Relativistic topological molecular crystals

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Topological phases usually are difficult to realize in molecular solids because the intermolecular interactions are in general too weak to mediate band inversion. In this work, however, we propose that nontrivial electronic topology may ubiquitously emerge in a class of molecular crystals that contain interstitial electron orbitals and heavy elements, whereby spin-orbit coupling drives band inversion between the interstitial and the molecular orbitals. We provide guidelines to hunt for such relativistic topological molecular crystals, and utilize first-principles calculations to illustrate the extraordinary characteristics of the representative candidate K$_2$[SnBi$_4$]: (1) It hosts cleavable surfaces along multiple orientations, with pronounced topological boundary states free from dangling bonds. (2) Strong response to external pressure or strain, whereby topological phase transition may occur under relatively low pressure. (3) High-efficiency thermoelectricity, with the Seebeck coefficient as high as 240 $\mu$VK$^{-1}$, and the lattice thermal conductivity around 0.22 - 0.23 Wm$^{-1}$K$^{-1}$ at 300 K. (4) Ultralow work function (2.2 eV) caused by the active interstitial orbitals. Our work suggests a pathway of realizing topological phases in molecular materials.

The peculiarity of molecular crystals lies in the constituent units, which are mainly discrete molecules instead of atoms, bound together by the relatively weak noncovalent forces (e.g., van der Waals bonding for neutral molecules, ionic bonding for charged molecules) \cite{1,2}. The molecular behavior of crystals would become significant, especially in the case that the dimensionality of molecules is down to zero [which renders the crystal quasi-zero dimensionality (quasi-0D)]. Quintessential examples include fullerides \cite{3}, metal-halide perovskites of quasi-0D \cite{4}, and versatile organic crystals.

Over the last decade, the topology embedded in quantum-mechanical wave functions has aroused paradigm renovations in condensed matter physics \cite{5-9} and many other fields \cite{10-12}. However, in molecular crystals, particularly those of quasi-0D, the band structure is widely gapped and dispersionless because of the weak electron hopping among molecules, obstructing any possible band touching (Fig. 1a). Thus, molecular crystals of quasi-0D are typically topologically trivial, akin to the ordinary atomic insulators \cite{13}, which has restricted the realm of molecular materials in regards to gaining consecutive profits from the recent bloom of topological physics. Indeed, only a limited number of quasi-low-dimensional molecular crystals with nontrivial band topology have been reported, and for some members the topological phases are manifested only when driven by external pressure (e.g., $\alpha$-(BEDT-TTF)$_2$I$_3$ at 1.5 GPa \cite{14}, [Pd(dddt)$_2$] at 12.6 GPa \cite{15}). Besides, most of these molecular materials host graphene-type Dirac points \cite{14,15} or nodal lines \cite{16}, restricted to nonrelativistic origins. Intriguing qualities induced by spin-orbit coupling (SOC), such as chiral spin textures, spin-polarized boundary states \cite{5,6} and the Rashba effect \cite{17}, are absent. Even in Bi-rich systems \cite{18}, relativistic topological nature is rarely found for those composed of isolated building blocks, since SOC solely is far insufficient in front of the large gap.

In this Article, however, we show that topological phases could universally arise in certain molecular crystals, given the existence of electron orbitals that are located in interstitial regions. The interstitial electrons work as a bridge, extensively overlapping with orbitals of surrounding molecules, so that the intersite hopping and hence the band dispersions are greatly enhanced, giving rise to possible band touching or inversion (Fig. 1b). We put forward rules of thumb to seek for the molecular crystals that are likely to host interstitial states. The systems containing heavy elements are the primary interest, by which the strong relativistic effects and resultant phenomena like the topological insulator (TI) phase can be mediated, since the gap is exceedingly squeezed via interstitial states. The combination of molecular crystals with interstitial electrons and topological nature would engender exceptional properties. We dub such sort of molecular solids as relativistic topological molecular crystals (RTMCs).

In the following, we start with the introduction of interstitial orbitals to delineate the idea of RTMCs, and then describe how we can find candidate systems in ma-
Interstitial electrons are the hallmark of an unusual class of solids named electrides, where some excess electrons detach from atomic orbitals, confined within the interstitial space and stabilized by the surrounding cations \[19–21\]. Since electrons in the interstitial orbital loosely interact with the nuclei, the corresponding band usually has a high energy and is thus distributed around the Fermi level \(E_F\). Further, by virtue of the large spatial spread \(s\text{-orbital-like}\) \[22\], the interstitial band is rendered a large width, capable of admixing the highest occupied and the lowest unoccupied states \[23\]. Now provided the presence of interstitial orbitals in a molecular crystal, the valence and conduction bands could touch and hybridize through the dispersive interstitial band (Fig. 1b). The stability of interstitial electrons is accompanied by the surrounding cationic units, which could be positively charged molecules or intercalated ions. Finally, the relativistic topological effects may be obtained if heavy atoms sit beside the interstitial sites. As discussed later, the electronic behavior of the RTMCs may resemble that of electrides due to the interstitial states, since they can be categorized as a generalized form of electrides \[20\]. Although we aim to find materials that intrinsically host interstitial orbitals and heavy atoms throughout this work, it is possible to modify a given molecular crystal into an RTMC by virtue of the well-developed molecular engineering \[3\] (e.g., removing certain molecules to create interstitial space), which remains open to be explored.

Based on the preceding analyses, we provide the following guidelines to seek for the RTMCs. (1) The target materials are mainly composed of discrete molecular blocks, and permissively additional intercalated ions; the latter could be indispensable to maintain the structural stability. (2) The lattice has void regions enrobed by cations that produce and stabilize the excess electrons. (3) Atoms with a large atomic number are present and near the void region. Following the rules above, we concentrate on a handful of Zintl phase compounds as the RTMC candidates in this Article. Zintl phases are a family of intermetallic compounds where electronegative cations donate electrons to support the formation of covalently bonded polyanions that consist of more electronegative elements \[24\]. Albeit seldom studied by the molecular materials community, they essentially match the characteristics of molecular crystals as elaborated in the beginning part. Once the cations surround the interstitial space, the detached electrons are likely to reside there. We herein choose the polyanions constituted by Sn and Bi to be the isolated molecular structures; the heavy Bi can guarantee strong relativistic effects. Next, we analyze the example material \(K_4\)\(Ba_2[SnBi_4]\).

