Two-dimensional (2D) topological insulators (TIs) are currently creating a surge of research activity [1–5]. In the presence of time-reversal symmetry (TRS), spin-orbit coupling (SOC) locks the momentum and spin directions of electrons in the metallic edge states of 2D TIs, leading to the quantum spin Hall (QSH) effect [6,7]. On the other hand, when a ferromagnetic (FM) exchange interaction is introduced, TRS is broken and the chemical potentials of two metallic channels with opposite spin polarizations can be unbalanced, giving rise to the quantum anomalous Hall (QAH) effect. The spin-polarized edge electron channel of QAH insulators is of crucial importance because of its incredibly precise quantization, robustness against defects, disorder and surface contamination over hundreds of micrometers, and relatively low energy consumption [6], which are highly promising in spintronic devices, quantum micrometers, and relatively low energy consumption[6]. Although computation, and low-power electronic devices.

The quantum anomalous Hall (QAH) insulator is a novel topological state of matter characterized by a nonzero quantized Hall conductivity without an external magnetic field. Using first-principles calculations, we predict the QAH state in monolayers of covalent-organic frameworks based on the newly synthesized \(X_3(C_{18}H_{12}N_6)_{2}\) structure where \(X\) represents 5d transition metal elements Ta, Re, and Ir. The \(\pi\) conjugation between \(X\) \(d_{\sigma}\) and \(d_{\pi}\) orbitals, mediated by \(N\) \(p_z\) and \(C\) \(p_z\), gives rise to a massive Dirac spectrum in momentum space with a band gap of up to 24 meV due to strong spin-orbit coupling. We show that the QAH state can appear by chemically engineering the exchange field and the Fermi level in the monolayer structure, resulting in nonzero Chern numbers. Our results suggest a reliable pathway toward the realization of a QAH phase at temperatures between 100 K and room temperature in covalent-organic frameworks.

**DOI**: 10.1103/PhysRevLett.116.096601

Two-dimensional (2D) topological insulators (TIs) are currently creating a surge of research activity [1–5]. In the presence of time-reversal symmetry (TRS), spin-orbit coupling (SOC) locks the momentum and spin directions of electrons in the metallic edge states of 2D TIs, leading to the quantum spin Hall (QSH) effect [6,7]. On the other hand, when a ferromagnetic (FM) exchange interaction is introduced, TRS is broken and the chemical potentials of two metallic channels with opposite spin polarizations can be unbalanced, giving rise to the quantum anomalous Hall (QAH) effect. The spin-polarized edge electron channel of QAH insulators is of crucial importance because of its incredibly precise quantization, robustness against defects, disorder and surface contamination over hundreds of micrometers, and relatively low energy consumption [6], which are highly promising in spintronic devices, quantum micrometers, and relatively low energy consumption[6]. Although computation, and low-power electronic devices.

The study of the QAH effect is still in its formative stage, due to the lack of suitable material realizations. Although the QAH phase has been observed in Cr- or V-doped (Bi, Sb)$_2$Te$_3$ thin films, it survives only at low temperatures (≈30–85 mK) [8,9,10,11], and the Hall conductance completely vanishes when the temperature is above 2 K [8,10,11]. Moreover, the molecular beam epitaxy synthesis method of such thin films [8–11] is expensive and thus inadequate for mass production. To date, diverse inorganic [12–19] and organic [20] materials have been theoretically proposed for the QAH effect, but the experimental observation based on these materials remains elusive due to their generic structural complexity [21,22]. Therefore, it is imperative to find more stable materials that can be fabricated using easy and inexpensive methods. Here we propose that organic 2D \(\pi\)-conjugated polymer networks could satisfy these criteria as they can be synthesized using chemical solution or vapor deposition techniques [23]. Most importantly, it is feasible to manipulate their molecular structure and the chemical elements of functional groups for desired orbital hybridization, magnetic exchange field, and/or SOC strength, all of which are essential ingredients to realize the QAH effect.

In this Letter, we demonstrate that the QAH phase can be achieved by rationally engineering the structure of the newly synthesized \(X_3(\text{HITP})_2\) covalent-organic framework (COF), where \(X\) is a transition metal and HITP is the 2, 3, 6, 7, 10, 11-hexamethylnonphenylene (C$_{18}$H$_{12}$N$_6$) functional group [24,25]. We carry out density functional theory (DFT) calculations to show that a proper 5d transition metal element (Ta, Re, or Ir) in an \(X_3(\text{HITP})_2\) monolayer gives rise to both a FM exchange field and strong SOC. To drive the system into a QAH insulating phase, the N atoms in the HITP functional group are fully or partially replaced by O atoms to tune the Fermi level \((E_F)\), so that the occupied bands have a nonzero Chern number. Our calculations show that the QAH effect can be realized if \(X = \text{Ta}\) and all N atoms are replaced by O atoms [i.e., in Ta$_3$(C$_{18}$H$_{12}$O$_6$)$_2$]. With \(E_F\) residing in a SOC-induced band gap of 24 meV, Ta$_3$(C$_{18}$H$_{12}$O$_6$)$_2$ can potentially host the QAH state at much higher temperatures than that of the previously reported QAH experiments [8–10]. Another system that can host the QAH effect is Ir$_3$(C$_{18}$H$_{12}$N$_3$O$_3$)$_2$ (i.e., \(X = \text{Ir}\) and half of the N atoms are replaced by O atoms), wherein \(E_F\) can be tuned to within an SOC-induced band gap (8 meV) via electric gating, enabling a gate-voltage tunable QAH effect. These results indicate that the structural derivatives of \(X_3(\text{HITP})_2\) are promising material realizations of a 2D magnetic TI.
We expect that these materials can expedite experimental research in the QAHE and its practical applications in electronic devices.

