Composition-controllable Topological Nodal-line Semimetals in Honeycomb Disilabenzene-linked Covalent Organic Frameworks with Six-band Models

Xinyong Cai,[1,2,3] Jun Zhou,[2,*] Panlong Kong,[4] Wencai Yi,[5] Haifei Qin,[6] Yuxiang Ni,[1] Yuanzheng Chen,[1,**] Hongyan Wang,[1,7,***]

[1]School of Physical Science and Technology, Southwest Jiaotong University, Chengdu 610031, China

[2]Institute of Materials Research and Engineering (IMRE), Agency for Science, Technology and Research (A*STAR), 2 Fusionopolis Way, Innovis #08-03, Singapore 138634

[3]School of Science, Key Laboratory of High Performance Scientific Computation, Xihua University, Chengdu 610039, China

[4]School of Mathematics and Physics, Jingchu University of Technology, Jingmen 448000, China

[5]Laboratory of High Pressure Physics and Material Science (HPPMS), School of Physics and Physical Engineering, Qufu Normal University, Qufu, Shandong, China

[6]School of Physics and Astronomy, Key Laboratory of Artificial Structures and Quantum Control (Ministry of Education) and Shanghai Jiao Tong University, Shanghai 200240, China

[7]Lead contact

*Correspondence: zhouj@a-star.edu.sg

**Correspondence: cyz@swjtu.edu.cn

***Correspondence: hongyanw@swjtu.edu.cn

SUMMARY

Covalent organic frameworks (COFs) are mainly normal insulators characterized by composite band models above and below the Fermi level. To introduce a strategy for creating COFs with unique topological states based on the composite band models, we rationally design the first topological nodal-line semimetallic COF (i.e., HBAT-COF) based on a recently synthesized precedent. Topology and frontier molecular orbital analysis reveal that N-containing heteroacene/acene-linked COFs typically exhibit an inherent diatomic Kagome band model, a six-band structure. First-principles calculations show that the coupling effect between pyridinic-N atoms and the Si-Br units facilitates the topological semimetallic phase transitions in the band model of HBAT-COF. More importantly, the Si-Br unit also enables a composition-controllable semimetal with the six-band model in the disilabenzene-linked COF without N atoms. The discovery of the Si-Br-induced topological phase transition in the six-band model offers an approach to transforming normal insulating COFs into nodal-line semimetal states with composite band models.

KEYWORDS

Covalent organic framework, topological nodal-line semimetal, Tight-binding model, Normal insulator, Topological transition, Organic topological materials.

INTRODUCTION

Following the establishment and extensive research of the inorganic topological materials database,[1-3] increasing focus has shifted to two-dimensional (2D) organic topological materials, e.g., covalent organic frameworks (COFs).[4,5] These materials have garnered significant attention and are being investigated at an accelerated pace due to their porosity-induced large surface area, designability, and high controllability with the diversity of organic molecules. However, these materials primarily have conventional insulating states in the form of decisive composite band models near the Fermi level. It is mainly ascribed to the decreased orbital overlapping from delocalized π electrons between non-metal element components and

their low-energy outer orbitals.

According to frontier molecular orbital theory analysis, the composite band models are generated by the lowest unoccupied molecular orbital (LUMO)/highest occupied molecular orbital (HOMO) and LUMO+1/HOMO-1 of linkers or/and knots.[6] Only a few intrinsic topological semimetal (insulator) materials have been identified, mainly presenting as simple band models to constitute a composite band model, i.e., two-band or three-band models in honeycomb structures (Schemes 1A-1D).[7-9] These models exist in honeycomb lattices, akin to graphene, or Kagome lattices, with a single orbital contribution on each atomic site.[6,10] Topological states, such as topological insulating states[9] and topological semimetallic (TSM) states[11], usually exist in the intersection points between the Dirac bands (flat bands) and the Fermi level in honeycomb COFs.[12] If there are two orbital contributions on each atomic site in a honeycomb lattice, a four-band model will be applied (Schemes 1E-1F).[13] A composite band model arises from a combination of two of these three basic band models, separated by the Fermi level.[6,7,12,14,15] The specific individual models can be manipulated through the selection of the linkers and/or knots of COFs. Theoretically, new topological semimetal states may emerge if the two individual models intersect with each other around the Fermi level.[16] For example, a topological nodal-line semimetallic state exists at the intersecting points at the Fermi level between a two-band model from the honeycomb sub-lattice and a three-band model from the Kagome sub-lattice in C_9N_4 monolayer (Schemes 1G-1H).[17] However, the underlying mechanism to form such an interwoven five-band model was elusive, impeding the design and discovery of more advanced topological COFs.

In this context, we concentrate our research on honeycomb COFs with organic molecules as knots in C3 rotation symmetry and linkers in C2 symmetry. Beyond the four types of band models mentioned above, a six-band model initiated from the Star lattice[18,19] is also widely used (Scheme 1I). It can be formed either by a combination of a two-band model and a four-band model or a combination of two three-band models.[6,12,20] The latter (also called the diatomic Kagome band model[21,22]) has theoretically been found to exhibit multiple higher-order topological insulating states and is attracting increasing attention.[20,23-27] Nowadays, COFs are mainly composed of C, H, B, N, O, S (Se), and halogen elements.[28] In the honeycomb COFs, a variety of heteroacene-linked COFs[29-43] have been synthesized over the past few years, showing great controllability and designability with C3 rotation symmetrical benzene-based molecules. However, similar to the aforementioned higher-order topological insulators, the honeycomb heteroacene-linked COFs have large bulk band gaps, which are unfavorable for the realization and application of topological materials. The normally insulating states they exhibit often appear in the form of six-band models, i.e., the bulk bandgap is determined by the six-band model bands.[29,31-43] Currently, researchers primarily concentrate on individual models within the six-band model, such as the commonly studied three-band model.[44,45] In contrast, few studies have focused on the entire six-band model or proposed to discover new topological states within it, including topological semimetal and the resulting first-order topological insulator under spin-orbit coupling (SOC), neglecting the universality and tunability demonstrated by the whole composite six-band model based on molecular compositions of COFs.

Here, based on first-principles calculations, we designed a honeycomb disilabenzene-linked COF (i.e., HBAT-COF) through the reaction between 1,4,5,8,9,12-hexabromoazatriphenylene (HBAT)[46] and Si atoms in the feasible synthetic method. HBAT-COF has a similar structural configuration to the honeycomb heteroacene-linked COFs, but they exhibit different topological properties. By introducing Si elements with high-energy outer orbitals to COFs, we realize the first topological nodal-line semimetallic COF through composite band models. It is also the first time that a gapless semimetal structure in the Star lattice has been discovered in the form of the whole six-band model. Frontier MO theory and tight-binding models are further used to explore the mechanism for the formation of topological nodal line semimetals, providing a new perspective for generating topologically non-trivial structures from trivially topologically insulating COFs in the form of composite band models.