### 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 \[25\]. It crystallizes in a hexagonal lattice \((a = 11.395(2)\ \text{Å} \text{ and } c = 8.320(2)\ \text{Å} \text{ at ambient pressure})\), with the noncentrosymmetric space group \(P6_3mc\) (No. 186), as shown in Fig. 2a. This compound consists of discrete molecular clusters, the \([SnBi_4]^8−\) tetrahedra, separated by inserted ions, \(K^+\) and \(Ba^{2+}\), showing quasi-0D; see Supplementary Section A for the analysis of its identity as a molecular crystal. Importantly, the \(K^+\) cations form a hollow at the center of the hexagon, with a diameter about 5.8 \(\text{Å}\), extending along [0001] (the lower panel of Fig. 2a), which provides sufficient space for...
to accommodate possible excess electrons.

We determine the electronic structure of $K_4Ba_2[SnBi_4]$ by means of the density functional theory (DFT) with the Perdew-Burke-Ernzerhof (PBE) type functional [26]; see Methods for details. Figure 2c depicts the nonrelativistic band structure, where the high-symmetry $k$ points are given in Fig. 2b. Although most bands are rather flat, in line with the quasi-0D nature, we immediately notice that two bands around the $\Gamma$ point highly disperse and even invert in the vicinity of $E_F$. These two inverted bands mainly emanate from the Bi $p$ orbitals and interstitial states at the hollow, as seen through the local orbital weights in the Bloch states (Fig. 2c), also supported by the visualization of wave functions at $\Gamma$ (Figs. 2e and 2f). The interstitial states enhance the intermolecular hopping and lead to band inversion in $K_4Ba_2[SnBi_4]$ as expected. It is noteworthy that the band structure near $E_F$ is dictated by the orbitals of the molecular cluster $[SnBi_4]^{8-}$ and interstitial states (Fig. 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 character of interstitial states, we construct Wannier functions [27] of the atomic and interstitial orbitals. The interstitial orbital is shown to be $\mathbf{K}^+$ and even invert in the vicinity of $E_F$. These two inverted bands around the $\Gamma$ point highly disperse and even invert in the vicinity of $E_F$. These two inverted bands mainly emanate from the Bi $p$ orbitals and interstitial states at the hollow, as seen through the local orbital weights in the Bloch states (Fig. 2c), also supported by the visualization of wave functions at $\Gamma$ (Figs. 2e and 2f). The interstitial states enhance the intermolecular hopping and lead to band inversion in $K_4Ba_2[SnBi_4]$ as expected. It is noteworthy that the band structure near $E_F$ is dictated by the orbitals of the molecular cluster $[SnBi_4]^{8-}$ and interstitial states (Fig. 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.

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In most realistic materials, nevertheless, the examination of such topological surface states (TSS) is hindered by dangling bonds on some surfaces (e.g., lateral cleavage of the layered TI Bi₂Te₃ [29, 30]). On the contrary, by virtue of the noncovalent interactions between constituent molecules and ions, the RTMC K₄Ba₂[SnBi₄] can be cut along multiple surfaces, namely, (0001) and (1010), free from breaking the covalent bonds, as indicated in Fig. 3a. Figures 3d and 3e display 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 the Supplementary Section C), which involves a more reasonable treatment of charge redistribution at the surface. We remark that the availability of cleavage along multiple directions is of even greater importance if the RTMC is a weak TI, in which case the TSS appear only on a certain surface [5, 6, 31].

**Pressure-induced topological phase transition**

Molecular solids generally exhibit large compressibility owing to the absence of an extended covalent network. As a direct result, a new topological phase might appear under relatively small mechanical perturbations [9, 32, 33]. 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 GPa and 2.5 GPa, but carrying an odd and an even Z₂, respectively (Fig. 4a), indicative of topological phase transition midway. In common with the universal phase diagram for noncentrosymmetric TIs [9, 32], a Weyl semimetal (WSM) phase is shown to lie in between the low-pressure TI and the high-pressure normal insulator (NI) states (Fig. 4a). Figure 4b presents 6 pairs of Weyl points distributed on the k_z = 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 an intermediate condition and rather 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 [34]. 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 RTMC as a testbed of multiple topological phases.

**Thermoelectricity**

Thermoelectric (TE) materials can realize energy conversion between heat and electricity [35], the capability of which is characterized by the dimensionless figure of merit, $zT = \sigma S^2 T / (\kappa_e + \kappa_l)$, where $\sigma$, $S$, $T$, $\kappa_e$, and $\kappa_l$ represent the electrical conductivity, Seebeck coefficient, absolute temperature, electronic and lattice component of the thermal conductivity, respectively. Just like many TIs (e.g., Bi₂Te₃, one of the best-performance room-temperature TE materials) [30, 35–37], K₄Ba₂[SnBi₄] exhibits the potential of extraordinary TE efficiency, considering the fact that the SOC-induced non-parabolic dis-
Different topological phases in K$_4$Ba$_2$[SnBi$_4$]. a, TI-WSM-NI phase transition in K$_4$Ba$_2$[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 in the vicinity of 2.5 GPa. b, Distribution of the Weyl points for the WSM phase. The chirality of each Weyl point is indicated.

While the intimate TI-TE relation is embodied in RTMCs too, it is much beyond the extent in conventional TIs. One distinction stems from the active interstitial electrons, which are weakly coupled with the crystal framework and are hence prone to high mobility, as commonly seen in electrides [20]. Thus, a considerable $\sigma$, in particular along the [0001] direction (the extended vacant channel), can be expected for K$_4$Ba$_2$[SnBi$_4$]. Figure 5d shows that 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 [35, 38], can be successfully achieved in RTMCs. In addition, being a quasi-zero-dimensional molecular crystal, K$_4$Ba$_2$[SnBi$_4$] bears a structural complexity which may trap heat, akin to the other Zintl compounds for thermoelectrics [24, 39]. The loosely coupled heavy [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 (Fig. 5e), whereby $\kappa_l$ can be drastically suppressed [39]. For comparison, $\kappa_l$ of K$_4$Ba$_2$[SnBi$_4$] is calculated to be 0.22 - 0.23 Wm$^{-1}$K$^{-1}$ at 300 K (Fig. 5f), even lower than that of Bi$_2$Te$_3$ (with in-plane and out-of-plane components 1.2 Wm$^{-1}$K$^{-1}$ and 0.4 Wm$^{-1}$K$^{-1}$, respectively [40]). Hence, we see that the interstitial orbitals that are relatively independent of the lattice or phonons may enable a high $\sigma$ while maintaining a low $\kappa_l$, giving birth to the distinguishing “phonon-glass electron-crystal” behavior [41] for RTMCs. Moreover, the linearized TSS that are robust against backscattering can further enhance $zT$ if thin films are exploited [36]. In short, the triple identity (i.e., TIs, generalized form of electrides, and molecular crystals of quasi-0D) could endow RTMCs with an inherent state-of-the-art TE performance.

