Topological phases are usually unreachable in molecular solids, which are characterized by weakly dispersed energy bands with a large gap, in contrast to topological materials. In this work, however, it is proposed that nontrivial electronic topology may ubiquitously emerge in a class of molecular crystals that contain interstitial electronic states, the bands of which are prone to be inverted with those of molecular orbitals. Guidelines are provided to hunt for such interstitial-electron-induced topological molecular crystals, especially in the topological insulating state. They exhibit a variety of exceptional qualities, as brought about by the intrinsic interplay of molecular crystals, interstitial electrons, and topological nature: 1) They may host cleavable surfaces along multiple orientations, with pronounced topological boundary states free from dangling bonds. 2) Strong response to moderate mechanical perturbations, whereby topological phase transition would occur under relatively low pressure. 3) Inherent high-efficiency thermoelectricity as jointly contributed by the non-parabolic band structure (therewith high thermopower), highly mobile interstitial electrons (high electrical conductivity), and soft phonons (small lattice thermal conductivity). 4) Ultralow work function owing to the active interstitial electrons. First-principles calculations are utilized to demonstrate these properties with the representative candidate K₄Ba₂[SnBi₄]. This work suggests a pathway of realizing topological phases in bulk molecular systems, which may advance the interdisciplinary research between topological and molecular materials.

1. Introduction

The peculiarity of molecular crystals lies in the building blocks, which are primarily discrete zero-dimensional (0D) molecules instead of isolated atoms, bound together by the comparatively weak noncovalent interactions (e.g., van der Waals bonding for neutral molecules, ionic bonding for charged molecules).[1,2] Quintessential examples include fullerides,[3] 0D halide perovskites,[4,5] and versatile organic crystals.[6] In comparison with atoms whose internal characteristics cannot be altered, molecules that are in essence tightly bonded atomic clusters, exhibit more diverse chemistry and higher flexibility through engineering the clusters at the bottom level, offering the promise of bottom-up materials design with customized functionalities.[3,6–8] The molecular crystals also motivate us to define the structural dimensionality of a solid if its primary building blocks are multi-atom substructures. Namely, molecular solids are considered 0D, and systems comprised of infinite chain-like motifs show one-dimensional (1D) character, and so forth.

The molecules typically have a closed electronic shell to reach the stability, which entails a wide gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).[7] Resulting from the small overlap of intersite wavefunctions as the molecules form a crystal, the band structure exhibits weak dispersions and therewith retains the large HOMO-LUMO gap (Figure 1a). Reflected in the real space, the electrons are fairly localized at each molecular site, as if constrained by the structural dimensionality. Such electronic structure is in stark contrast to that in topological materials, which have aroused paradigm renovations in condensed matter physics[9–12] and many other fields[13–15] over the last decade. A prerequisite of nontrivial electronic topology is gap closing or further reopening.[9,10] In this regard, molecular crystals tend to stand on the opposite side against topological materials,[9–12,16,17] which has restricted the realm of molecular materials from gaining consecutive profits through the recent bloom of topological physics. Indeed, the molecular crystals carrying nontrivial topology are very limited so far, and for some members the topological phases do not show up unless driven by external pressure in order to amplify the intersite interactions (e.g., α-(BEDT-TTF)₂I₃ at 1.5 GPa,[18] [Pd(dddT)₂] at 12.6 GPa[19]). Besides, most of
these molecular materials host graphene-type Dirac points\cite{18,19} or nodal lines,\cite{20} with the novel relativistic phenomena (e.g., spin-polarized boundary states, Rashba effect) absent.

In this article, however, we show that topological phases could universally arise in certain molecular crystals, given some electron orbitals located in interstitial regions. As discussed above, weak interactions between molecules are the main obstacle to topological nontriviality. To address this issue, herein the interstitial electrons, which are relatively unbound from nuclei, could work as a bridge, extensively overlapping with orbitals of surrounding molecules, and hence greatly enhancing the intersite hopping. The resulting dispersive band would narrow down or even close the gap (Figure 1b), through which the system may reach topological point- or line-nodal semimetal states. We take one step further to focus on systems containing heavy elements, so that the strong spin–orbit coupling (SOC) could mediate topological insulator (TI) phase. We also put forward rules of thumb to seek for such interstitial-electron-induced topological molecular crystals (ITMCs).

Intertwined with interstitial electrons and topological phases, molecular crystals may exhibit extraordinary properties. First, the ITMCs hold multiple dangling-bond-free surfaces, each of which allows the access to the topological surface states (TSS), because of the 0D character. For the same reason, they tend to show evident response to mechanical perturbations. An important consequence is, for example, that topological phase transition may be achieved under comparatively low pressure. Moreover, we see that interstitial orbitals enable the breakthrough of electronic dimensionality against the constraint imposed by the lattice. In other words, while the periodically aligned molecules remain localized and loosely coupled, the interstitial electrons could be extended throughout the crystal. As a result, ITMCs fulfill the “phonon-glass electron-crystal” criteria,\cite{21} intrinsically exhibiting high thermoelectric (TE) performance. Also due to the active interstitial electrons, the work function of ITMCs is generally lower than that of conventional TIs, enabling the doping of TSS to large-gap insulators or molecules and other promising applications.