RESULTS

Feasible design for the experimental realization of disilabenzene-linked HBAT-COF monolayer

In the previous works, most COFs have mainly involved C, B, H, N, O, S (Se), and halogen group atoms and exhibited as normal insulators, including the synthesized honeycomb heteroacene-linked COFs (Figure S1). The honeycomb COFs mainly take the benzene ring as the knot, and the linker is heteroacene molecules with two equivalent heteroatoms at opposite positions on the benzene ring (e.g., N, O, and S)[29-41] (Figure 1A). In some materials, the linker has edge functional groups, such as carbonyl groups (=O) in the 1,4-Benzoquinone units (Figure 1B).[41,42,47-54] Very recently, the first Si-containing heteroacene-linked COF (referred to as HBTP-COF) was synthesized through the reaction between 2,3,6,7,10,11-hexabromotriphenylene (HBTP) and Si atoms by Sun *et al* in 2023 (Figures 1D-1E).[55] The freestanding HBTP-COF (C_6H_2SiBr) monolayer also has a honeycomb lattice and a low bandgap by first-principles calculations. After that, we proposed novel disilabenzene-linked COF monolayers (Figure 1C) with topological semimetallic properties, such as a novel disilabenzene-linked COF derived from HBAT[46] (referred to as HBAT-COF in Figures 1F-1G). Because of the same terminal functional group (i.e., -Br group) of HBAT as HBTP, the realization of HBAT-COF is very feasible in a similar synthetic method from the view of chemistry. Analogous to the honeycomb COFs with edge functional groups in Figure 1B, HBAT-COF (C_4N_2SiBr) has two pyrazine units fused with 1,4-disilabenzene in the linker, whereas the edge functional group is the -Br group, binding with Si instead of C atoms. As shown in Figures 1E and 1G, these two disilabenzene-linked COFs can be seen as simple honeycomb structures, akin to flat graphene consisting of single elements, belonging to the P6/mmm space group (No. 191). Note that we have also taken into account the possibility of Si atoms forming sp^3 hybridized orbitals. The computational results of the optimization indicate that Si atoms exist more stably in the form of sp^2 hybridized bonds within the COFs. For HBTP-COF and HBAT-COF monolayers, the constituent elements are HBTP and HBAT, and their lattice constants of freestanding monolayers are $a_1=b_1=18.32$ Å and $a_2=b_2=17.73$ Å, respectively. The smaller atomic radius of N atoms results in the smaller lattice constants of HBAT-COF monolayer. From the electron localization function (ELF) of Figures S2A-S2B, we can see the strong covalent bonds between C and C(N) atoms, polar covalent bonds between Si and Br due to their sharp electronegativity difference, and the uniformly distributed lone electron pairs of N atoms at the edge of inner pores, suggesting similarly stable structures. The calculated elastic constants show $C_{11}=C_{22}=43$ N m^{-1} (45 N m^{-1}), $C_{12}=30$ N m^{-1} (30 N m^{-1}), $C_{44}=6$ N m^{-1} (7 N m^{-1}) for HBAT-COF (HBTP-COF) monolayer. Both $C_{11}C_{22}-C_{12}^2 > 0$ meet the Born Criteria. They imply the good mechanical stability of the freestanding HBAT-COF monolayer and their similar structural robustness, which stems from the structural feature of isoelectronic species between pyridinic-N atoms and C-H units. Moreover, the absence of an imaginary phonon further proves the HBAT-COF monolayer's dynamic stability (Figure S2C).

Non-trivial topological state of the disilabenzene-linked HBAT-COF monolayer

According to the synthesis of HBTP-COF,[55] HBTP-COF is a semiconductor similar to honeycomb heteroacene-linked COFs[14]. Our first-principles calculations based on the PBE method further confirm its semiconducting nature, demonstrating a direct bandgap of 0.22 eV at the Γ point (Figures 2A and S3A). As C atoms are the main atoms in the framework, the density of state (DOS) demonstrates that they contribute the most among the four constituent elements of the HBTP-COF monolayer, while H atoms, possessing only a low-energy shell with a 1s orbital electron, do not contribute near the Fermi level. Due to the large electronegativity difference between Br and Si atoms, Br primarily forms localized conjugated π bonds. Its electrons concentrate around Br atoms, resulting in significantly less contribution to the bands near the Fermi level compared to Si. In contrast, for HBAT-COF, we surprisingly discovered that it possesses semimetallic properties (Figures 2B and S3B). A linearly intersecting degeneracy point D1 can be clearly observed between the Γ and M points, while another point with an extremely small bandgap (0.025 eV) appears between the K and Γ points. The zero contribution of the DOS at the Fermi level in the HBAT-COF monolayer provides additional evidence for the existence of an intersection at the Fermi level. Although C atoms remain the most abundant component atoms, their contribution near the Fermi level is surpassed slightly by N atoms.

To gain a more precise understanding of the band structure compositions of HBAT-COF and HBTP-COF monolayers, we further compute their atom-orbital projected band structures. From Figures 2A and S4, it can be observed that the bands around the Fermi level in the HBTP-COF monolayer are primarily composed of p_z orbitals of C, Si, and Br atoms, which form the conjugated and delocalized π bonds above and below the structural framework. p_z orbitals can also be seen in the partial charge density of its valence band maximum (VBM) and conduction band minimum (CBM) at the Γ point (Figures S5A-B). In addition to the initially identified linear band intersection between the Γ and M points in HBAT-COF monolayer, which arises mainly from the CB formed by the p_z orbitals of N atoms and the VB by the p_z orbitals of Si atoms, we have also discovered another intersection (D2) between the K and Γ points, which is also formed by the atomic contributions from the same bands (Figure 2B). As a result, D2 exists with D1 synchronously. According to the arguments by Weng et al.,[56,57] it originates from spatial inversion (Π) and time reversal ($\mathbf{T}$) symmetries in HBAT-COF monolayer. Such two Dirac points can result in a nodal-line semimetal.[57] The "valley" formed by the CB and the "peak" formed by the VB simultaneously cross the Fermi surface and overlap with each other. The intersection between the VB and the CB occurs precisely at the Fermi level, creating electron and hole pockets.

Besides, we calculate the partial charge density of six electronic states (V_1, V_2, V_3, V_4, C_1, and C_2) around D1 and D2 above and below the Fermi level (Figure 2B). The result shows that V_1 and V_2 within the overlapping zone are the same as V_3 and V_4 outside the overlapping zone, belonging to the same band, while C_1 and C_2 within the overlapping zone are different from them, gathering in another one (Figures 2B-2C). It further ensures the existence of the intersection. Within the overlapping zone, the isoelectronic structural feature endows HBTP-COF and HBAT-COF monolayers with their similar partial charge density in the band near the Fermi level, such as CBM (VBM) of the latter and VBM (CBM) of the former at the Γ point (Figures S5C-D). Through symmetry analysis, we know that the HBAT-COF monolayer belongs to the point group D_{6h}, containing one vertical mirror plane σ_v and one C2 rotation axis along K-Γ and Γ-M, respectively. Under the point group, the nodal loop can be formed in the whole first Brillouin zone, as shown in Figure 2D. For example, when M (0.5, 0, 0) in the path of the calculated band structure was altered with an arbitrary point M_1(0.45, 0.1, 0) bewteen K and M points, the third crossing point (D3) can be found at a similar distance away from the Γ point as those between D1 (D2) and Γ point (Figure S6).