**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 RTMCs, the interstitial electron originating from alkali atoms would significantly lift the position of the highest occupied states, leading to a lowered work function. Indeed, the low work function is a common feature among electrides, also due to the interstitial electrons [20]. As an example, the work function of K$_4$Ba$_2$[SnBi$_4$] for the (1010) surface is calculated to be 2.2 eV in the presence of SOC (see the Supplementary Section D), akin to alkali metals, which is
FIG. 5. Thermoelectricity of K₄Ba₂[SnBi₄]. a, Band structure of K₄Ba₂[SnBi₄] with SOC in the vicinity of the Γ point, which is calculated with the HSE06 functional. This figure is a magnified view of Fig. 2d. b, Isoenergy surface centered at the Γ point, with the corresponding energy marked in a. The size is exaggerated for easy visualization. c, Seebeck coefficient S of K₄Ba₂[SnBi₄] versus the carrier concentration nₑ at 300 K. Both p-type and n-type doping are plotted. The dashed grey lines indicate the threshold of |S| = 156 µVK⁻¹. d, Electrical conductivity σ against nₑ at 300 K. σ is evaluated in the unit of the scattering time τ under the constant scattering time approximation, due to lacking the information of τ. Only the 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 Fig. 2b. For the spectrum of κₗ, only the z component is shown. Note that the frequencies of the low-lying optical modes, which produce scattering via anharmonic coupling with acoustic modes, are merely around 30 cm⁻¹. f, Lattice thermal conductivity κₗ versus the temperature, based on the calculation of anharmonic phonons.

unprecedented in TIs so far (e.g., the work function value of Bi₂Te₃ is around 5.3 eV [42] on the contrary). Consequently, the helical Dirac carries could easily transfer to the contact system by constructing heterostructures (see the Supplementary Section E). We propose a promising application in catalysis. TSS have been shown to boost some chemical reactions by serving as an electron bath [43]. Here the RTMCs, further equipped with a low work function, are expected to activate very inert molecules that even has a shallow lowest unoccupied molecular orbital (LUMO), thus being potential high-efficiency catalysts [20].

Other RTMC candidates
We briefly present other [Sn, Bi]-polyanion-based Zintl compounds that belong to the RTMCs. The first one is K₁₀[Sn₂Bi₆] in a monoclinic lattice (space group P2₁/c, No. 14). Each unit cell contains two discrete [Sn₂Bi₆]¹⁰⁻ molecular clusters in addition to the inserted K⁺ ions (Fig. 6a), being of quasi-0D. The interlayer region offers space for interstitial states, as indicated by the yellow bubbles at the cell edge (the upper panel of Fig. 6a). Owing to the interstitial states, the electronic bands are highly dispersive around the Γ point (Fig. 6c). Further driven by SOC, the valence band maximum and conduction band minimum invert as unveiled by the PBE functional (Fig. 6e), and the system turns out to be a strong TI, with a gap around 60.7 meV. Although the additional HSE06 calculation predicts a trivial non-inverted band structure (Fig. 6e), the gap is merely about 33.2 meV, thus we can still expect a topological phase only through exposing a relatively low pressure, by making use of the weak intermolecular bonding of RTMCs. The work function is merely 2.3 eV for the (100) surface, similar to that of K₄Ba₂[SnBi₄].

K₃Na₂[SnBi₃] is a quasi-one-dimensional RTMC candidate. The lattice is orthorhombic (Ibca, No. 73), with the [Sn₂Bi₆]¹⁰⁻ chain extending along the [100] direction (Fig. 6b). The intercalation of K⁺ and Na⁺ ions provides excess electrons at interstitial sites (blue bubbles in the upper panel of Fig. 6b). Consequently, band inversion arises at Γ, between a molecular orbital and the interstitial state (Figs. 6d and 6f), resulting in a strong TI phase, as supported by the DFT calculations with either
FIG. 6. Other RTMC 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 function of the lowest unoccupied state (upper panel) and highest occupied state (lower panel) at the $\Gamma$ point with no SOC. The corresponding position in the spectrum is also marked in c or d. Yellow and navy bubbles represent the positive and negative parts 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 the inclusion of 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 of K$_3$Na$_2$[SnBi$_3$] (not shown), while b presents the conventional cell for clear visualization.

Conclusions
We have elucidated the concept of RTMCs, which bear the triple identity of topological materials, molecular crystals, and the generalized form of electrides. Based on first-principles calculations, we have demonstrated a variety of exceptional properties, namely, multiple dangling-bond-free surfaces, topological phase transition under small mechanical perturbations, high-performance thermoelectricity, and ultralow work function. The discussed phenomena and applications are within current experimental reach. Our results suggest that some long-known molecular solids would get renewed through the topological nature once recognized as RTMCs, meanwhile the well-established theories and technologies in the community of molecular crystals (e.g., flexible bottom-up materials design via molecular engineering [3]) might enable functionality tailoring for topological materials.