In the following, we start with the introduction of interstitial orbitals to delineate the idea of ITMCs, and then describe how we can find candidate systems in materials databases. For clarity and concreteness, we use first-principles modeling to identify the existing material $K_{x}Ba_{y}[SnBi_{4}]$ as an ITMC candidate, and take it as the primary example to demonstrate the striking signatures of ITMCs. The same idea is applied to other candidates additionally.

2. Results

2.1. Interstitial-Electron-Induced Topological Molecular Crystals

Interstitial electrons are the hallmark of an unusual class of solids named electrides, where some excess electrons are confined within the interstitial space and stabilized by the surrounding cations, not attached to any atom, bond, or molecule.\cite{22–24} Since the interstitial orbital loosely interacts with nuclei, the corresponding band usually has a high energy and is thus distributed around the Fermi level ($E_F$). Furthermore, by virtue of the large spatial spread (s-orbital-like),\cite{25} the interstitial band is rendered a large width, capable of admixing the highest occupied and the lowest unoccupied states.\cite{18} Now provided the presence of interstitial orbitals in a molecular crystal, the gap is possible to be closed by the dispersive interstitial band (Figure 1b). The stability of interstitial electrons is accompanied by the surrounding cationic units, which could be positively charged molecules or intercalated ions. Finally, strong SOC may be obtained if heavy atoms sit beside the interstitial sites, since we concentrate on the relativistic topological states.

We draw two remarks before proceeding. First, one should differentiate the interstitial electrons from the ordinary overlap of adjacent atomic electrons, with the latter commonly seen in solids. In comparison, interstitial electrons are more independent and off the parent atoms, although it is difficult to draw an
absolute border line between these two concepts merely based on the density distribution. Exotic phenomena of electrides (e.g., high mobility and large nonlinear optical response)\cite{23} are a manifestation of the unicity of interstitial electrons. Ideally, contribution from interstitial orbitals to the electronic structure cannot be replaced by a superposition of atomic orbitals.\cite{27} See Section S1 (Supporting Information) for more details. Second, although we borrow the idea from electrides, ITMCs need not to be typically electrides, but are more a generalized form (see Section S1, Supporting Information). In addition, electrides are rarely found among bulk molecular solids. While some electrides have been proposed as a platform for topological materials recently,\cite{26} none of them consist of 0D molecular units to exhibit the unique qualities of ITMCs.

Based on the preceding analyses, we provide the following guidelines to seek for the ITMCs. 1) The target materials are mainly composed of discrete molecular units, and permissively additional intercalated ions; the latter could be indispensable to maintain the structural stability. 2) The lattice has vacancies envir- oned by cations with small electronegativity, which donate and stabilize interstitial electrons. 3) Heavy atoms are present and near the vacancies. Following the rules above, we concentrate on a few Zintl phase compounds as the ITMC candidates in this article. Zintl phases are a family of semiconductors where electropositive cations (generally alkali or alkaline earth cations) donate electrons to support the filled valence (e.g., following the octet rule, namely, eight electrons in the valence shell) of more electronegative elements.\cite{28,29} When the donated electrons are insufficient, the electronegative atoms would form polyanionic structures via covalent bonds in order to close the shell. These polyanions behave as molecular units if they are spatially local- ized. Here, we choose the polyanions constituted by Sn and Bi to be the molecular units. The heavy nucleus of Bi could offer strong relativistic effects; additionally, the large radius of its va- lence electron orbitals (6p) is conducive to intersite electron hopping compared to that of light elements. Next, we analyze the example material K$_4$Ba$_2$[SnBi$_4$].

### 2.2. Crystal and Electronic Structures of K$_4$Ba$_2$[SnBi$_4$]

The experimental synthesis of K$_4$Ba$_2$[SnBi$_4$] was reported in 2000.\cite{30} It crystallizes in a hexagonal lattice ($a = 11.395(2)$ Å and $c = 8.320(2)$ Å at ambient pressure), with the noncentrosymmetric space group $P6_3/mc$ (No. 186), as shown in Figure 2a. The primary structural motifs are discrete [SnBi$_4$]$^{8-}$ tetrahedra, located at the Wyckoff site 2b and oriented along the [0001] direction, separated by K$^+$ and Ba$^{2+}$ cations at Wyckoff sites 6c. The crystal thus shows the 0D character (see Section S2, Supporting Information, for comprehensive analyses) that we will echo and make use of frequently in the subsequent discussions. Importantly, the K$^+$ cations form a hollow at the edge of unit cell, extending along [0001], with a diameter $\approx$5.8 Å (the lower panel of Figure 2a), which provides sufficient space to accommodate possible inter- stitial electronic states.