Our DFT calculations are performed using the *vasp* code [26] with projector augmented wave pseudopotentials [27] and Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) [28]. Other computational details can be seen in the Supplemental Material [29]. All atoms in \( X_3(\text{HITP})_2 \) monolayers are coplanar [Fig. 1(a)], thus preserving the mirror symmetry \((M_x)\) about the basal plane. The three \( X \) atoms per unit cell form a kagome lattice [Fig. 1(b)]. Among this material family, \( \text{Ni}_3(\text{HITP})_2 \) and \( \text{Cu}_3(\text{HITP})_2 \) have been recently synthesized via solution-based chemical reactions and isolated via extensive washing [24,25]. Therefore, we believe that \( X_3(\text{HITP})_2 \) with other transition metal elements should be accessible using similar processes. In this study, we focus on \( X_3(\text{HITP})_2 \), where \( X \) is a 5\( d \) transition metal from Hf to Au, as they are heavier, and hence have stronger SOC. The lattice parameters \(|a_1| = |a_2| = a\) of \( \text{Ni}_3(\text{HITP})_2 \) and \( \text{Cu}_3(\text{HITP})_2 \) are calculated as 21.91 and 21.75 Å, respectively, agreeing well with previous DFT studies [24,25,38,39]. \( a \) for \( X = 5d \) transition metal elements is listed in Table S1 in the Supplemental Material [29].

We first consider the magnetic configurations of \( X_3(\text{HITP})_2 \). Our calculations show that it energetically favors an FM state with a spontaneous magnetic moment \( \mu = 1 \mu_B \) per \( X \) atom, where \( X \) has an odd number of valence electrons \( n_X \) \((X = \text{Ta}, \text{Re}, \text{Ir}, \text{or} \ \text{Au})\), as seen in Table S1 in the Supplemental Material [29], while it favors a nonmagnetic ground state for \( X \) with an even \( n_X \) \((X = \text{Hf}, \text{W}, \text{Os}, \text{or} \ \text{Pt})\). The origin of magnetism can be understood from the low-energy band configurations (Fig. 2). States near \( E_f \) comprise the \( X \) 5\( d \) atomic orbitals and the HITP \( s \) and \( p \) orbitals. Each \( X \) atom is surrounded by four nearest-neighbor nitrogen atoms, generating a deformed square planar crystal field in the basal (N-N distance in the \( y \) direction is longer than that in the \( x \) direction, Fig. 2). By the crystal field, the \( X \) 5\( d \) orbitals \((d^{A,B,C})\) split into five distinct energy levels, denoted by \( d_{xz}^{A,B,C}, \ d_{yz}^{A,B,C}, \ d_{z^2}^{A,B,C}, \ d_{x^2−y^2}^{A,B,C}, \ \text{and} \ d_{x^2−y^2}^{A,B,C} \) from the lowest to the highest in the energy spectrum. The \( N \ p_z \) orbitals form \( \pi \) bonds with the \( X \) \( d_{xz}^{A,B,C} \) and \( d_{yz}^{A,B,C} \) orbitals, due to the same odd parity under \( M_z \) about the \( xy \) plane, while the other \( d \) orbitals, which have an even parity of \( M_z \), do not join the \( \pi \)-bond network of HITP. The interaction between \( p_z \) and \( d_{xz} \) and \( d_{yz} \) produces lower-lying bonding states (blue box in Fig. 2), which are primarily the \( p_z \) orbitals of HITP) and higher-lying antibonding states (red box in Fig. 2, which are mainly composed of the \( d_{xz}^{A,B,C} \) and \( d_{yz}^{A,B,C} \) orbitals). Next considered are the SOC of the \( X \) atoms at the \( A \), \( B \), and \( C \) sites, which coupled to the \( \pi \)-bonding network, splitting the degenerate antibonding orbitals \( d_{xz}^{A,B,C} \) and \( d_{yz}^{A,B,C} \) into discrete energy bands marked as \( d_{xz}^{1,2,3} \) and \( d_{yz}^{1,2,3} \) in Fig. 2, respectively. The highest occupied electronic bands and thus the position of \( E_f \) in Fig. 2 are determined by \( n_X \). If \( n_X \) is even, the exchange-split occupied bands are filled equally with electrons of both spins, and therefore \( \mu = 0 \mu_B \) in this material. On the contrary, if \( n_X \) is odd, in \( \text{Ta}_3(\text{HITP})_2 \) for instance, the \( d_{xz}^{A,B,C} \) bands of the three \( \text{Ta} \) atoms are each half filled, allowing for the FM spin alignment as the ground state of the system with \( \mu = 1 \mu_B \) per \( \text{Ta} \) atom. Similar phenomena occur in \( \text{Re}_3(\text{HITP})_2 \) \((d_{xz}^{A,B,C} \ \text{half filled})\), \( \text{Ir}_3(\text{HITP})_2 \) \((d_{xz}^{1,2,3} \ \text{half filled})\), and \( \text{Au}_3(\text{HITP})_2 \) \((d_{xz}^{1,2,3} \ \text{half filled})\) as well. Such an effective