References
[1] A. Kitaigorodsky, Molecular crystals and molecules, Vol. 29 (Elsevier, 2012).
[2] L. Kronik and J. B. Neaton, Excited-state properties of molecular solids from first principles, Annual Review of Physical Chemistry 67, 587 (2016).
[3] S. A. Claridge, A. Castlemale Jr, S. N. Khanna, C. B. Murray, A. Sen, and P. S. Weiss, Cluster-assembled materials, ACS nano 3, 244 (2009).
[4] J. Yin, P. Maity, M. De Bastiani, I. Dursun, O. M. Bakr, J.-L. Brédas, and O. F. Mohammed, Molecular behavior of zero-dimensional perovskites, Science advances 3, e1701793 (2017).
[5] M. Z. Hasan and C. L. Kane, Colloquium: Topological insulators, Rev. Mod. Phys. 82, 3045 (2010).
[6] Y. Ando, Topological insulator materials, Journal of the Physical Society of Japan 82, 102001 (2013).
[7] X.-L. Qi and S.-C. Zhang, Topological insulators and superconductors, Rev. Mod. Phys. 83, 1057 (2011).
[8] N. P. Armitage, E. J. Mele, and A. Vishwanath, Weyl and dirac semimetals in three-dimensional solids, Rev. Mod. Phys. 90, 015001 (2018).
[9] M. Hirayama, R. Okugawa, and S. Murakami, Topological semimetals studied by ab initio calculations, Journal of the Physical Society of Japan 87, 041002 (2018).
[10] C. Nayak, S. H. Simon, A. Stern, M. Freedman, and S. Das Sarma, Non-abelian anyons and topological quantum computation, Rev. Mod. Phys. 80, 1083 (2008).
[11] T. Ozawa, H. M. Price, A. Amo, N. Goldman, M. Hafezi, L. Lu, M. C. Rechtsman, D. Schuster, J. Simon, O. Zilberberg, and I. Carusotto, Topological photonics, Rev. Mod. Phys. 91, 015006 (2019).
[12] E. J. Bergholtz, J. C. Budich, and F. K. Kunst, Ex-
ceptional topology of non-Hermitian systems, Rev. Mod. Phys. 93, 015005 (2021).

[11] B. Bradlyn, L. Elcoro, J. Cano, M. Vergniory, Z. Wang, C. Felser, M. I. Aroyo, and B. A. Bernevig, Topological quantum chemistry, Nature 547, 298 (2017).

[12] K. Kajita, Y. Nishio, N. Tajima, Y. Suzumura, and A. Kobayashi, Molecular dirac fermion systems — theoretical and experimental approaches —, Journal of the Physical Society of Japan 83, 072002 (2014).

[13] R. Kato, H. Cui, T. Tsumuraya, T. Miyazaki, and Y. Suzumura, Emergence of the dirac electron system in a single-component molecular conductor under high pressure, Journal of the American Chemical Society 139, 1770 (2017).

[14] B. Zhou, S. Ishibashi, T. Ishii, R. Takehara, B. Bradlyn, L. Elcoro, J. Cano, M. Vergniory, Z. Wang, S. M. Kauzlarich, A. Zevalkink, E. Toberer, and G. J. M. Hirayama, S. Matsuishi, H. Hosono, and S. M. Kauzlarich, A. Zevalkink, E. Toberer, and G. J. M. Hirayama, S. Matsuishi, H. Hosono, and S. Mu-

[15] A. Isaeva, B. Rasche, and M. Ruck, Bismuth-based candidates for topological insulators: Chemistry beyond bi2te3, physica status solidi (RRL) – Rapid Research Letters 7, 39 (2013).

[16] J. L. Dye, Electrons as anions, Science 301, 607 (2003).

[17] H. Hosono and M. Kitano, Advances in materials and applications of inorganic electrides, Chemical Reviews 121, 3121 (2021).

[18] T. Yu, M. Hirayama, J. A. Flores-Livas, M.-T. Huebsch, T. Nomoto, and R. Arita, First-principles design of halide-reduced electrodes: Magnetism and topological phases, Phys. Rev. Materials 5, 044203 (2021).

[19] S. Matsuishi, Y. Toda, M. Miyakawa, K. Hayashi, T. Kamiya, M. Hirano, I. Tanaka, and H. Hosono, High-density electron anions in a nanoporous single crystal: [Ca24Al28O44]4+[4e−], Science 301, 626 (2003).

[20] M. Hirayama, S. Matsuishi, H. Hosono, and S. Murakami, Electrides as a new platform of topological materials, Phys. Rev. X 8, 031067 (2018).

[21] S. M. Kauzlarich, A. Zavalkink, E. Toberer, and G. J. Snyder, Zintl phases: Recent developments in thermoelectrics and future outlook, in Thermoelectric Materials and Devices, Vol. 2017-January (Royal Society of Chemistry, United Kingdom, 2017) pp. 1–26.

[22] B. Eisenmann and U. Rössler, Pniktogenidostannate(IV) with isolated Tetraeder-Anionen: Neue Vertreter (E1)4(E2)2Sn[Sn15]4 (mit E1= Na, K; E2= Ca, Sr, Ba; E15= P, As, Sb, Bi) vom Na4[ZnO4]-Typ und die Überstrukturvariante von K3Sr2[SnAs4], Zeitschrift für anorganische und allgemeine Chemie 626, 1373 (2000).

[23] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77, 3865 (1996).

[24] N. Marzari, A. A. Mostofi, J. R. Yates, I. Souza, and D. Vanderbilt, Maximally localized wannier functions: Theory and applications, Rev. Mod. Phys. 84, 1419 (2012).

[25] J. Heyd, G. E. Scuseria, and M. Ernzerhof, Hybrid functionals based on a screened coulomb potential, The Journal of chemical physics 118, 8207 (2003).

[26] Y. Chen, J. G. Analytis, J.-H. Chu, Z. Liu, S.-K. Mo, X.-L. Qi, H. Zhang, D. Lu, X. Dai, Z. Fang, et al., Experimental realization of a three-dimensional topological insulator, Bi2Te3, science 325, 178 (2009).

[27] J. P. Heremans, R. J. Cava, and N. Samarth, Tetradymites as thermoelectrics and topological insulators, Nature Reviews Materials 2, 1 (2017).

[28] J. Huang, S. Li, C. Yoon, J. S. Oh, H. Wu, X. Liu, N. Dhale, Y.-F. Zhou, Y. Guo, Y. Zhang, M. Hashimoto, D. Lu, J. Denlinger, X. Wang, C. N. Lao, R. J. Birgeneau, F. Zhang, B. Ly, and M. Yi, Room-temperature topological phase transition in quasi-one-dimensional material bi4+4, Phys. Rev. X 11, 031042 (2021).

[29] J. Liu and D. Vanderbilt, Weyl semimetals from non-centrosymmetric topological insulators, Phys. Rev. B 90, 155316 (2014).

[30] M. Ochi, R. Arita, N. Trivedi, and S. Okamoto, Strain-induced topological transition in srru206 and caos206, Phys. Rev. B 93, 195149 (2016).