We determine the electronic structure of K$_4$Ba$_2$[SnBi$_4$] by means of the density functional theory (DFT) with the Perdew–Burke–Ernzerhof (PBE) type functional;\cite{31} see Section 4 Experimental Section for details. Figure 2c depicts the nonrelativis- tic band structure, where the high-symmetry $k$ points are given in Figure 2b. Although dispersions of most bands are comparatively weak, in line with the 0D feature, we immediately notice a highly dispersive band around $E_F$, emanating from the inter- stitial orbital (see the orbital-resolved bands in Figure 2c) and mostly unoccupied. Only a tiny portion at the bottom of the interstitial band is below $E_F$ through inversion with the Bi 6p band (Figures 2e,f); the tiny occupation at the interstitial site indicates that the electron transfer from cations to polyanions is not complete, and therewith offers an opportunity of nontrivial topology in the electronic states. It is also noteworthy that the band structure near $E_F$ is dictated by the orbitals of [SnBi$_4$]$^{8-}$ and interstitial states (Figure 2c), while the inserted ions have negligible impact and merely play the role of preserving the electroneutrality and lattice stability, as molecular crystals ought to be.

To further demystify the signature of interstitial states, we construct Wannier functions\cite{32,33} of the atomic and interstitial orbitals. The interstitial orbital is shown to be centered at the hollow with a large spread (Figure 2g), as it should be. A tight-binding Hamiltonian built from these localized orbitals (Figure 2h) can immediately replicate the DFT band structure (Figure 2i). However, supposing that the interstitial states were absent from this crystal, as imitated by excluding the components related to the interstitial orbitals from the Hamiltonian (Figure 2h), the band edge would vanish substantially and leave a comparatively large gap ($\approx$0.5 eV), as unveiled by the solid green lines in Figure 2i. This simulation evidences the decisive role of interstitial states for the strong band dispersion and inversion in K$_4$Ba$_2$[SnBi$_4$].

At last, by including SOC in the calculations, we predict that K$_4$Ba$_2$[SnBi$_4$] is a strong TI with an intermediate gap (75.4 meV) around $\Gamma$ (Figure 2d). To avoid the false-positive prediction of TIs caused by the well-known gap underestimation in DFT,\cite{34} we provide the band structure at the level of the nonlocal Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional\cite{35} as reference (Figure 2d), that shows no critical disparity and preserves the odd Z$_g$ and a slightly larger gap (85.7 meV). Interestingly, the band gap of K$_4$Ba$_2$[SnBi$_4$] to our knowledge, tops all the noncentrosymmetric TIs hitherto known at ambient pressure within the level of DFT (see Section S3, Supporting Information), which may let the surface transport of K$_4$Ba$_2$[SnBi$_4$] fairly free from the bulk carrier disturbance and trigger a variety of applications.

### 2.3. Multiple Cleavable Surfaces

It is known that the gapless Dirac cone could be manifested on any surface of a strong TI in principle.\cite{9,10} In most realistic materials, nevertheless, the examination of such TSS is hindered by dangling bonds for some terminations (e.g., lateral cleavage of the layered TI Bi$_2$Te$_3$\cite{36,37}). On the contrary, by virtue of the noncovalent interactions between constituent molecules and ions, the ITMC K$_4$Ba$_2$[SnBi$_4$] can be cut along multiple surfaces, namely, [0001] and [1010], free from breaking the covalent bonds, as indicated in Figure 3a. Figure 3d,e displays the clean pronounced TSS on the (0001) and (1010) surfaces, respectively, as predicted by the Wannier function model. This is compatible with the DFT prediction (see Section S4, Supporting Information), which involves a more reasonable treatment of charge redistribution at the surface. We remark that the availability of
2.4. Pressure-Induced Topological Phase Transition

Molecular solids generally exhibit large compressibility owing to the absence of a global covalently bonded network. As a direct result, a different topological phase might appear under intermediate mechanical perturbations.\cite{12,39,40} We fully relax the crystal structure of K₄Ba₂[SnBi₄] at a series of increasing pressures within DFT, and monitor the Z₂ index if gapped. The gap opens at 2.3 and 2.5 GPa, but carrying an odd and an even Z₂, respectively (Figure 4a), indicative of topological phase transition midway. In common with the universal phase diagram for noncentrosymmetric TIs,\cite{12,39} a Weyl semim (WSM) phase is shown to lie in between the lower-pressure TI and the higher-pressure normal insulator (NI) states (Figure 4a). Figure 4b presents 6 pairs of Weyl points distributed on the k_y = 0 plane due to the time reversal and six-fold screw symmetries. Notice that the range of pressure for the WSM is within the interval of 2.3–2.5 GPa, which is a moderate condition and fairly accessible in the laboratory. We make a detour to mention that the isostructural compound K₄Ba₂[SnSb₄] (where Sb replaces Bi) is found to be an NI. Therefore, the phase transition can be realized also by doping Sb to K₄Ba₂[SnBi₄], just like the alloy Bi₁₋ₓSbₓ.\cite{41} In short, this system can be modulated into a WSM either under comparatively low pressure, or through chemical doping of Sb, suggesting the role of a single ITMC as a testbed of multiple topological phases.

