2-nodal net |
| 632026       | chains [0 0 1] with [PbI$_3$]$^-^$ | 2,6-c net with stoichiometry (2-c)(3-c)(6-c); 2-nodal net |
| 636241       | chains [0 0 1] with [PbI$_3$]$^-^$ | 2,6-c net with stoichiometry (2-c)(3-c)(6-c); 2-nodal net |
| 722539       | chains [0 0 1] with [PbI$_3$]$^-^$ | 2,6-c net with stoichiometry (2-c)(3-c)(6-c); 2-nodal net |
| 776897       | chains [0 0 1] with [PbI$_3$]$^-^$ | 2,6-c net with stoichiometry (2-c)(3-c)(6-c); 2-nodal net |
| 780403       | chains [0 0 1] with [PbI$_3$]$^-^$ | 2,6-c net with stoichiometry (2-c)(3-c)(6-c); 2-nodal net |
| 780404       | chains [0 0 1] with [PbI$_3$]$^-^$ | 2,6-c net with stoichiometry (2-c)(3-c)(6-c); 2-nodal net |
| 780405       | chains [0 0 1] with [PbI$_3$]$^-^$ | 2,6-c net with stoichiometry (2-c)(3-c)(6-c); 2-nodal net |
| 780408       | chains [0 0 1] with [PbI$_3$]$^-^$ | 2,6-c net with stoichiometry (2-c)(3-c)(6-c); 2-nodal net |
| 780409       | chains [0 0 1] with [PbI$_3$]$^-^$ | 2,6-c net with stoichiometry (2-c)(3-c)(6-c); 2-nodal net |
| 921641       | chains [0 0 1] with [PbI$_3$]$^-^$ | 2,6-c net with stoichiometry (2-c)(3-c)(6-c); 2-nodal net |
| 780410       | chains [0 0 1] with [PbI$_3$]$^-^$ | 2,6-c net with stoichiometry (2-c)(3-c)(6-c); 2-nodal net |
Table A1. Cont.

| CSD Ref Code | Type of Chain | Topology of the Net * |
|--------------|---------------|-----------------------|
| 785767       | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 785768       | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 785769       | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 818548       | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 834146       | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 836348       | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 917236       | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1012805      | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1123333      | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1869662      | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1869663      | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1135285      | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1962916      | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1183349      | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1308385      | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1400319      | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1400321      | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1400323      | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1400324-15701131 | chains [0 0 1] with [PbI3]^- | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1400324-15701131 | chains [0 0 1] with [PbI3]^- | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1400324-15701131 | chains [0 0 1] with [PbI3]^- | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1400324-15701131 | chains [0 0 1] with [PbI3]^- | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1400324-15701131 | chains [0 0 1] with [PbI3]^- | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1400324-15701131 | chains [0 0 1] with [PbI3]^- | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1400324-15701131 | chains [0 0 1] with [PbI3]^- | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1400324-15701131 | chains [0 0 1] with [PbI3]^- | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1400324-15701131 | chains [0 0 1] with [PbI3]^- | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1400324-15701131 | chains [0 0 1] with [PbI3]^- | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1526831      | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1532918-968126 | chains [0 0 1] with [PbI3]^- | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1547867      | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1570129      | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1590177      | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1819979      | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1828821      | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1828823      | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1835320      | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1869657-1869658 | chains [0 0 1] with [PbI3]^- | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1869657-1869658 | chains [0 0 1] with [PbI3]^- | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1869657-1869658 | chains [0 0 1] with [PbI3]^- | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| 1905762      | chains [0 0 1] with [PbI3]^-   | 2,6-c net with stoichiometry (2-c)(3c-6c); 2-nodal net |
| CSD Ref Code | Type of Chain | Topology of the Net * |
|-------------|---------------|-----------------------|
| 1909463     | chains [0 0 1] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1923364-1923365 | chains [0 0 1] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 193493-1934988 | chains [0 0 1] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 193493-1934988 | chains [0 0 1] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1944788     | chains [0 0 1] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1969340     | chains [0 0 1] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1992695     | chains [0 0 1] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 2072691-994664 | chains [0 0 1] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 2072691-994664 | chains [0 0 1] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 2072691-994664 | chains [0 0 1] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 2072691-994664 | chains [0 0 1] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 219758.cif. | chains [0 0 1] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 708406      | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 780407      | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 797634      | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 861679      | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1048276     | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1135285-1962916 | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1169102     | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1871034     | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1400322     | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1495872     | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1495874     | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1502217     | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1504241     | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1524688-1944787 | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1524688-1944787 | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1524689     | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1562186     | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1577162-1577163 | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1828819     | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1871034     | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1901048-612444 | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1901048-612444 | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1915775     | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1923364-1923365 | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1944787     | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1962916     | chains [0 1 0] with [PbI_3]^− | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |

* CSD Ref Code: Crystal Structure Database Reference Code.
* Type of Chain: Describes the type of chain in the crystal structure.
* Topology of the Net: Describes the topology of the network in the crystal structure.
Table A1. Cont.

| CSD Ref Code | Type of Chain | Topology of the Net * |
|--------------|--------------|-----------------------|
| 1977726      | chains [0 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1024906      | chains [0 1 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(3-c); 2-nodal net |
| 221315       | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 248812       | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(3-c); 2-nodal net |
| 776896       | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 776898       | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 776899       | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 900606       | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 958061       | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 967300       | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 998856       | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1015245      | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1047384      | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1251540      | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1274099      | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1447264      | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1447265      | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1447266      | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1483105-871217 | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1483105-871217 | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1495875      | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1523553-1523557 | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1523553-1523557 | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1523553-1523557 | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1523553-1523557 | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1523553-1523557 | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1533556      | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1535129-1535132 | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1535129-1535132 | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1535129-1535132 | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1577162-1577163 | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1590186      | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1828826      | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1846735      | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1874395      | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1877051      | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1877051-607736 | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1877051-607736 | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1877055-607737 | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1877055-607737 | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
| 1899647      | chains [1 0 0] with [Pbl3]^- | 2,6-c net with stoichiometry (2-c)(6-c); 2-nodal net |
### Table A1. Cont.