[31] D. Hsieh, D. Qian, L. Wray, Y. Xia, Y. S. Hor, R. J. Cava, and M. Z. Hasan, A topological dirac insulator in a quantum spin hall phase, Nature 452, 970 (2008).

[32] H. J. Goldsmid, Introduction to Thermoelectricity, Vol. 121 (Springer, Berlin, Heidelberg, 2010).

[33] N. Xu, Y. Xu, and J. Zhu, Topological insulators for thermoelectrics, npj Quantum Materials 2, 1 (2017).

[34] H. Shi, D. Parker, M.-H. Du, and D. J. Singh, Connecting thermoelectric performance and topological-insulator behavior: Bi2Te3 and Bi2Te2Se from first principles, Phys. Rev. Applied 3, 014004 (2015).

[35] K. Kuroki and R. Arita, “pudding mold” band drives large thermopower in Na8Co2O2, Journal of the Physical Society of Japan 76, 083707 (2007).

[36] L. Zhang, M.-H. Du, and D. J. Singh, Zintl-phase compounds with SnSb4 tetrahedral anions: Electronic structure and thermoelectric properties, Phys. Rev. B 81, 075117 (2010).

[37] O. Hellman and D. A. Broido, Phonon thermal transport in Bi2Te3 from first principles, Phys. Rev. B 90, 134309 (2014).

[38] G. A. Slack, in CRC Handbook of Thermoelectrics (CRC Press, Boca Raton, FL, 1995) pp. 407–440.

[39] D. Takane, S. Souma, T. Sato, T. Takahashi, K. Segawa, and Y. Ando, Work function of bulk-insulating topological insulator Bi2–2Sb2Te3–ySey, Applied Physics Letters 109, 091601 (2016).

[40] H. Chen, W. Zhu, D. Xiao, and Z. Zhang, Co oxidation facilitated by robust surface states on au-covered topological insulators, Phys. Rev. Lett. 107, 056804 (2011).
DFT calculations. The DFT calculations of the RTMC candidate materials are performed based on the projector augmented wave scheme [44] as implemented in the Vienna *ab initio* simulation package (VASP) [45]. For static calculations (i.e., self-consistent electronic relaxation, band structure, etc.), we employ the exchange-correlation functional given by the generalized gradient approximation (GGA) with the PBE parametrization [26]. The nonlocal HSE06 hybrid functional [28] is supplemented for phases at ammation (GGA) with the PBE parametrization [26]. The nonlocal correlation functional given by the generalized gradient wave scheme [44] as implemented in the Vienna

Wannier functions are

onto the

K

and Cs-Ba to approximate the mixed atom, in addition to K-Ba. We calculate the band structure using the mixing Rb-Sr, Rb-Ba, Cs-Sr, and other pairs of alkali and alkaline earth elements. Namely, we also perform a DFT calculation for an 8-layer (10¯10) slab (thickness 79 ˚A) in the presence of SOC. 20 ˚A of vacuum is adopted so that the outermost K

Ba

2+

ions and [SnBi]4− tetrahedra are relaxed; no significant improvement in the band structure can be seen if relaxing more atoms in the deeper layers. While the method of the first-order Methfessel-Paxton [62] is used for partial occupancies, the accurate position of the Fermi level is determined via the tetrahedron method with Blochl corrections [63].

Thermoelectricity. The Seebeck coefficient $S$ and electrical conductivity $\sigma$ are assessed in the framework of Boltzmann transport theory under the rigid band picture, with the help of the *Boltzmann* module [64] in *Wannier90*. The constant scattering time approximation is adopted, so that the scattering time $\tau$ can be extracted from $\sigma$, and cancels in the expression of $S$ [64]. $\sigma$ is estimated in the unit of $\tau$. The Wannier functions are obtained from the DFT results with SOC, under the HSE06 hybrid functional, since the hybrid functional is believed to describe the band edge more accurately in general, which is crucial to thermoelectrics [35]. A $50 \times 50$ fine $k$-grid is used.

To characterize the phononic transport properties of $K_4Ba_2[SnBi_4]$, we switch from VASP to the QUANTUM ESPRESSO package [65, 66], because computing interatomic force constants within the VCA is not supported in VASP. Since the lattice dynamics is relatively insensitive to the details of the electronic band edge, it suffices to use a pure functional instead of the expensive hybrid functional. The PBEsol pseudopotentials from *plibrary* [67] are applied. SOC has small impact on the lattice dynamics and is ignored to save the computational cost. The atomic coordinates are further relaxed with a force criterion of 0.1 meV/Å. A $1 \times 1 \times 2$ supercell is built for the evaluations of phononic spectrum and lattice thermal conductivity $\kappa_l$, since the lattice constants $a$ and $b$ are already quite large and over 10 Å. In particular, anharmonic phonons are computed to access $\kappa_l$, through the Boltzmann transport theory for phonons under the scattering time approximation, namely,

$$\kappa_l(T) = \frac{1}{V N_e} \sum_{q,j} c_{q,j}(T) v_{q,j} \otimes v_{q,j} \phi_{q,j}(T).$$

Here $T$ denotes the temperature, $q$ the wave vector, $j$ the polarization, $V$ the unit cell volume, $N_e$ the number of $q$ points, $c_{q,j} = \hbar q_{q,j} \partial \nu_{q,j} / \partial T$, with $\nu_{q,j}$ the phonon frequency and $q_{q,j}$ the occupation number, $v_{q,j}$ the phonon velocity, $\phi_{q,j}$ the phonon lifetime. The anharmonic interatomic force constants are computed up to the spacings around 10 Å. The calculations of $\kappa_l$ are done through the code ALAMODE [68], sampled on a $12 \times 12 \times 12$ fine $q$-grid.

**Work function.** We construct a slab along a given direction and calculate the Fermi energy ($E_F,_{slab}$) as well as the vacuum potential energy ($\phi_{vac}$) outside the material under the formalism of DFT. The work function ($W$) for the corresponding surface is thus expressed as $W = \phi_{vac} - E_F,_{slab}$ [69]. Since the bulk is insulating but the surface is metallic in TIs, we determine $E_F,_{slab}$ directly through the slab calculation, instead of deriving it from the bulk. In fact, the latter value, which is obtained by shifting the bulk Fermi level ($E_F,_{bulk}$) to align the average Hartree potential of the slab middle layers with that of the bulk [70], is tested to be almost equal to the former, within the range of the band gap (i.e., a few 10 meV).