2.5. Thermoelectricity

TE materials can realize energy conversion between heat and electricity,\cite{42} the capability of which is characterized by the dimensionless figure of merit, zT = σS²T/(νe + νl), where σ, S, T, κ_e, and κ_l represent the electrical conductivity, Seebeck

Figure 2. Crystal and electronic structures of K₄Ba₂[SnBi₄]. a) Front and top view of the unit cell of K₄Ba₂[SnBi₄]. The Wyckoff position 6c with the coordinate (0.517, 0.483, 0.226) is statistically filled by K⁺ (1/3) and Ba²⁺ (2/3), as indicated in the corresponding color. An extended hollow with a diameter of 5.8 Å is marked by a dashed orange circle. b) Brillouin zone of K₄Ba₂[SnBi₄], with the high-symmetry k points explicitly labeled. Two projected Brillouin zones along the a* and c* directions are indicated too. c) Orbital-resolved electronic band structure of K₄Ba₂[SnBi₄] in the absence of SOC, as predicted by the PBE pure functional within the DFT framework. The zero of energy is shifted to E_F. High-symmetry k points are given in (b). d) Electronic band structures of K₄Ba₂[SnBi₄] in the presence of SOC, as predicted by the PBE pure functional (solid black line) and by the HSE06 hybrid functional (dashed grey line), with the band gap 75.4 and 85.7 meV, respectively. e,f) Wave functions of the lowest unoccupied state (e) and the highest occupied state (f) at the Γ point with no SOC. They are dominated by the [SnBi₄]⁻⁻ orbitals and interstitial states, respectively. Their positions in the spectrum are labeled in (c). Yellow and light blue bubbles respectively stand for the positive and negative parts of the wave function. g) Wannier orbital of the interstitial state centered at the hollow in the absence of SOC, as plotted with (left panel) and without (right panel) the atoms. Yellow and light blue respectively denote the positive and negative parts of the orbital. h) Diagrammatic representation of the tight-binding Hamiltonian built from Wannier orbitals without SOC. The matrix components related to the atomic and interstitial orbitals are colored in green and orange, respectively. i) The band structures produced by the tight-binding Hamiltonian with (dashed orange line) and without (solid green line) the inclusion of interstitial orbitals. The zero of energy and high-symmetry k points are the same with those in (c).

cleavage along multiple directions is of even greater importance if the ITMC is a weak TI, in which case the TSS appear only on a certain surface.\cite{9,10,18}
The best-performance room-temperature TE materials were found to be $\text{Bi}_2\text{Te}_3$, with the maximal $S$-type doping $(a)$ at 300 K, $\sigma_{zz}$ prominently exceeds $\sigma_{xx}$ overall. Therefore, the cooccurrence of high $S$ and high $\sigma$, which have conflicting requirements to band dispersions, can be successfully achieved in ITMCs. In addition, being a molecular crystal, $\text{K}_4\text{Ba}_2[\text{SnBi}_4]$ bears a structural complexity that can trap heat, akin to the other Zintl compounds for thermoelectrics. The loosely coupled heavy $[\text{SnBi}_4]^{18-}$ clusters and intercalated ions result in soft phonons, namely, low-velocity acoustic modes and low-lying optical modes that govern the phonon-phonon scattering (Figure 5e), whereby $\kappa_1$ can be drastically suppressed. Indeed, by calculating anharmonic phonons (see Section 4 Experimental Section), we evaluate $\kappa_1$ of $\text{K}_4\text{Ba}_2[\text{SnBi}_4]$ to be $\sim W \cdot m^{-1} \cdot K^{-1}$ at 300 K (Figure 5f), even lower than that of $\text{Bi}_2\text{Te}_3$ (with in-plane and out-of-plane components 1.2 and 0.4 $W \cdot m^{-1} \cdot K^{-1}$ respectively); also notice the high isotropy of the low $\kappa_1$ in $\text{K}_4\text{Ba}_2[\text{SnBi}_4]$ relative to that in the layered $\text{Bi}_2\text{Te}_3$, which again justifies the 0D nature of $\text{K}_4\text{Ba}_2[\text{SnBi}_4]$ from the viewpoint of phonons. Hence, we conclude that while the phonons behave as being trapped, the electrons remain mobile across the crystal by means of the comparatively independent interstitial electrons, giving birth to the distinguishing “phonon-glass electron-crystal” behavior for ITMCs. Moreover, the linearized TSS that are robust against backscattering can further enhance $zT$ if thin films are exploited. In short, the triple identity (i.e., TIs, generalized form of electrides, and molecular crystals) could endow ITMCs with an inherent state-of-the-art TE performance.

2.6. Work Function

The knowledge of work function is crucial to heterostructures, with the mismatch between the contact systems dominating the interface properties through the electron transfer, band bending, etc. In the ITMCs, the work function is routinely small due to the active interstitial electrons. As an example, the work function of $\text{K}_4\text{Ba}_2[\text{SnBi}_4]$ for the (1010) surface is calculated to be 2.2 eV in the presence of SOC (see Section S5, Supporting Information), akin to alkali metals, which is unprecedented in TIs so far (e.g., the work function of $\text{Bi}_2\text{Te}_3$ is $\approx 5.3$ eV on the contrary). Consequently, the helical surface Dirac carries could easily transfer to the contact system by constructing heterostructures (see Section S6, Supporting Information). We propose a promising application in catalysis. TSS have been shown to have the potential of boosting certain chemical reactions by serving as an electron bath. Here the ITMCs, further equipped with a low work function, are expected to activate very inert molecules that has a shallow LUMO, thus being prospective high-efficiency catalysts.