Next, to confirm whether the nodal-line semimetal in HBAT-COF is symmetry-protected, we further analyze its band parties. For simplicity, we can regard HBAT-COF as the self-assembly of the disilabenzene-linked heteroacene molecule (Figure S7), which has the same D_{2h} symmetry as that of HBTP-COF. As presented in Figures 2E-F and S7B, the wave functions of the frontier MOs of two molecules have the same irreducible representations (symmetry) for LUMO+1, LUMO, HOMO, and HOMO-1, due to similar and isoelectronic configurations. For the linker molecule of HBTP-COF, its HOMO has a lower energy than LUMO by 1.24 eV. When the molecule assembles semiconductive HBTP, the wave functions of the VBM and the CBM at the Γ point show that they mainly stem from HOMO and LUMO, respectively. For the N-containing molecule of HBAT-COF, the energy difference between HOMO and LUMO is smaller (0.91 eV). Distinctly from HBTP-COF, when the N-containing molecule constitutes HBAT-COF, its HOMO contributes predominantly to the CBM while LUMO forms the VBM in the band structure (Figures 2E-F and S5). It also demonstrates an inversion between the top VB and bottom CB near Γ point in HBAT-COF monolayer owing to their opposite parties (Figures 2B, E-F, and S5).[58] However, the irreducible representations of HOMO and LUMO indicate that the nodal-line semimetal is not protected by σ_h mirror symmetry but other crystal symmetries, as shown in Figure S8, and the low buckled HBAT-COF with p-31m space group (without σ_h mirror symmetry) is also a nodal-line semimetal. Thus, comparing the isoelectronic HBTP-COF and HBAT-COF monolayers, the topological phase transition from the semiconductor to the nodal-line semimetal originates from the substitution of high-energy electrons in N atoms (Figure 2G).

The nodal-line semimetal is protected by both time-reversal and spatial-inversion symmetries. When SOC is included in our first-principles calculations, we find that the semimetallic state remains stable (Figure

S9) and the changes on the topological nodal-line semimetal are negligible. This result is attributed to the fact that the structure is mainly composed of light elements (C and N), for which spin-orbit coupling is intrinsically weak. Additionally, the maximally localized Wannier functions[59] were also constructed to confirm the result. This nodal-line semimetallic state is significantly different from previously reported COFs, as most of them are semiconductors (Figure S1), with only a few intrinsic Dirac semimetals having been discovered.[7,8] Even few have been found in metal-organic frameworks. The porous graphitic carbon nitride, C_9N_4, is another nodal-line semimetal that has been theoretically reported in porous materials.[17] It is formed by combining the two-band model of Dirac fermions and the three-band model of Kagome bands to create a five-band model. Regrettably, its semimetallic property is topologically trivial. Consequently, we further examine the topological nature of the nodal-line semimetal by calculating the drumhead edge states and the topological index (Berry phase).[16,56,58] The edge states (Figure 2H) connecting two Dirac points and the Berry phase π indicate that the topological nodal-line semimetal is non-trivial.[60]

Topological nodal-line semimetal state transition from HBTP-COF to HBAT-COF monolayers by isoelectronic species

In addition to finding its topological nature, we further explore the origin of the topological nodal-line semimetal. In the band structures of both HBAT-COF and HBTP-COF monolayers, there are a total of six bands around the Fermi level, which are well separated from other bands (Figures 2A-B and 3A). These six bands consist of two sets of face-to-face Kagome bands above and below the Fermi level, which we refer to as the six-band model, to be exact, the diatomic Kagome band model. The “flat bands” in the Kagome bands exhibit significant dispersion, mainly owing to the inclusion of long-range electron coupling from delocalized π bonds between atoms in the DFT calculations, especially when influenced by higher-energy orbitals at closer distances, such as p orbitals of Si atoms. The similarly distinct six bands near the Fermi level and the resulting band structure are commonly found in the so-called Star lattice[18,19,61] and are sometimes referred to as diatomic Kagome lattices[21,22] owing to the presence of two sets of Kagome bands. For HBAT-COF and HBTP-COF monolayers, we indeed observe that their primitive cells are composed of three identical linkers (including the C atoms in the knots of Figure 3A) with D_{2h} point group, and both the linker molecules' LUMO and HOMO are non-degenerate. In addition, the primitive cells have C3 rotation symmetric monomers based on the knots, satisfying the basic requirement of the six-band model.[20] Meanwhile, isoelectronic species confer their similar LUMO (HOMO) and the band number in the calculation. Importantly, there is a significant energy gap between HOMO (LUMO) and HOMO-1(LUMO+1) levels (Figures 2E-F), which is the reason that the six bands are separate from the other bands.

In a honeycomb-like lattice, the occupancy of the three identical HOMOs (LUMOs) in the primitive cell forms a Kagome lattice (Scheme 1D), leading to the formation of the isolated lower (upper) three-band (Kagome) model with suitable structural symmetry.[6,12] According to the partial charge density plots of the other two bands that are further away from the Fermi level (Figure S10), we also confirm that they are formed by only the HOMOs (LUMOs) of the linker in HBAT-COF and HBTP-COF monolayers. In light of the above analysis, we have ascertained that the honeycomb COFs connected by heteroacene units can form a six-band model, whereas the six-band model encompasses different configurations in the form of semicondutor[6,20] (Figure S11). A straightforward and expeditious approach to discern these configurations involves assessing the degeneracy of the LUMO (LUMO+1) and HOMO (HOMO-1) levels from the monomer with C3 rotation symmetry within the Star lattice (Figure 3B and Figure S12). The degeneracy at the Γ point often persists in the energy band structure of the resulting COFs.[20] Furthermore, a deeper analysis of the structural MO hybridization and symmetry reveals that the diatomic Kagome model of HBAT-COF monolayer is notably scarce. To date, all atoms within (hetero)acene in corresponding structures have featured sp^2 hybridized orbitals (Figure 3C), with the p_z orbitals being half-filled, such as benzo-CMPs[62], C2P-5[29], and aza-COF-2[32] in Figure 3.

We observe that in the HBTP-COF monolayer, the upper three bands and the lower three bands are well-separated, with the smallest distance at the same Γ point, that is, forming a narrow direct bandgap. The two sets of Dirac bands of the diatomic Kagome bands in the HBTP-COF monolayer will intersect if

the upper three bands and the lower three bands can be brought closer together. HBAT-COF achieves the effect by replacing the C-H groups in the linker of HBTP-COF with the isoelectronic pyridinic-N atoms. From a physical perspective, we can also treat the linker (including the C atoms in the knot) as a diatomic molecule with only two single-orbital contributions (e.g., p_z in Figure 3D) near the Fermi level. By constructing a tight-binding model for the diatomic Kagome lattice and establishing the Hamiltonian matrix, the requirements can be determined for the diatomic Kagome band model (Tight-binding calculations of diatomic Kagome lattices in Supplemental Information).[20] In the analysis of the band structures of HBTP-COF and HBAT-COF monolayers, we have determined the on-site energies (ε) and hopping energies (t_0 /t_1 and t_2) associated with their p_z orbitals (Figure S13). The decreased t_0 and the increased $t_1(\varepsilon)$ make the upper three bands and the lower three bands close, presenting the increase of bandwidth in the upper three bands and the rise of the lower three bands.