The 8-layer (1010) slab of $K_4Ba_2[SnBi_4]$ relaxed in the same way as in the surface state calculation is adopted. SOC is switched on. For $K_4[Sn_2Bi_6]$ and $K_4NaN_2[SnBi_3]$, a 6-layer (100) slab and a 6-layer (010) slab are built, respectively. The thickness of the vacuum is 20 Å in both cases. The outermost ions and molecular units are relaxed.

**References**
[44] G. Kresse and D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, Phys. Rev. B 59, 1758 (1999).

[45] G. Kresse and J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Phys. Rev. B 54, 11169 (1996).

[46] G. I. Csonka, J. P. Perdew, A. Ruzsinszky, P. H. T. Philipsen, S. Lebègue, J. Paier, O. A. Vydrov, and J. G. Angyán, Assessing the performance of recent density functionals for bulk solids, Phys. Rev. B 79, 155107 (2009).

[47] V. Wang, N. Xu, J.-C. Liu, G. Tang, and W.-T. Geng, Vaspkit: a user-friendly interface facilitating high-throughput computing and analysis using vasp code, Computer Physics Communications, 108033 (2021).

[48] U. Herath, P. Tavadze, X. He, E. Bousquet, S. Singh, F. Muñoz, and A. H. Romero, Pyrocars: A python library for electronic structure pre/post-processing, Computer Physics Communications 251, 107080 (2020).

[49] S. Curtarolo, W. Setyawan, G. L. Hart, M. Jahnatek, R. V. Chepulskii, R. H. Taylor, S. Wang, J. Xue, K. Yang, O. Levy, et al., Afflow: An automatic framework for high-throughput materials discovery, Computational Materials Science 58, 218 (2012).

[50] A. Togo and I. Tanaka, Spglib: a software library for crystal symmetry search, arXiv preprint arXiv:1808.01590 (2018).

[51] R. K. Momma and F. Izumi, Vesta: a three-dimensional visualization system for electronic and structural analysis, Journal of Applied Crystallography 41, 653 (2008).

[52] M. Kawamura, Fermisurfer, Fermi-surface viewer providing multiple representation schemes, Computer Physics Communications 239, 197 (2019).

[53] L. Nordheim, Zur elektronentheorie der metalle. i, Annalen der Physik 401, 607 (1931).

[54] L. Bellaiche and D. Vanderbilt, Virtual crystal approximation revisited: Application to dielectric and piezoelectric properties of perovskites, Phys. Rev. B 61, 7877 (2000).

[55] N. Marzari and D. Vanderbilt, Maximally localized generalized wannier functions for composite energy bands, Phys. Rev. B 56, 12847 (1997).

[56] I. Souza, N. Marzari, and D. Vanderbilt, Maximally localized wannier functions for entangled energy bands, Phys. Rev. B 65, 035109 (2001).

[57] G. Pizzi, V. Vitale, R. Arita, S. Blügel, F. Freimuth, G. Gréanton, M. Gibertini, D. Gresch, C. Johnson, T. Koretsune, J. Ibañez-Azpiroz, H. Lee, J.-M. Lim, D. Marchand, A. Marrazzo, Y. Mokrousov, J. I. Mustafa, Y. Nohara, Y. Nomura, L. Paulatto, S. Ponce, T. Ponweiser, J. Qiao, F. Thöle, S. S. Tsirkin, M. Wierzbowska, N. Marzari, D. Vanderbilt, I. Souza, A. A. Mostofi, and J. R. Yates, Wannier90 as a community code: new features and applications, Journal of Physics: Condensed Matter 32, 165902 (2020).

[58] D. Gresch, Q. Wu, G. W. Winkler, R. Häuselmann, M. Troyer, and A. A. Soluyanov, Automated construction of symmetrized wannier-like tight-binding models from ab initio calculations, Phys. Rev. Materials 2, 103805 (2018).

[59] A. A. Soluyanov and D. Vanderbilt, Computing topological invariants without inversion symmetry, Phys. Rev. B 83, 235401 (2011).

[60] Q. Wu, S. Zhang, H.-F. Song, M. Troyer, and A. A. Soluyanov, Wanniertools: An open-source software package for novel topological materials, Computer Physics Communications 224, 405 (2018).

[61] M. P. L. Sancho, J. M. L. Sancho, J. M. L. Sancho, and J. Rubio, Highly convergent schemes for the calculation of bulk and surface green functions, Journal of Physics F: Metal Physics 15, 851 (1985).

[62] M. Methfessel and A. T. Paxton, High-precision sampling for Brillouin-zone integration in metals, Phys. Rev. B 40, 3616 (1989).

[63] P. E. Blöchl, O. Jepsen, and O. K. Andersen, Improved tetrahedron method for brillouin-zone integrations, Phys. Rev. B 49, 16223 (1994).

[64] G. Pizzi, D. Volja, B. Kozinsky, M. Fornari, and N. Marzari, Boltz2Wann: A code for the evaluation of thermoelectric and electronic transport properties with a maximally-localized wannier functions basis, Computer Physics Communications 185, 422 (2014).

[65] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Ciocci, M. Cocciconi, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, L. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Schlauzer, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials, Journal of Physics: Condensed Matter 21, 395502 (19pp) (2009).

[66] P. Giannozzi, O. Andreussi, T. Brumme, O. Bünau, M. B. Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cocciconi, N. Colonna, I. Carnimeo, A. D. Corso, S. de Gironcoli, P. Delugas, R. A. D. Jr, A. Ferretti, A. Floris, G. Fratesi, G. Fugallo, R. Gebauer, U. Gerstmann, F. Giustino, T. Gorni, J. Jia, M. Kawamura, H.-Y. Ko, A. Kokalj, E. Küçükbenli, M. Lazzere, M. Marsili, N. Marzari, F. Mauri, N. L. Nguyen, H.-V. Nguyen, A. O. de-la Roza, L. Paulatto, S. Ponce, D. Rocca, R. Sabatini, B. Santra, M. Schlipf, A. P. Seitsonen, A. Smogunov, I. Timrov, T. Thonhauser, P. Umari, N. Vast, X. Wu, and S. Baroni, Advanced capabilities for materials modelling with QUANTUM ESPRESSO, Journal of Physics: Condensed Matter 29, 465901 (2017).

[67] A. Dal Corso, Pseudopotentials periodic table: From H to Pu, Computational Materials Science 95, 337 (2014).