2.7. Other Candidate Systems

We briefly present another $[\text{Sn}, \text{Bi}]-\text{polyanion-based ITMC, K}_{10}[\text{Sn}_2\text{Bi}_4]$.

$\text{K}_{10}[\text{Sn}_2\text{Bi}_4]$ forms in a monoclinic lattice (space group $P2_1/c$, No. 14), the unit cell of $\text{K}_{10}[\text{Sn}_2\text{Bi}_4]$ contains two discrete

Figure 3. Cleavage and surface states of $\text{K}_4\text{Ba}_2[\text{SnBi}_4]$. a) Dangling-bond-free surfaces of $\text{K}_4\text{Ba}_2[\text{SnBi}_4]$, as indicated by black arrows and green ticks. b,c) Slabs of $\text{K}_4\text{Ba}_2[\text{SnBi}_4]$ terminated with the (0001) surface (b) and (1010) surface (c). d,e) Momentum-resolved density of states of a semi-infinite (0001) slab (d) and (1010) slab (e) predicted based on the Wannier functions with SOC.
Figure 4. Different topological phases in $K_4Ba_2[SnBi_4]$. a) TI-WSM-NI phase transition in $K_4Ba_2[SnBi_4]$ with the increasing external pressure. Momentum-resolved density of states of a semi-infinite (0001) slab (upper panel) with a schematic bulk band structure (lower panel) is depicted for each phase. The WSM phase arises within the range of 2.3–2.5 GPa. b) Distribution of the Weyl points for the WSM phase. The chirality of each Weyl point is indicated.

Figure 5. Thermoelectricity of $K_4Ba_2[SnBi_4]$. a) Band structure of $K_4Ba_2[SnBi_4]$ with SOC in the vicinity of the $\Gamma$ point, which is calculated with the HSE06 functional. This figure is a magnified view of Figure 2d. b) Isoenergy surface centered at the $\Gamma$ point, with the corresponding energy marked in (a). The size is exaggerated for easy visualization. c) Seebeck coefficient $S$ of $K_4Ba_2[SnBi_4]$ versus the carrier concentration $n_c$ at 300 K. Both $p$-type and $n$-type doping are plotted. The dashed grey lines indicate the threshold of $|S| = 156 \mu V K^{-1}$. d) Electrical conductivity $\sigma$ against $n_c$ at 300 K. $\sigma$ is evaluated in the unit of the scattering time $\tau$ under the constant scattering time approximation. Only $p$-type doping is shown. e) Phononic band structure (left panel) and frequency-resolved lattice thermal conductivity (right panel). High-symmetry $k$ points are given in Figure 2b. For the spectrum of $\kappa_l$ (right panel), the $z$ component is shown alone. Note that the frequencies of the low-lying optical modes, which produce scattering via anharmonic coupling with acoustic modes, are merely $\approx 30$ cm$^{-1}$. f) Lattice thermal conductivity $\kappa_l$ versus the temperature, based on the calculation of anharmonic phonons.
Figure 6. Other ITMC systems. a,b) Crystal structure of K$_{10}$[Sn$_2$Bi$_6$] (a) and K$_3$Na$_2$[SnBi$_3$] (b) together with their wave functions of the lowest unoccupied state (upper panel) and highest occupied state (lower panel) at the Γ point with no SOC. The corresponding position in the spectrum is also marked in (c) or (d). Yellow and light blue bubbles represent the positive and negative components of the wave function, respectively. c,d) Electronic band structure of K$_{10}$[Sn$_2$Bi$_6$] (c) and K$_3$Na$_2$[SnBi$_3$] (d) in the absence of SOC. The energy is measured from the Fermi level. e,f) Band structure of K$_{10}$[Sn$_2$Bi$_6$] (e) and K$_3$Na$_2$[SnBi$_3$] (f) with SOC. The HSE06 result is offered in addition to the PBE. Note that the band structure in (d) or (f) is based on the primitive cell (not shown) of K$_3$Na$_2$[SnBi$_3$], while (b) presents the conventional cell.

We also show the application of the ITMC idea to 1D crystals, which is quite straightforward. K$_3$Na$_2$[SnBi$_3$] (space group Iba$ar{a}$, No. 73) is a 1D Zintl material with the [Sn$_3$Bi$_6$]$^{10-}$ chain extending along the [100] direction (Figure 6b). The intercalation of K$^+$ and Na$^+$ ions provides excess electrons at interstitial spaces (light blue bubbles in the upper panel of Figure 6b). Consequently, band inversion arises at Γ, between a molecular orbital and the interstitial state (Figures 6d,f), resulting in a strong TI phase, as supported by either a pure or a hybrid functional calculation, notwithstanding a small indirect gap (<10 meV). Cleavage or strain on the surfaces (010) and (001) is available, though the operation on the (100) surface is obstructed by the [Sn$_3$Bi$_6$]$^{10-}$ chain. We find that the work function along the (010) surface is as low as 2.1 eV.

3. Conclusions and Discussion

We have elucidated the concept of ITMCs based on first-principles calculations, and demonstrated their remarkable properties as a result of the characteristic unification of molecular crystals, interstitial states, and topological phases, namely, multiple dangling-bond-free surfaces, topological phase transition under moderate mechanical perturbations, high-performance thermoelectricity, and ultralow work function. The discussed phenomena and applications are within current experimental reach.