Furthermore, as depicted in Figure 3E-3G, the band structures of benzo-CMP[62], C2P-5[29], and aza-COF-2[32] indicate that N atoms exert a limited influence on decreasing the band gap of COFs derived from benzo-CMP. Inversely, aza-COF-2 demonstrates a minor enhancement in the band gap compared to benzo-CMP. In comparison with benzo-CMP, the HBTP-COF monolayer displays a substantial decrease in the band gap, which is attributed to the heavy element effect of Si and Br atoms (Figure 3H). In the COFs primarily composed of carbon atoms, elements from the same group with a larger atomic number have the same number of valence electrons in their outermost shell. The valence electrons can form similar sp^2 hybridized orbitals and offer larger on-site energy, reducing the band gap between the upper three bands and the lower three bands. Br atoms make a relatively small contribution to the composition of the six-band model, but their high-energy outer orbital plays a guiding role in approaching the Fermi level for the composite six-band model, similar to Si atoms. Therefore, the Si-Br unit is regarded as the principal factor responsible for the topological phase transition from the semiconducting HBTP-COF to the nodal-line semimetallic HBAT-COF (Figure 3h). Additionally, the isoelectronic pyridinic-N is hypothesized to induce a unique coupling effect between the p_z orbitals in conjunction with the Si-Br unit, thereby facilitating the semimetallic topological phase transition in the tunable six-band model of HBAT-COF through the substitution of C-H with pyridinic-N in HBTP-COF. Moreover, our investigation extends to the role of the Si-Br unit in alternative six-band models. Computational results reveal that in the case of HFB/BT-COF, the substitution of the central C-H unit in the linker with the Si-Br unit does not precipitate a topological phase transition. Instead, it leads to a significant increase in the band gap compared with HBAT-COF (Figure S14). This observation can be ascribed to the propensity of sulfur atoms to form sp^3 hybrids, which diminishes the overlap with orbitals from sp^2-hybridized atoms, thereby impeding electronic transport.

Composition-dependent topological semimetal states in disilabenzene-linked COF monolayers

From the above analysis, we have learned that the Si-Br unit provides a groundbreaking premise for the formation of topological semimetals in the normally insulating COFs, the band structure of which features composite band models around the Fermi level (Figure 4A). The substitution of C-H with isoelectronic pyridinic-N, i.e., the transition from benzene to pyrazine in the linker, realizes the topological semimetallic state, primarily by intersecting the upper three bands with the lower three bands based on HBTP-COF and HBAT-COF (Figures 4B and 4D). Therefore, we consider the influence of different N contents on the band structure of disilabenzene-linked COFs. Since HBTP and HBAT organic units have the same terminal functional groups, they can be easily combined through similar chemical reactions, similar to the combination of elements in the same group with the same number of valence electrons in inorganic materials.[63] Thus, we focus on the most common combination of HBTP/HBAT = 1:1 (Figure 4C and Figure S15), with the two elements distributed alternately in the hexagon vertex (referred to as $C_5NHSiBr$), the structural configuration of which has the minimum energy in the isomers. First-principles calculations show that its band structure also forms a six-band model similar to those of HBTP-COF and HBAT-COF. However, due to the reduction in symmetry (from D_{6h} symmetry to D_{3h} symmetry),[12] one of the two degenerate conduction bands (at the Γ point) in the upper three bands has broken away from the bottom VB at the K point, eliminating the degeneracy (Figure S15B). The bottom CB is also tangent to the top VB

of the lower three bands at the Γ point, forming a quadratic linear Dirac semimetallic state (Figure 4E). Notably, the quadratic linear Dirac degeneracy point in $C_5NHSiBr$ is unstable, and examples in inorganic materials have shown that non-trivial topological insulating states may emerge at the degeneracy point.[64] This implies that when considering SOC, a bandgap may open at this point, which is indeed confirmed by the calculation result (Figure S15C).

In addition, over recent years, multiple N-containing heteroacene-linked COFs[29,30,32-36] (Figure S1) have been synthesized with triphenylene-derived molecules (including HBTP), which show great suitability. It has inspired us to discover another approach to attain new intrinsic topological states in COFs with Br-substituted trinaphthylenes, i.e., 2,3,6,7,10,11-hexabromotrinaphthylene (HBTT). By combining HBTP and HBTT with Si (Figures 4G and S16C), we can obtain HBTP/HBTT-COF (C_8H_3SiBr). Band structure calculations reveal that it is also a quadratic linear semimetal (Figure S16D). Similarly, its structure exhibits symmetry reduction, leading to the complete disappearance of the Dirac linear degeneracy point in the two sets of Kagome bands. When HBTT reacts with Si alone (Figures 4G and S16E), it can generate HBTT-COF ($C_{10}H_4SiBr$). It possesses the same symmetry as HBAT-COF and a similar nodal-line semimetal formed by the diatomic Kagome model (Figure S16F). Note that we can also attain another nodal-line semimetal by replacing a benzene unit in the linker of HBTP/HBTT-COF (Figures S16G-16H) with a pyrazine. By constructing hydrocarbon COFs corresponding to HBTP/HBTT-COF and HBTT-COF with naphthacene and pentacene as linkers (analogous to anthracene-based benzo-CMP[62] in Figure 3E), respectively, and comparing their band structure with those of HBTP/HBTT-COF and HBTT-COF (Figure S17), we find that the Si-Br unit also has a direct effect on altering the topological state in the diatomic Kagome band model, without the assistance of the pyrazine unit. The relevant information of the above-mentioned (hetero)acene-linked COFs is presented in Table S1.

All of these findings demonstrate that the Si-Br unit has the potential to alter the topological state in honeycomb acene-linked hydrocarbon COFs. The most important reason lies in the heavy element effect of the two elements. Consequently, considering the elements involved in the study of covalent organic materials (including three-dimensional ones), the fourth main group includes Ge, and the halogen group includes F and Cl. The former has already been synthesized in organic molecules like 1,4-Digermabenzene. The latter two are also relatively common in COFs. We consider replacing Br with Cl, F, and H, as well as replacing Si with Ge to form different COFs. Band structure calculations show that when Br is replaced with F and H, the resulting new COFs (i.e., C_4N_2SiF and C_4N_2SiH) are, respectively, similar to HBAT-COF as the nodal-line semimetal and HBTP as the low-bandgap semiconductor; whereas all new COFs (i.e., C_4N_2GeH, C_4N_2GeF, C_4N_2GeCl, and C_4N_2GeBr) formed by replacing Si with Ge are nodal-line semimetals. This demonstrates that Si and its isoelectronic elements with larger atomic numbers have a significant impact on the structural properties. The larger the atomic number, the stronger the effect on drawing the two sets of Kagome bands closer together within the six-band model. However, when we replace Si with Ge in HBTP-COF, forming C_6H_2GeBr, we find that without the presence of N atoms, Ge or Br alone is insufficient to modify the topological state of the structure, further showing the supporting role of N atoms.

DISCUSSION

To propose a rational design concept for the realization of new topological semimetallic COFs based on composite band models, we designed a new honeycomb disilabenzene-linked COF (named HBAT-COF). Due to the identical terminal functional groups (-Br) between HBAT and HBTP molecules, the realization of HBAT-COF is endowed with high feasibility by the synthesis of HBTP-COF. Through the calculations of the corresponding ELF, elastic constants, and stable phonon spectrum of HBAT-COF, we further confirm the high stability of HBAT-COF. Computational band structure and electronic states analysis reveal that HBAT-COF is a topological nodal-line semimetallic material. Subsequently, topological structure and frontier molecular orbital theory analysis indicate that the semimetallic state is formed by a set of diatomic Kagome bands of six-band models above and below the Fermi level in the Star lattice. After the comparisons between structural components of honeycomb heteroacene-linked COFs, it is found that the Si-Br units play a pivotal role in transforming a semiconductive composite band model into that of a nodal-line

semimetal. The presence of pyridinic-N alone is insufficient to orchestrate the topological phase transition within the composite band model; however, the synergistic interplay between pyridinic-N and the Si-Br unit has successfully induced a semimetallic state in HBAT-COF. This architectural configuration fosters the formation of diatomic Kagome bands at the Fermi energy level. Furthermore, by modifying the linkers in the COF, i.e., the control of pyridinic-N and acenes, it is feasible to design a series of disilabenzene-linked COFs that inherently exhibit topological semimetallic properties. The Si-Br unit's ability to facilitate the transition from a semiconductive composite band model to a semimetal offers a novel avenue for uncovering additional topological states within COFs, which are predominantly characterized by normally insulating states.