[68] T. Tadano, Y. Gohda, and S. Tsuneyuki, Anharmonic force constants extracted from first-principles molecular dynamics: applications to heat transfer simulations, Journal of Physics: Condensed Matter 26, 225402 (2014).

[69] D. Cahn and A. Kahn, Electron energetics at surfaces and interfaces: Concepts and experiments, Advanced Materials 15, 271 (2003).

[70] C. J. Fall, N. Binggeli, and A. Baldereschi, Deriving accurate work functions from thin-slab calculations, Journal of Physics: Condensed Matter 11, 2689 (1999).

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Supplementary Information for
Relativistic topological molecular crystals

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A. Chemical bonds in K\textsubscript{4}Ba\textsubscript{2}[SnBi\textsubscript{4}]

This section clarifies the chemical bonding types in K\textsubscript{4}Ba\textsubscript{2}[SnBi\textsubscript{4}] to ascertain its identity as a molecular crystal. As K and Ba are much more electropositive (with the electronegativity 0.82 and 0.89, respectively) than Sn and Bi (electronegativity: 1.96 and 2.02), the valence electrons in the outermost s shell of the former transfer to the latter, so that K and Ba become isolated cations altogether, and [SnBi\textsubscript{4}]\textsuperscript{8−} as a whole show the oxidation number −8. Further, within the substructure of [SnBi\textsubscript{4}]\textsuperscript{8−}, covalent bonds are established between Sn and Bi, resulting from their close electronegativities. Indeed, the orbitals of Sn (5s\textsuperscript{2}5p\textsuperscript{2}) are hybridized into sp\textsuperscript{3}, filled with four electrons. Each sp\textsuperscript{3} electron is then paired with one p electron of Bi (6s\textsuperscript{2}6p\textsuperscript{3}), and four Bi atoms are thus connected with the central Sn in a tetrahedral shape through covalent bonding. The remaining two p orbitals of each Bi that are half-occupied receive two extra electrons captured from cations (four Bi atoms are then assigned with eight electrons exactly), forming two lone pairs, whereby the [SnBi\textsubscript{4}]\textsuperscript{8−} polyanion reaches a full valence. In this way, [SnBi\textsubscript{4}]\textsuperscript{8−} is a molecular unit glued by the Sn-Bi covalent bonding, and interacts with K\textsuperscript{+} and Ba\textsuperscript{2+} through ionic bonding. In fact, the spacings between neighboring [SnBi\textsubscript{4}]\textsuperscript{8−} clusters (5.3 - 5.6 Å) are considerably greater than the intracluster Sn-Bi bond length (2.9 Å), also suggesting the hallmark of molecular crystals \cite{1}. Similar analysis can be addressed to other RTMC candidates as well.

Our first-principles calculation supports the arguments above. Electron localization function (ELF) is a variant of electron density, aiming to describe the degree of electron localization in real space \cite{2,3}. The local minimum of ELF is called the bonding attractor, with its occurrence between atomic shells indicative of shared-electron interactions (e.g., covalent bond), and its absence on the bond path reflecting unshared-electron interactions (e.g., ionic bond) \cite{4,5}. Figure S1 gives the ELF of K\textsubscript{4}Ba\textsubscript{2}[SnBi\textsubscript{4}]. While bonding attractors appear in the middle region of Sn and Bi, the [SnBi\textsubscript{4}]\textsuperscript{8−} tetrahedra are completely separated from K\textsuperscript{+} and Ba\textsuperscript{2+} cations, as the evidence of ionic bonding in-between.

B. Band gaps of noncentrosymmetric TIs

We obtain large-gap noncentrosymmetric TIs from the topological materials database Materiae \cite{6}. Only those with the estimated band gap (E\textsubscript{g}) larger than 50 meV are selected. Note that TIs with broken inversion symmetry generally have a smaller band gap than inversion-symmetric ones; while for the latter E\textsubscript{g} can reach hundreds of meV (e.g., tetradymites), for the former E\textsubscript{g} > 100 meV is hardly found. Since the band structures in the materials database are estimated via a high-throughput flow and numerical inadequacy would thus be unavoid-

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figS1.png}
\caption{ELF of K\textsubscript{4}Ba\textsubscript{2}[SnBi\textsubscript{4}]. The yellow bubble represents the ELF. Views from several different directions are shown.}
\end{figure}

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Fig. S2. Band structures of noncentrosymmetric TIs. Calculations are performed in the framework of DFT with the PBE parametrization. For CdSnSb₂, the indirect gap is evaluated to be zero, despite the finite direct gap.

We additionally characterize the work function for the polar (0001) slab. To circumvent the intricate setting of defects or adatoms that is required to simulate the significant reconstruction of the charged surface, we restrict our scope to a thin film (3 layers, thickness ≈25 Å) as a compromise, as shown in Fig. S4c. The effective screening medium method [8] is implemented to eliminate the spurious dipole interactions between periodic images. Atoms in the outermost layers are relaxed. Figure S4d depicts the unbalanced work function for each end [3.8 eV for (0001), and 2.5 eV for (0001)], as typically seen in polar slabs. Here the (0001) vacuum potential is greatly lifted by the electric field of the negative charge on this surface. A low work function can be retrieved through surface neutralization.

D. Work function of K₄Ba₂[SnBi₄]

The work function of K₄Ba₂[SnBi₄] (1010) is estimated through an 8-layer slab (Fig. S4a) with the inclusion of SOC. The averaged Hartree potential energy along the [1010] direction is presented in Fig. S4b, showing that the vacuum level is 2.2 eV above E_F, indicative of the work function.

We additionally characterize the work function for the polar (0001) slab. To circumvent the intricate setting of defects or adatoms that is required to simulate the significant reconstruction of the charged surface, we restrict our scope to a thin film (3 layers, thickness ≈25 Å) as a compromise, as shown in Fig. S4c. The effective screening medium method [8] is implemented to eliminate the spurious dipole interactions between periodic images. Atoms in the outermost layers are relaxed. Figure S4d depicts the unbalanced work function for each end [3.8 eV for (0001), and 2.5 eV for (0001)], as typically seen in polar slabs. Here the (0001) vacuum potential is greatly lifted by the electric field of the negative charge on this surface. A low work function can be retrieved through surface neutralization.