We address more comments on molecular crystals to highlight their superiority in terms of materials design. As initially noted in Section 1, molecular crystals stand out owing to molecules as building blocks. Indeed, the individual molecules, if stably existing when extracted from the bulk, can exhibit physical and chemical properties akin to or even beyond elements in the periodic table, like the superhalogenic nature with an extremely shallow LUMO (e.g., NO$_3^{-}$). In this context, such atomic clusters are particularly dubbed superatoms, to emphasize the crucial fact that they may mimic atoms. Bulk solids built from superatoms show more versatile features as inherited from these clusters, than those with purely atomic components. Furthermore, unlike atoms with fixed attributes, the characters of a superatom may be precisely tuned by engineering the cluster (e.g., adding, removing, or replacing a single atom). Hence, materials hierarchically assembled from superatoms allow tailored properties and functionalities, like lattice constants and band gap.

Interstitial states are key to the topological phases of ITMCs, the mechanism of which can be heuristically understood from...
the gap closing due to the dispersive interstitial band, as elaborated in Sections 1 and 2.1. Indeed, we can gain deeper insight by focusing on real space. The ordinary molecular crystals, with each molecular orbital exponentially localized at the site, can be adiabatically connected to the atomic limit (more technically, the obstructed atomic limit\cite{51}), where the the molecular units are at infinite separation. Consequently, molecular crystals are topologically trivial in general. With electron orbitals located at vacancies, however, the system is naturally driven away from the atomic limit\cite{26,27} leading to a high propensity for nontrivial topology.

Now, it is natural to emphasize that the character of being a molecular crystal stands on the foremost position for the novelty of ITMCs, which is indispensable for their diverse prominent features, and for the promise of tailoring the functions of the materials as assembled from molecules. Then followed by the participation of interstitial electrons that are tightly connected with topological phases, the systems become distinguishing from normal molecular solids. This is the vital logic lying in the name ITMC. Therefore, ITMCs are immediately differentiated from other families whose main components are not discrete molecular units, such as ionic solids comprised of isolated atoms alone, metals with globally delocalized bondings, and crystals with extended networks of covalent bonds. As an example, some 1D solids were reported to hold topological band structure, such as \( A\{\text{MoX}\}_3 \) (\( A = \text{Na, K, Rb, In, TI}; \ X = \text{S, Se, Te} \))\cite{54} \( \text{Bi}_2 \text{I}_{10} \)\cite{38,55} and \( \{\text{TaSe}_3\}_2 \)\cite{56}. But they lose some degrees of freedom and flexibility as hindered by infinite chains compared to molecular solids that show the 0D nature. On top of that, the energy bands originating from the extended covalent bonds can be easily dispersed, and importantly contribute to the topological band structure of these 1D systems.\cite{54,56} In particular, networks of hypervalent bonding, a type of electron-rich multicontiner bonding beyond the octet rule.\cite{57} are characteristic of folded half-filled bands, and there with show high tendency towards band crossing or inversion.\cite{58} In contrast, for molecular solids, due to the lack of any global covalent network, alternative ways to nontrivial band topology are desired—this is the very moment at which interstitial states come in handy.

Although we have chosen to demonstrate the idea and superiority of ITMCs as realized in the selected Zintl compounds in this work, the signatures of ITMCs are distinctive from those that are of substantial study for the general Zintl family. For instance, in spite of topological phases predicted in a couple of Zintl compounds with polyanions, the polyanionic frameworks are two-dimensional (2D) sheets (e.g., \( \text{AlN}_2 \text{As}_2 \) with \( A = \text{Ca, Sr, Eu} \))\cite{59} or 1D chains (e.g., \( \text{Eu}_2 \text{In}_3 \text{Bi}_2 \))\cite{60}, with isolated anionic clusters not reported yet. They are distinct from ITMCs just like the 1D topological materials as discussed above. It is widely known that Zintl materials are also considered suitable for thermo-electrics, since they tend to exhibit the “phonon-glass electron-crystal” behavior.\cite{28,29} Nonetheless, the “electron-crystal” electronic structure commonly relies on the global structural motifs of covalent bonds (i.e., 1D or 2D polyanions),\cite{28} despite the fact that the weak coupling of polyanions produces the “phonon-glass” character in the same way with ITMCs. The electronic and phononic transports are thus more interdependent. In ITMCs, on the contrary, interstitial electrons and molecular units, that are loosely bound to each other, may work as relatively independent components, govern the electrical mobility and lattice thermal conductivity more separately, further enabling a large \( \sigma \) while preserving a small \( \kappa \). Besides, the interstitial electrons provide one additional tunable parameter for the molecular materials design, which may be controlled by engineering the confinement geometry via strain or substitution of atoms.