METHODS

Structural optimization and electronic band calculations were carried out within the framework of density functional theory (DFT) using the Vienna *ab initio* simulation package (VASP).[65] The Perdew–Burke–Ernzerhof (PBE) functional of generalized gradient approximation was adopted. The projector-augmented wave method was utilized to describe ion-electron interactions. The plane-wave energy cutoff was set to 600 eV, and the energy convergence criterion in the self-consistency process was 10^{-5} eV. A 20 Å thick slab layer was introduced along the direction to prevent interactions between periodic images. The Brillouin zone was sampled with a resolution of 0.025 × 2π $Å^{-1}$. The phonon spectrum was computed using a supercell with the Phonopy code. Molecular properties were calculated using pre- and post-processing tools qvasp[66] and VASPKIT[67]. Topological edge states and Berry phase were calculated using the WANNIER90 code,[68,69] where a tight-binding Hamiltonian based on maximally localized Wannier functions was fitted to the first-principles band structure.

RESOURCE AVAILABILITY

Lead contact

Further information and resource requests should be sent to the lead contact, Hongyan Wang (hongyanw@swjtu.edu.cn).

Materials availability

All unique materials generated in this study are available from the lead contact with a completed materials transfer agreement.

Data and code availability

All data are available in the article and its supplemental information files or from the corresponding authors upon request.

ACKNOWLEDGMENTS

This work was supported by the Sichuan Science and Technology Program (2022ZYD0024; 2021YFG0228), the China Scholarship Council, and the A*STAR Computational Resource Centre through the use of its high-performance computing facilities.

AUTHOR CONTRIBUTIONS

X. C. and J. Z. conceived the idea, performed the DFT calculations, and wrote the original draft. P. K and W. Y installed and tested the software. H. Q. and Y. N. analyzed the data. Y. C. and H. W. reviewed and edited the paper.

DECLARATION OF INTERESTS

The authors declare no competing financial interest.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at

REFERENCES

1. Vergniory, M.G., Elcoro, L., Felser, C., Regnault, N., Bernevig, B.A., and Wang, Z. (2019). A complete catalogue of high-quality topological materials. Nature *566*, 480-485. https://doi.org/10.1038/s41586-019-0954-4.
2. Tang, F., Po, H.C., Vishwanath, A., and Wan, X. (2019). Comprehensive search for topological materials using symmetry indicators. Nature *566*, 486-489. https://doi.org/10.1038/s41586-019-0937-5.
3. Zhang, T.T., Jiang, Y., Song, Z.D., Huang, H., He, Y.Q., Fang, Z., Weng, H.M., and Fang, C. (2019). Catalogue of topological electronic materials. Nature *566*, 475-479. https://doi.org/10.1038/s41586-019-0944-6.
4. Huang, N., Wang, P., and Jiang, D. (2016). Covalent organic frameworks: a materials platform for structural and functional designs. Nat. Rev. Mater. *1*, 1-19. https://doi.org/10.1038/natrevmats.2016.68.
5. Liang, R.R., Jiang, S.Y., A, R.H., and Zhao, X. (2020). Two-dimensional covalent organic frameworks with hierarchical porosity. Chem. Soc. Rev. *49*, 3920-3951. https://doi.org/10.1039/d0cs00049c.
6. Ni, X., Li, H., Liu, F., and Bredas, J.L. (2022). Engineering of flat bands and Dirac bands in two-dimensional covalent organic frameworks (COFs): relationships among molecular orbital symmetry, lattice symmetry, and electronic-structure characteristics. Mater. Horiz. *9*, 88-98. https://doi.org/10.1039/d1mh00935d.
7. Jing, Y., and Heine, T. (2019). Two-Dimensional Kagome Lattices Made of Hetero Triangulenes Are Dirac Semimetals or Single-Band Semiconductors. J. Am. Chem. Soc. *141*, 743-747. https://doi.org/10.1021/jacs.8b09900.
8. Adjizian, J.-J., Briddon, P., Humbert, B., Duvail, J.-L., Wagner, P., Adda, C., and Ewels, C. (2014). Dirac Cones in two-dimensional conjugated polymer networks. Nat. Commun. *5*, 5842, 5842. https://doi.org/10.1038/ncomms6842.
9. Wang, Z.F., Liu, Z., and Liu, F. (2013). Organic topological insulators in organometallic lattices. Nat. Commun. *4*, 1471. https://doi.org/10.1038/ncomms2451.
10. Jiang, W., Ni, X., and Liu, F. (2021). Exotic Topological Bands and Quantum States in Metal-Organic and Covalent-Organic Frameworks. Acc. Chem. Res. *54*, 416-426. https://doi.org/10.1021/acs.accounts.0c00652.
11. Schoop, L.M., Pielnhofer, F., and Lotsch, B.V. (2018). Chemical Principles of Topological Semimetals. Chem. Mater. *30*, 3155-3176. https://doi.org/10.1021/acs.chemmater.7b05133.
12. Thomas, S., Li, H., Zhong, C., Matsumoto, M., Dichtel, W.R., and Bredas, J.-L. (2019). Electronic Structure of Two-Dimensional π-Conjugated Covalent Organic Frameworks. Chem. Mater. *31*, 3051-3065. https://doi.org/10.1021/acs.chemmater.8b04986.
13. Zhou, M., Ming, W., Liu, Z., Wang, Z., Li, P., and Liu, F. (2014). Epitaxial growth of large-gap quantum spin Hall insulator on semiconductor surface. Proc. Natl. Acad. Sci. *111*, 14378-14381. https://doi.org/10.1073/pnas.1409701111.
14. Zhou, T., Wu, X., Deng, T., Li, H., Gao, Z., and Shi, W. (2023). Atomistic design of two-dimensional covalent organic frameworks with high thermoelectric performance. J. Mater. Chem. A *11*, 15821-15832. https://doi.org/10.1039/d3ta02146g.
15. Wang, S., Xu, X., Yue, Y., Yu, K., Shui, Q., Huang, N., and Chen, H. (2020). Semiconductive Covalent Organic Frameworks: Structural Design, Synthesis, and Application. Small Struct. *1*, 2000021. https://doi.org/https://doi.org/10.1002/sstr.202000021.
16. Singh, B., Lin, H., and Bansil, A. (2023). Topology and Symmetry in Quantum Materials. Adv. Mater. *35*, e2201058. https://doi.org/10.1002/adma.202201058.