Fig. S2. Band structures of noncentrosymmetric TIs. Calculations are performed in the framework of DFT with the PBE parametrization. For CdSnSb₂, the indirect gap is evaluated to be zero, despite the finite direct gap.

We calculate the band structure of an 8-layer (1010) K₄Ba₂[SnBi₄] slab (thickness ≈79 Å) with SOC under DFT, as illustrated in Fig. S3. The linear gapless TSS are consistent with the prediction by Wannier functions (Fig. 3e), despite the slight difference of the projected bulk bands due to the boundary effect. The asymmetric (0001) slab is skipped because complicated setup of surface defects or adatoms is needed to cure the energy divergence caused by the polar surface [7]. Still, we can expect a surface spectrum akin to the tight-binding model after neutralizing the surface, just like the correspondence in the (1010) slab.

C. DFT band structure of the K₄Ba₂[SnBi₄] slab

We calculate the band structure of an 8-layer (1010) K₄Ba₂[SnBi₄] slab (thickness ≈79 Å) with SOC under DFT, as illustrated in Fig. S3. The linear gapless TSS are consistent with the prediction by Wannier functions (Fig. 3e), despite the slight difference of the projected bulk bands due to the boundary effect. The asymmetric (0001) slab is skipped because complicated setup of surface defects or adatoms is needed to cure the energy divergence caused by the polar surface [7]. Still, we can expect a surface spectrum akin to the tight-binding model after neutralizing the surface, just like the correspondence in the (1010) slab.
E. Interfaces of K$_4$Ba$_2$[SnBi$_4$] with molecules

We investigate the interface of K$_4$Ba$_2$[SnBi$_4$] with the fullerene C$_{60}$. The C$_{60}$ molecule occupies the interstitial region on the (1010) surface of K$_4$Ba$_2$[SnBi$_4$], as shown in the left panel of Fig. S5a. As the diameter of C$_{60}$ is quite large ($\approx 7.1$ Å) and close to the lattice constant $c$ ($\approx 8.3$ Å) of K$_4$Ba$_2$[SnBi$_4$], we double the unit cell along the $c$ direction (i.e., [0001]). To reduce the computational expense, only a 2-layer slab of K$_4$Ba$_2$[SnBi$_4$] is used, and SOC is switched off; we aim at a qualitatively heuristic result rather than pursuing the quantitative rigor. The outermost cations and polyanions, together with the distance of C$_{60}$ to the surface are fully relaxed. The position of C$_{60}$ along [0001] is optimized (as given in the right panel of Fig. S5a) so that the total energy of the interface system is at the minimum. Figure S5c displays the band structure of this interface system. The LUMOs of C$_{60}$ are successfully doped, owing to the low work function of K$_4$Ba$_2$[SnBi$_4$]. Importantly, the doped C$_{60}$ orbitals are next to the surface Dirac cone of K$_4$Ba$_2$[SnBi$_4$] (not manifested in Fig. S5c as SOC is absent), revealing the intriguing possibility that the massless Dirac Fermions might interact with the fullerene molecule or fulleride crystal with further fine tuning.

A (1010) K$_4$Ba$_2$[SnBi$_4$] slab interfaced with a polytetrafluoroethylene (PTFE) (C$_2$F$_4$)$_n$ chain is studied as well, as shown in Fig. S5b. The PTFE is a stable fluorocarbon polymer with a small electron affinity. When contacted with K$_4$Ba$_2$[SnBi$_4$], the LUMO of (C$_2$F$_4$)$_n$ is filled and adjacent to the Dirac cone (Fig. S5d), just like C$_{60}$, as a reflection of doping TSS to molecules or non-topological insulators even with a large gap.

F. Justification of the VCA

The mixed-atom sites in K$_4$Ba$_2$[SnBi$_4$] (Fig. 2a) are described with the pseudopotential interpolated by those of K and Ba (i.e., VCA). To justify this approximation, the band structure is evaluated under the pseudopotentials interpolated also by other pairs of alkali and alkaline earth elements. Here we take Rb-Sr, Rb-Ba, Cs-Sr, and Cs-Ba. Figure S6 shows that the band structures in the vicinity of $E_F$ keep almost unchanged regardless of the mixing type, no matter whether SOC is included or not. We can, therefore, safely harness the VCA, to which the electronic properties of K$_4$Ba$_2$[SnBi$_4$] are insensitive.

Fig. S5. Interface systems of K$_4$Ba$_2$[SnBi$_4$] with other molecules. a, b A (1010) K$_4$Ba$_2$[SnBi$_4$] slab with the adsorption of fullerene C$_{60}$ (a) and PTFE (C$_2$F$_4$)$_n$ (b). Both front and side views are illustrated. c, d Band structures of the interface system with C$_{60}$ (c) and (C$_2$F$_4$)$_n$ (d). SOC is not included. States arising from the adsorbed molecules are highlighted in red.

Fig. S6. Band structures of K$_4$Ba$_2$[SnBi$_4$] under different settings of the VCA. The first row (K-Ba) means that the pseudopotential is obtained by the interpolation of 1/3 K and 2/3 Ba; analogously for the remaining rows.
List of references

[1] A. Kitaigorodsky, *Molecular crystals and molecules*, Vol. 29 (Elsevier, 2012).
[2] A. D. Becke and K. E. Edgecombe, A simple measure of electron localization in atomic and molecular systems, *The Journal of Chemical Physics* 92, 5397 (1990).
[3] A. Savin, The electron localization function (ELF) and its relatives: interpretations and difficulties, *Journal of Molecular Structure: THEOCHEM* 727, 127 (2005).
[4] B. Silvi and A. Savin, Classification of chemical bonds based on topological analysis of electron localization functions, *Nature* 371, 683 (1994).
[5] S. Zhao, E. Kan, and Z. Li, Electride: from computational characterization to theoretical design, *WIREs Computational Molecular Science* 6, 430 (2016).
[6] T. Zhang, Y. Jiang, Z. Song, H. Huang, Y. He, Z. Fang, H. Weng, and C. Fang, Catalogue of topological electronic materials, *Nature* 566, 475 (2019).
[7] P. W. Tasker, The stability of ionic crystal surfaces, *Journal of Physics C: Solid State Physics* 12, 4977 (1979).
[8] M. Otani and O. Sugino, First-principles calculations of charged surfaces and interfaces: A plane-wave nonrepeated slab approach, *Phys. Rev. B* 73, 115407 (2006).