Following the searching guidelines as summarized in Section 2.1, more ITMC candidates can be picked out from materials databases (possibly in conjunction with high-throughput techniques\cite{61}), or even artificially designed, which remains to be an open question. For example, a variety of Bi clusters\cite{62} can take the role of polyanions in order for strong SOC; the option of anions is even broader if the relativistic topological states are not of particular interest. Other than isolated atoms, alkali superatomons (e.g., \( K_4 \text{O} \))\cite{61}, the properties of which can be flexibly controlled, also have the potential to provide and stabilize the interstitial electrons on account of their ultra small electronegativity. Compared to atomic cations, they may enlarge the spacings and reduce interactions between molecules, so that the solid maintains more of the molecular character. Our results suggest that some long-known molecular solids would recapture attention once recognized as ITMCs, meanwhile the well-established theories and technologies in the community of molecular crystals (e.g., flexible bottom-up materials design\cite{3,6,8}) might enable functionality tailoring for topological materials.

4. Experimental Section

DFT Calculations: The DFT calculations of the ITMC candidate materials were performed based on the projector augmented wave scheme\cite{64} as implemented in the Vienna ab initio simulation package (VASP).\cite{65} For static calculations (i.e., self-consistent electronic relaxation, band structure, etc.), the exchange-correlation functional was employed, given by the generalized gradient approximation (GGA) with the PBE parametrization.\cite{31} The nonlocal HSE06 hybrid functional\cite{35} was supplemented for the check of band topology at ambient pressure. The energy cutoff of the plane wave was chosen as 30% above the maximum value recommended in the pseudopotential library. The Brillouin zones were sampled by a \( \Gamma \)-centered grid with the resolution of \( 2\pi \times 0.024 \text{ Å}^{-1} \) such that not only the total energy but also the bandgap were converged (see Section S7, Supporting Information). The PBEsol\cite{66} instead of PBE parametrization was applied for the lattice relaxation, since the former could reproduce the lattice constants closer to the experimental values at ambient pressure (the lattice constants predicted by PBEsol were \( a = 11.379 \text{ Å}, c = 8.282 \text{ Å} \), and by PBE were \( a = 11.555 \text{ Å}, c = 8.519 \text{ Å} \), while recalling that the experimental values were \( a = 11.395(2) \text{ Å}, c = 8.320(2) \text{ Å} \). The internal coordinates of all atoms were fully relaxed with a force criterion of 0.01 eV Å\(^{-1}\). Since the molecules of candidate ITMCs were not neutral but charged (e.g., \( [\text{SnBi}_3]^– \)), ionic bonding governs the intermolecular interactions. As a result, van der Waals forces, that were comparatively much weaker, were not included in the calculations. Indeed, the empirical dispersion correction to DFT (i.e., DFT-D)\cite{67,68} was tested for \( K_4 \text{Ba}_2[\text{SnBi}_4] \), which showed no further improvements, and produced identical band structure and gap to those without DFT-D. Pre/post-processing tools and utilities\cite{61,69–74} were used to aid the calculations.

Virtual crystal approximation (VCA)\cite{75,76} was exploited for the fractionally occupied Wyckoff position \( 6c \) (0.517, 0.483, 0.226) in \( K_4 \text{Ba}_2[\text{SnBi}_4] \), with the ratios of \( K \) and \( Ba \) being 1/3 and 2/3, respectively, in the pseudopotential, since they possessed similar ionic radii (\( K^+: 1.33 \text{ Å}, Ba^+: 1.35 \text{ Å} \)) and electronic shells. The VCA was further validated by combinations of other pairs of alkali and alkaline earth elements. Namely, The band structure was also calculated using the mixing \( \text{Rb}-\text{Rb}, \text{Rb}-\text{Ba}, \text{Cs}-\text{Sr}, \) and \( \text{Cs}-\text{Ba} \) to approximate the mixed atom, in addition to \( K-\text{Ba} \). In all cases, the bands near \( E_F \) remained almost unaffected either with or without SOC (see Section S8, Supporting Information). This is consistent with the fact
that the intercalated ions show negligible influence on the electronic structure around \( E_F \) (as pointed out in Section 2.2), indicative of the expedient exemption from more sophisticated treatments (e.g., special quasirandom structures[77] or coherent potential approximation[78,79]) for the fractional occupation.

To assess the weight of interstitial orbitals in Bloch states in \( K_4 Ba_2 [S n B i_4] \) and to get a hint on the electronic edge, its sufficed to use a pure functional [82] and to take into account the contribution from interstitial states.

**Wannier Functions and Band Topology:** Wannier functions were built via the code Wannier90[32,13,80]. The maximal localization procedure was not applied, and a post-processing symmetrization[81] was conducted, so that the Wannier functions could respect the symmetries of the crystal and atomic orbitals, which was crucial to high-quality band interpolation and surface state prediction. The projection operators for \( K_4 Ba_2 [S n B i_4] \) were chosen as interstitial \( s\), \( S n\) sp³, \( B i\) \( p\), and mixed-atom \( d\) orbitals; the \( d\) orbital was selected because of the bottom of the corresponding band was entangled with the top of \( B i\) \( p\) band (Figure 2c), albeit with a small overlap. The \( Z_2\) invariants were evaluated through Wannier charge centers occupied the occupied bands.[82] The chirality of Weyl points was computed by integrating the Berry flux over a surface enclosing the Weyl point.[11,12] Both calculations (\( Z_2\) and chirality) were performed based on the Wannier tight-binding Hamiltonian as implemented in the WannierTools package.[83]

**Surface States:** The iterative Green’s function method[84] was utilized to compute the (1010) and (0001) surface states of \( K_4 Ba_2 [S n B i_4] \), by constructing a semi-infinite slab on the basis of Wannier functions. The calculation was conducted with WannierTools. Note that it might needed to shift the positions of all Wannier functions in order to keep the \([S n B i_4]^8–\) tetrahedron as an entirety inside a unit cell, otherwise the Sn-Bi covalent bond would be cut and thus produced trivial surface states.