| CSD Ref Code | Type of Chain | Topology of the Net * |
|--------------|---------------|-----------------------|
| 1902819      | chains [1 0 0] with [PbI$_3$]$^-$ | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1934897-1934902 | chains [1 0 0] with [PbI$_3$]$^-$ | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1934897-1934902 | chains [1 0 0] with [PbI$_3$]$^-$ | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1934902      | chains [1 0 0] with [PbI$_3$]$^-$ | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1944781      | chains [1 0 0] with [PbI$_3$]$^-$ | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1944784      | chains [1 0 0] with [PbI$_3$]$^-$ | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1944785      | chains [1 0 0] with [PbI$_3$]$^-$ | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 776895       | chains [1 0 1] with [PbI$_3$]$^-$ | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1483104      | chains [1 0 1] with [PbI$_3$]$^-$ | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1869657-1869658 | chains [1 0 1] with [PbI$_3$]$^-$ | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1869657-1869658 | chains [1 0 1] with [PbI$_3$]$^-$ | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 114129       | chains [1 1 1] with [PbI$_3$]$^-$ | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 734814       | chains [1 1 1] with [PbI$_3$]$^-$ | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 735413       | chains [1 1 1] with [PbI$_3$]$^-$ | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 745950       | chains [1 1 1] with [PbI$_3$]$^-$ | 2,6-c net with stoichiometry (2-c)3(6-c); 2-nodal net |
| 1400320      | chains [1 0 0] with [PbI$_3$]$^-$ | 2,6-c net with stoichiometry (1-c)(2-c)(3-c)(6-c); 4-nodal net |
| 1894399      | chains [1 0 0] with [PbI$_3$]$^-$ | 2,6-c net with stoichiometry (1-c)(2-c)(3-c)(6-c); 4-nodal net |
| 1968137      | chains [0 0 1] with [PbI$_3$]$^-$ | 1,2,3,6-c net with stoichiometry (1-c)(2-c)(3-c)(6-c); 4-nodal net |
| 1432454      | chains [1 0 0] with [PbI$_4$]$^{2-}$ | 1,2,6-c net with stoichiometry (1-c)2(2-c)2(6-c); 3-nodal net |
| 1846083      | chains [0 1 0] with [PbI$_4$]$^{2-}$ | 1,2,6-c net with stoichiometry (1-c)2(2-c)2(6-c); 3-nodal net |
| 1938185      | chains [0 0 1] with [PbI$_4$]$^{2-}$ | 1,2,6-c net with stoichiometry (1-c)2(2-c)2(6-c); 3-nodal net |
| 1307516      | chains [0 0 1] with [PbI$_5$]$^{3-}$ | 1,2,6-c net with stoichiometry (1-c)4(2-c)(6-c); 3-nodal net |
| 1429047      | chains [0 0 1] with [PbI$_5$]$^{3-}$ | 1,2,6-c net with stoichiometry (1-c)4(2-c)(6-c); 3-nodal net |
| 1910573      | chains [0 0 1] with [PbI$_5$]$^{3-}$ | 1,2,6-c net with stoichiometry (1-c)4(2-c)(6-c); 3-nodal net |
| 1860735-1861695 | chains [0 0 1] with [PbI$_5$]$^{3-}$ | 1,2,6-c net with stoichiometry (1-c)4(2-c)(6-c); 3-nodal net |
| 1860735-1861695 | chains [0 0 1] with [PbI$_5$]$^{3-}$ | 1,2,6-c net with stoichiometry (1-c)4(2-c)(6-c); 3-nodal net |
| 1860735-1861695 | chains [0 0 1] with [PbI$_5$]$^{3-}$ | 1,2,6-c net with stoichiometry (1-c)4(2-c)(6-c); 3-nodal net |
| 1048274      | chains [0 1 0] with [PbI$_5$]$^{3-}$ | 1,2,6-c net with stoichiometry (1-c)4(2-c)(6-c); 3-nodal net |
| 1505390      | chains [0 1 0] with [PbI$_5$]$^{3-}$ | 1,2,6-c net with stoichiometry (1-c)4(2-c)(6-c); 3-nodal net |

* Network stoichiometry means the number of different independent nodes in the net.

### Table A2. The geometrical distortions and calculated band gaps for hybrid perovskite-derived structures with [PbI$_5$]$^{3-}$ vertex-connected chains.

| Reference | Organic Cation                  | Distortion of Octahedra ($\Delta d$) | Distance between Chains, Å | Pb-Pb-Pb Angle, ° | Shortest I-I Distance in a Chain of Octahedra, Å | The Volume of the Organic Cation in the Structure, Å$^3$ | Calculated Band Gap, eV |
|-----------|--------------------------------|-------------------------------------|-----------------------------|-------------------|------------------------------------------------|-----------------------------------------------------|-------------------------|
| [28]      | piperazine-1,4-diium            | $7.27 \times 10^{-4}$               | 7.08                        | 83.127            | 4.16                                            | 179.94                                              | 2.15                    |
| [29]      | methylammonium, DMSO            | $5.72 \times 10^{-4}$               | 4.334                       | 173.73            | 4.614                                           | 120.36                                              | 2.26                    |
| [30]      | guanidinium                     | $2.48 \times 10^{-5}$               | 6.65                        | 180               | 6.36                                            | 112.99                                              | 2.01                    |
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