17. Chen, H., Zhang, S., Jiang, W., Zhang, C., Guo, H., Liu, Z., Wang, Z., Liu, F., and Niu, X. (2018). Prediction of two-dimensional nodal-line semimetals in a carbon nitride covalent network. J. Mater. Chem. A *6*, 11252-11259. https://doi.org/10.1039/c8ta02555j.
18. Chen, M., and Wan, S. (2012). The quantum anomalous Hall effect on a star lattice with spin-orbit coupling and an exchange field. J. Phys. Condens. Matter. *24*, 325502, 325501-325506. https://doi.org/10.1088/0953-8984/24/32/325502.
19. Chen, W.-C., Liu, R., Wang, Y.-F., and Gong, C.-D. (2012). Topological quantum phase transitions and topological flat bands on the star lattice. Phys. Rev. B *86*, 085311-085314. https://doi.org/10.1103/PhysRevB.86.085311.
20. Hu, T., Zhang, T., Mu, H., and Wang, Z. (2022). Intrinsic Second-Order Topological Insulator in Two-Dimensional Covalent Organic Frameworks. J. Phys. Chem. Lett. *13*, 10905-10911. https://doi.org/10.1021/acs.jpclett.2c02683.
21. Zhou, Y., Sethi, G., Liu, H., Wang, Z., and Liu, F. (2022). Excited quantum anomalous and spin Hall effect: dissociation of flat-bands-enabled excitonic insulator state. Nanotechnology *33*, 415001-415007. https://doi.org/10.1088/1361-6528/ac7a4b.
22. Sethi, G., Zhou, Y., Zhu, L., Yang, L., and Liu, F. (2021). Flat-Band-Enabled Triplet Excitonic Insulator in a Diatomic Kagome Lattice. Phys. Rev. Lett. *126*, 196403. https://doi.org/10.1103/PhysRevLett.126.196403.
23. Ni, X., Huang, H., and Bredas, J.L. (2022). Organic Higher-Order Topological Insulators: Heterotriangulene-Based Covalent Organic Frameworks. J. Am. Chem. Soc. *144*, 22778-22786. https://doi.org/10.1021/jacs.2c11229.
24. Zhang, T., Hu, T., Zhang, Y., and Wang, Z. (2023). Pseudospin Polarized Dual-Higher-Order Topology in Hydrogen-Substituted Graphdiyne. Nano Lett. *23*, 8319-8325. https://doi.org/10.1021/acs.nanolett.3c02684.
25. Liu, F., Deng, H.Y., and Wakabayashi, K. (2019). Helical Topological Edge States in a Quadrupole Phase. Phys. Rev. Lett. *122*, 086804. https://doi.org/10.1103/PhysRevLett.122.086804.
26. Hu, T., Zhong, W., Zhang, T., Wang, W., and Wang, Z.F. (2023). Identifying topological corner states in two-dimensional metal-organic frameworks. Nat. Commun. *14*, 7092. https://doi.org/10.1038/s41467-023-42884-1.
27. Xue, Y., Huan, H., Zhao, B., Luo, Y., Zhang, Z., and Yang, Z. (2021). Higher-order topological insulators in two-dimensional Dirac materials. Phys. Rev. Res. *3*, L042044-042047. https://doi.org/10.1103/PhysRevResearch.3.L042044.
28. Liu, Y., Liu, X., Su, A., Gong, C., Chen, S., Xia, L., Zhang, C., Tao, X., Li, Y., Li, Y., et al. (2024). Revolutionizing the structural design and determination of covalent-organic frameworks: principles, methods, and techniques. Chem. Soc. Rev. *53*, 502-544. https://doi.org/10.1039/d3cs00287j.
29. Jhulki, S., Kim, J., Hwang, I.-C., Haider, G., Park, J., Park, J.Y., Lee, Y., Hwang, W., Dar, A.A., Dhara, B., et al. (2020). Solution-Processable, Crystalline π-Conjugated Two-Dimensional Polymers with High Charge Carrier Mobility. Chem *6*, 2035-2045. https://doi.org/10.1016/j.chempr.2020.05.026.
30. Wang, J., Liu, Z., Wang, H.-g., Cui, F., and Zhu, G. (2022). Integrated pyrazine-based porous aromatic frameworks/carbon nanotube composite as cathode materials for aqueous zinc ion batteries. Chem. Eng. J. *450*, 138051-138059. https://doi.org/10.1016/j.cej.2022.138051.

31. Ong, W.J., and Swager, T.M. (2018). Dynamic self-correcting nucleophilic aromatic substitution. Nat. Chem. *10*, 1023-1030. https://doi.org/10.1038/s41557-018-0122-8.
32. Meng, Z., Aykanat, A., and Mirica, K.A. (2018). Proton Conduction in 2D Aza-Fused Covalent Organic Frameworks. Chem. Mater. *31*, 819-825. https://doi.org/10.1021/acs.chemmater.8b03897.
33. Kandambeth, S., Jia, J., Wu, H., Kale, V.S., Parvatkar, P.T., Czaban‐Jóźwiak, J., Zhou, S., Xu, X., Ameur, Z.O., Abou‐Hamad, E., et al. (2020). Covalent Organic Frameworks as Negative Electrodes for High‐Performance Asymmetric Supercapacitors. Advanced Energy Mater. *10*, 2001673-2001679. https://doi.org/10.1002/aenm.202001673.
34. Meng, L., Ren, S., Ma, C., Yu, Y., Lou, Y., Zhang, D., and Shi, Z. (2019). Synthesis of a 2D nitrogen-rich pi-conjugated microporous polymer for high performance lithium-ion batteries. Chem. Commun. *55*, 9491-9494. https://doi.org/10.1039/c9cc04036f.
35. Parvatkar, P.T., Kandambeth, S., Shaikh, A.C., Nadinov, I., Yin, J., Kale, V.S., Healing, G., Emwas, A.-H., Shekhah, O., Alshareef, H.N., et al. (2023). A Tailored COF for Visible-Light Photosynthesis of 2,3-Dihydrobenzofurans. J. Am. Chem. Soc. *145*, 5074-5082. https://doi.org/10.1021/jacs.2c10471.
36. Noh, H.-J., Chung, S., Okyay, M.S., Im, Y.-K., Kim, S.-W., Kweon, D.-H., Jeon, J.-P., Seo, J.-M., Kim, N.-H., Yu, S.-Y., et al. (2022). Hydrophenazine-linked two-dimensional ladder-type crystalline fused aromatic network with high charge transport. Chem *8*, 3130-3144. https://doi.org/10.1016/j.chempr.2022.08.001.
37. Li, S., Liu, Y., Dai, L., Li, S., Wang, B., Xie, J., and Li, P. (2022). A stable covalent organic framework cathode enables ultra-long cycle life for alkali and multivalent metal rechargeable batteries. Energy Storage Mater. *48*, 439-446. https://doi.org/10.1016/j.ensm.2022.03.033.
38. Kim, J., Kim, S., Park, J., Kang, S., Seo, D.J., Park, N., Lee, S., Kim, J.J., Lee, W.B., Park, J., and Lee, J.C. (2024). Covalent-Frameworked 2D Crown Ether with Chemical Multifunctionality. J. Am. Chem. Soc. *146*, 4532-4541. https://doi.org/10.1021/jacs.3c11182.
39. Cai, X., Chen, J., Wang, H., Ni, Y., Chen, Y., and King, R.B. (2023). C(3)N(2): the missing part of highly stable porous graphitic carbon nitride semiconductors. Nanoscale Horiz. *8*, 662-673. https://doi.org/10.1039/d2nh00440b.
40. Iqbal, R., Majeed, M.K., Hussain, A., Ahmad, A., Ahmad, M., Jabbar, B., Akbar, A.R., Ali, S., Rauf, S., and Saleem, A. (2023). Boosting the Crystallinity of Novel Two-Dimensional Hexamine Dipyrazino Quinoxaline-Based Covalent Organic Framework for Electrical Double-Layer Supercapacitor. Mater. Chem. Front. *7*, 2464-2474. https://doi.org/10.1039/d3qm00169e.
41. Zhang, B., Wei, M., Mao, H., Pei, X., Alshmimri, S.A., Reimer, J.A., and Yaghi, O.M. (2018). Crystalline Dioxin-Linked Covalent Organic Frameworks from Irreversible Reactions. J. Am. Chem. Soc. *140*, 12715-12719. https://doi.org/10.1021/jacs.8b08374.
42. Xu, S., Wang, C., Song, T., Yao, H., Yang, J., Wang, X., Zhu, J., Lee, C.S., and Zhang, Q. (2023). A Dithiin-Linked Covalent Organic Polymer for Ultrahigh Capacity Half-Cell and Symmetric Full-Cell Sodium-Ion Batteries. Adv. Sci. *10*, e2304497. https://doi.org/10.1002/advs.202304497.
43. Kim, S.W., Jung, H., Okyay, M.S., Noh, H.J., Chung, S., Kim, Y.H., Jeon, J.P., Wong, B.M., Cho, K., Seo, J.M., et al. (2023). Hexaazatriphenylene-Based Two-Dimensional Conductive Covalent Organic Framework with Anisotropic Charge Transfer. Angew. Chem. Int. Ed. Engl. *62*, e202310560. https://doi.org/10.1002/anie.2