To take the charge redistribution at the surface into account, a DFT calculation was also performed for an 8-layer (1010) slab (thickness \( \approx 79\) Å) in the presence of SOC. A vacuum (20 Å) was adopted, so that the vacuum level was tested to converge. The outermost \( K^+ / B a^2+\) ions and \([S n B i_4]^8–\) tetrahedra were relaxed; no significant improvement in the band structure can be seen if relaxing more atoms in the deeper layers.

**Thermoelectricity:** The Seebeck coefficient \( S\) and electrical conductivity \( \sigma\) were assessed in the framework of Boltzmann transport theory under the rigid band picture, with the help of BoltzmannWann modul[85] in Wannier90. The constant scattering time approximation was adopted, so that the scattering time \( \tau\) (that was unknown for \( K_4 Ba_2 [S n B i_4] \), not measured in experiment yet and highly intricate to computationally estimate) could be extracted from \( S\) and canceled in the expression of \( S[86]\). \( \sigma\) was estimated in the unit of \( \Omega^{-1}\). The Wannier functions were obtained from the DFT results with SOC, under the HSE06 hybrid functional, since the hybrid functional was believed to describe the band edge more accurately in general, which was crucial to thermoelectrics.[42] A 50 \( \times \) 50 \( \times \) 50 fine \( k\)-grid was used.

To characterize the phononic transport properties of \( K_4 Ba_2 [S n B i_4] \), the authors switched from VASP to the QUANTUM ESPRESSO package[86,87] because computing interatomic force constants within the VCA was not supported in VASP. Since the lattice dynamics was relatively insensitive to the details of the electronic band edge, it sufficed to use a pure functional (PBEsol) instead of the expensive hybrid functional (HSE06). The PBEsol pseudopotentials from pa1library[88] were applied. SOC had small impact on the lattice dynamics and was ignored to save the computational cost. The atomic coordinates were further relaxed with a force criterion of 0.1 meV Å⁻¹. A 1 \( \times \) 1 \( \times \) 2 supercell was built for the evaluations of phononic spectrum and lattice thermal conductivity \( k_\parallel\), since the lattice constants \( a\) and \( b\) were already quite large and over 10 Å. In particular, anharmonic phonons were computed to access \( k_\parallel\), through the Boltzmann transport theory for phonons under the scattering time approximation, namely,

\[
\kappa_\parallel(T) = \frac{1}{V N_q} \sum_{q_j} \langle v_\parallel(T) n_j \rangle \otimes \langle v_\parallel(T) n_j \rangle
\]

Here \( T\) denotes the temperature, \( q\) the wave vector, \( j\) the polarization, \( V\) the unit cell volume, \( N_q\) the number of \( q\) points, \( c_{\parallel q} = h c_{\parallel q} / k_B T\), with \( \omega_{\parallel q}\) the phonon frequency and \( n_{\parallel q}\) the occupation number, \( k_\parallel\) the phonon velocity, and \( \tau_{\parallel q}\) the phonon lifetime. The anharmonic interatomic force constants were computed up to the spacings \( \approx 10\) Å. The calculations of \( k_\parallel\) were done through the code ALAMODE[89] sampled on a \( 12 \times 12 \times 12\) fine \( q\)-grid.

**Work Function:** A slab along a given direction was constructed, and the Fermi energy \( (E_{\text{F,slab}})\) as well as the vacuum potential energy \( (\phi_{\text{vac}})\) outside the material under the formalism of DFT was calculated. The work function \( (w)\) for the corresponding surface is thus expressed as \( W = \phi_{\text{vac}} - E_{\text{F,slab}}\).[90] Since the bulk was insulating but the surface was metallic in TIs, \( E_{\text{F,slab}}\) was determined directly through the slab calculation, instead of deriving it from the bulk. In fact, the latter value, which was obtained by shifting the bulk Fermi level \( (E_{\text{F, bulk}})\) to align the averaged Hartree potential of the slab middle layers with that of the bulk,[91] was tested to be almost equal to the former, within the range of the bandgap (i.e., a few 10 meV).

The 8-layer (1010) slab of \( K_4 Ba_2 [S n B i_4] \) relaxed in the same way as in the surface state calculation was adopted. SOC was switched on. For \( K_4 [S n B i_2]\) and \( K_4 N a_2 [S n B i_4]\), a 6-layer (100) slab and a 6-layer (010) slab were built, respectively. The thickness of the vacuum was 20 Å in both cases. The outermost ions and molecular units were relaxed.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available in the supplementary material of this article.

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first-principles calculations, interstitial electrons, molecular crystals, thermoelectrics, topological materials, zintl phases

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