02310560.
44. Guo, H.M., and Franz, M. (2009). Topological insulator on the kagome lattice. Phys. Rev. B *80*, 113102-113109. https://doi.org/10.1103/PhysRevB.80.113102.
45. Wei, L., Zhang, X., Liu, X., Zhou, H., Yang, B., and Zhao, M. (2017). Tunable Dirac cones in two-dimensional covalent organic materials: C2N6S3 and its analogs. RSC Adv. *7*, 52065-52070. https://doi.org/10.1039/c7ra10950d.
46. Iqbal, R., Ali, S., Yasin, G., Ibraheem, S., Tabish, M., Hamza, M., Chen, H., Xu, H., Zeng, J., and Zhao, W. (2022). A novel 2D Co3(HADQ)2 metal-organic framework as a highly active and stable electrocatalyst for acidic oxygen reduction. Chem. Eng. J. *430*, 132642-132648. https://doi.org/10.1016/j.cej.2021.132642.
47. Wu, M., Zhao, Y., Sun, B., Sun, Z., Li, C., Han, Y., Xu, L., Ge, Z., Ren, Y., Zhang, M., et al. (2020). A 2D covalent organic framework as a high-performance cathode material for lithium-ion batteries. Nano Energy *70*, 104498-104498. https://doi.org/10.1016/j.nanoen.2020.104498.
48. Guan, X., Li, H., Ma, Y., Xue, M., Fang, Q., Yan, Y., Valtchev, V., and Qiu, S. (2019). Chemically stable polyarylether-based covalent organic frameworks. Nat. Chem. *11*, 587-594. https://doi.org/10.1038/s41557-019-0238-5.
49. Chen, X.L., Xie, M., Zheng, Z.L., Luo, X., Jin, H., Chen, Y.F., Yang, G.Z., Bin, D.S., and Li, D. (2023). Multiple Accessible Redox-Active Sites in a Robust Covalent Organic Framework for High-Performance Potassium Storage. J. Am. Chem. Soc. *145*, 5105-5113. https://doi.org/10.1021/jacs.2c11264.
50. Mahmood, J., Ahmad, I., Jung, M., Seo, J.M., Yu, S.Y., Noh, H.J., Kim, Y.H., Shin, H.J., and Baek, J.B. (2020). Two-dimensional amine and hydroxy functionalized fused aromatic covalent organic framework. Commun. Chem. *3*, 31. https://doi.org/10.1038/s42004-020-0278-1.
51. Li, T., Zhang, P.L., Dong, L.Z., and Lan, Y.Q. (2024). Post-synthetic Rhodium (III) Complexes in Covalent Organic Frameworks for Photothermal Heterogeneous C-H Activation. Angew. Chem. Int. Ed. Engl. *63*, e202318180. https://doi.org/10.1002/anie.202318180.
52. Haldar, S., Wang, M., Bhauriyal, P., Hazra, A., Khan, A.H., Bon, V., Isaacs, M.A., De, A., Shupletsov, L., Boenke, T., et al. (2022). Porous Dithiine-Linked Covalent Organic Framework as a Dynamic Platform for Covalent Polysulfide Anchoring in Lithium-Sulfur Battery Cathodes. J. Am. Chem. Soc. *144*, 9101-9112. https://doi.org/10.1021/jacs.2c02346.
53. Ouyang, Z., Tranca, D., Zhao, Y., Chen, Z., Fu, X., Zhu, J., Zhai, G., Ke, C., Kymakis, E., and Zhuang, X. (2021). Quinone-Enriched Conjugated Microporous Polymer as an Organic Cathode for Li-Ion Batteries. Acs Appl. Mat. Interfaces *13*, 9064-9073. https://doi.org/10.1021/acsami.1c00867.
54. Zhang, M., Tong, Y., Sun, Z., Wang, J., Lin, Y., Kang, F., Zhang, Q., and Huang, W. (2023). Two-Dimensional Covalent Organic Framework with Synergistic Active Centers for Efficient Electrochemical Sodium Storage. Chem. Mater. *35*, 4873-4881. https://doi.org/10.1021/acs.chemmater.3c00983.
55. Sun, K., Silveira, O.J., Ma, Y., Hasegawa, Y., Matsumoto, M., Kera, S., Krejčí, O., Foster, A.S., and Kawai, S. (2023). On-surface synthesis of disilabenzene-bridged covalent organic frameworks. Nat. Chem. *15*, 136-142. https://doi.org/10.1038/s41557-022-01071-3.
56. Fang, C., Weng, H.M., Dai, X., and Fang, Z. (2016). Topological nodal line semimetals. Chinese Physics B *25*, 117106. https://doi.org/10.1088/1674-1056/25/11/117106.

57. Xu, Q., Yu, R., Fang, Z., Dai, X., and Weng, H. (2017). Topological nodal line semimetals in the CaP_3 family of materials. Phys. Rev. B *95*, 045136. https://doi.org/10.1103/PhysRevB.95.045136.
58. Ni, X., Huang, H., and Brédas, J.-L. (2022). Emergence of a Two-Dimensional Topological Dirac Semimetal Phase in a Phthalocyanine-Based Covalent Organic Framework. Chem. Mater. *34*, 3178-3184. https://doi.org/10.1021/acs.chemmater.1c04317.
59. Marzari, N., and Vanderbilt, D. (1997). Maximally localized generalized Wannier functions for composite energy bands. Phys. Rev. B *56*, 12847-12865. https://doi.org/10.1103/PhysRevB.56.12847.
60. Pan, B., Zhou, P., Xiao, H., Yang, X., and Sun, L. (2024). Prediction of two-dimensional carbon nitride materials with semimetal states and flat bands. Carbon *228*, 119277. https://doi.org/10.1016/j.carbon.2024.119277.
61. Guo, X., Liu, Z., Liu, B., Li, Q., and Wang, Z. (2020). Non-Collinear Orbital-induced Planar Quantum Anomalous Hall Effect. Nano Lett. *20*, 7606-7612. https://doi.org/10.1021/acs.nanolett.0c03136.
62. Yang, Z.-D., Wu, W., and Zeng, X.C. (2014). Electronic and transport properties of porous graphenes: two-dimensional benzo- and aza-fused π-conjugated-microporous-polymer sheets and boron–nitrogen co-doped derivatives. J. Mater. Chem. C *2*, 2902-2907. https://doi.org/10.1039/c3tc32363c.
63. Cai, X., Chen, Y., Sun, B., Chen, J., Wang, H., Ni, Y., Tao, L., Wang, H., Zhu, S., Li, X., et al. (2019). Two-dimensional Blue-AsP monolayers with tunable direct band gap and ultrahigh carrier mobility show promising high-performance photovoltaic properties. Nanoscale *11*, 8260-8269. https://doi.org/10.1039/C9NR01261C.
64. Zhang, H., Wang, Y., Yang, W., Zhang, J., Xu, X., and Liu, F. (2021). Selective Substrate-Orbital-Filtering Effect to Realize the Large-Gap Quantum Spin Hall Effect. Nano Lett. *21*, 5828-5833. https://doi.org/10.1021/acs.nanolett.1c01765.
65. Kresse, G., and Furthmüller, J. (1996). Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput. Mater. Sci. *6*, 15-50. https://doi.org/https://doi.org/10.1016/0927-0256(96)00008-0.
66. Yi, W., Tang, G., Chen, X., Yang, B., and Liu, X. (2020). qvasp: A flexible toolkit for VASP users in materials simulations. Comput. Phys. Commun. *257*, 107535. https://doi.org/10.1016/j.cpc.2020.107535.
67. Wang, V., Xu, N., Liu, J.-C., Tang, G., and Geng, W.-T. (2021). VASPKIT: A user-friendly interface facilitating high-throughput computing and analysis using VASP code. Comput. Phys. Commun. *267*, 108033. https://doi.org/10.1016/j.cpc.2021.108033.
68. Mostofi, A.A., Yates, J.R., Pizzi, G., Lee, Y.-S., Souza, I., Vanderbilt, D., and Marzari, N. (2014). An updated version of wannier90: A tool for obtaining maximally-localised Wannier functions. Comput. Phys. Commun. *185*, 2309-2310. https://doi.org/10.1016/j.cpc.2014.05.003.
69. Wu, Q., Zhang, S., Song, H.-F., Troyer, M., and Soluyanov, A.A. (2018). WannierTools: An open-source software package for novel topological materials. Comput. Phys. Commun. *224*, 405-416. https://doi.org/10.1016/j.cpc.2017.09.033.

FIGURE TITLES AND LEGENDS

Scheme 1. The semimetal band models in organic materials.

The reported (A-B) two-band, (C-D) three-band, (E-F) four-band, and (G-H) five-band models with intrinsic topological semimetal states in honeycomb-like lattices. (I) The Star lattice with six-band models in this work. The arrow shows the main constituent elements in synthesized COFs before 2023.

Figure 1. The progress of honeycomb heteroacene-linked COFs.

Schematic illustration of honeycomb heteroacene-linked COFs without (A) and with (B) edge functional groups X=O, OH, NH_2, CN, COOH, CNH_2, and halogen group (e.g., edge carbonyl groups, i.e., X is O atoms) in previous works. The COFs are normal insulators and involve N, O, and S (Se) heteroatoms. (C) Schematic illustration of honeycomb disilabenzene-linked COFs with topological semimetallic properties in this work. (D) The synthesis of the reported HBTP-COF (***Nature Chemistry 15, 136-142, 2023***) by the reaction between HBTP and Si atoms, as well as (F) the possible synthesis pathway of HBAT-COF. Schematic illustration of the honeycomb (E) HBTP-COF and (G) HBAT-COF, where the little rose-bengal cakes and the little light-blue cakes are HBTP and HBAT as the building blocks, respectively. The grey rhombus is the primitive cell.

Figure 2. Band structures of HBTP-COF and HBAT-COF monolayers.

(A-B) The atom orbital projected band structures along the high-symmetry path M(0.5, 0, 0)-K(0.3333, 0.3333, 0)-Γ(0, 0, 0)-M(0.5, 0, 0) in HBTP-COF and HBAT-COF monolayers. "**+**" and "**−**" indicate the even and odd parities of bands for C2(z) rotation symmetry (blue signs) with the z-axis as the rotation axis, C2(x) rotation symmetry (black signs) with the x-axis as the rotation axis, and σ(xz) mirror symmetry (green signs) at the Γ point near the Fermi level, respectively.

(C) The electronic states (V_1, V_2, C_1, and C_2) around Dirac crossing points (D1 and D2) in HBAT-COF monolayer.

(D) Schematic illustration of the first Brillouin zone in HBAT-COF monolayer. **a** light-blue and **b** rose-bengal solid line arrows are lattice vectors in direct space. a* and b* dotted lines are lattice vectors in reciprocal space. M_1 is a point between the high-symmetry points M and K. The orange circle is formed by the Dirac crossing points in the whole first Brillouin zone.

(E-F) The frontier MOs (irreducible representations) of disilabenzene-linked heteroacene molecules (linker units) and the wave functions of the electronic states (VBM and CBM) at the Γ point in HBTP-COF and HBAT-COF monolayers. A_u, B_{1u}, B_{gy}, and B_{gx} are irreducible representations of the MOs.

(G) Schematic illustration of the band inversion from HBTP-COF as a normal insulator to HBAT-COF as a nodal-line semimetal.

(H) Calculated surface spectrum for a semi-infinite HBAT-COF. The topologically non-trivial surface states of the two edges connecting the Dirac points are clearly visible.

Figure 3. The origin of the nodal-line semimetal in HBAT-COF monolayer.

(A) The potential Star lattice in the HBTP-COF and HBAT-COF monolayers. The linker (including C atoms in the benzene knot) is regarded as a diatomic molecule with non-degenerate HOMO (LUMO), taking HBAT-COF as an example.

(B) The energy difference and degeneracy between frontier LUMO (LUMO+1) and HOMO (HOMO-1) of the monomer with C3 rotation symmetry in the HBTP-COF monolayer.

(C) The monomer is formed by sp^2 hybridized orbitals with half-filled p_z as the schematic diagram shows.

(D) The single orbital tight-binding model interpretation from the diatomic molecule model of the linker (including C atoms in the benzene knot). t_0 /t_1 and t_2 are the nearest and the second-nearest hopping parameters of every site in the Star lattice, respectively.

(E-I) The linkers in (E) acene-linked benzo-CMP, (F-G) two N-containing heteroacene-linked COFs, (H) HBTP-COF, and (I) HBAT-COF, as well as band structures of their resulting COFs along the high symmetry path of the first Brillouin zone (Γ(0, 0, 0)-M(0.5, 0, 0)-K(0.3333, 0.3333, 0)-Γ(0, 0, 0)).

Figure 4. Two composition-controllable ways of topological states transition in the primitive cell of disilabenzene-linked COF monolayers.

(A) Semiconducting honeycomb COF monolayers and their band structures dependent on crucial composite band models above and below the Fermi level, where the two Dirac bands in the conduction bands can alone/together with different (color) flat bands form composite band models (e.g., four-, five-, six-, seven- and eight-band models) with those of valence bands. One of the ways is to realize different N contents (i.e., pyrazine units) in the linker of the COFs, such as from (B) HBTP-COF to (C) HBTP/HBAT-COF ($C_5NHSiBr$) to (D) HBAT-COF. (E) Schematic illustration of the topological state transition. The other is to increase the length of the linker in the HBTP-COF-like, such as from (F) HBTP-COF (C_6H_2SiBr) to (G) HBTP/HBTT-COF (C_8H_3SiBr) to (H) HBTT-COF ($C_{10}H_4SiBr$).