---

**FIG. 1.** (a) Top view of a unit cell of \( X_3(\text{HITP})_2 \) monolayer with lattice vectors \( a_1 \) and \( a_2 \) in the \( xy \) plane; (b) a schematic showing that \( X \) atoms form a kagome lattice with three atomic sites \( A \), \( B \), and \( C \) in a unit cell; and (c) the first Brillouin zone of the structure, with reciprocal lattice vectors \( b_1 \) and \( b_2 \) and high-symmetry points \( \Gamma \), \( M \), and \( K \).

**FIG. 2.** A schematic of the electronic band structure around the \( E_f \) that explains the origin of ferromagnetism in certain \( X_3(\text{HITP})_2 \) monolayers with magnetic exchange field \( \Delta \).
magnetic exchange field ($\Delta$) leads to an energy splitting between the majority (up, $\uparrow$) and minority (down, $\downarrow$) spin states. The strength of $\Delta$, defined as half the energy splitting between the up- and down-spin states of the highest occupied band, decreases as $n_X$ increases: it is 877, 752, 216, and 0 meV for $X = \text{Ta, Re, Ir, and Au}$, respectively. The FM Ta$_3$(HITP)$_2$, Re$_3$(HITP)$_2$, and Ir$_3$(HITP)$_2$ are candidate systems that can host the QAH effect.

Having described the magnetic ground states of $X_3$(HITP)$_2$ monolayers, we turn to their electronic properties. To realize the QAH phase in these materials, it is desirable to have their $E_f$ within or close to the SOC-induced band gaps, which occur among the antibonding $d^1_{xy}, d^1_{yz}, d^1_{dz^2}$ ($\uparrow$ or $\downarrow$) and $d^1_{xy}, d^1_{yz}, d^1_{dz^2}$ ($\uparrow$ or $\downarrow$). The Fermi levels of Ta$_3$(HITP)$_2$, Re$_3$(HITP)$_2$, and Ir$_3$(HITP)$_2$ monolayers are relatively far below such band gap openings (see Supplemental Material [29]), so it is imperative to elevate their $E_f$. Fortunately, the organic nature of these COFs offers the flexibility to engineer their electronic properties through chemical or structural manipulations. In this study, we use O atoms to fully or partially replace N atoms in the COF structure (Fig. 3) to introduce more electrons and consequently to raise $E_f$ to the desired energy.

We demonstrate the successful realization of the QAH effect by such a modification in two COF structures, namely, Ta$_3$(HITP)$_2$ and Ir$_3$(HITP)$_2$. In Ta$_3$(HITP)$_2$, all N atoms are substituted by O atoms [Fig. 3(a)]. This new COF—Ta$_3$(C$_{18}$H$_{12}$O$_6$)$_2$—is thermodynamically stable (see Supplemental Material [29]) and has a slightly larger lattice parameter than the original chemical formula Ta$_3$(C$_{18}$H$_{12}$N$_6$)$_2$. It is FM as well because the total number of valence electrons in the new system is still odd. Its spontaneous magnetic moment, however, is greatly enhanced ($3 \mu_B$ per X atom) as compared to that of Ta$_3$(C$_{18}$H$_{12}$N$_6$)$_2$ ($1 \mu_B$ per X atom). The increase in $\mu$ can be understood from Fig. 3(a). Before the substitution, only the $d_{xy}$ orbital is half filled in Ta$_3$(C$_{18}$H$_{12}$N$_6$)$_2$. After the substitution, four more electrons are introduced to the vicinity of each Ta atom as it has four nearest-neighbor O (or N) atoms. The added electrons in Ta$_3$(C$_{18}$H$_{12}$O$_6$)$_2$ first occupy the $d_{xy}$ orbital to make it fully filled and then half fill the $d_{x^2-y^2}$, $d_{xz}$, and $d_{yz}$ orbitals [Fig. 3(a)], leaving $\mu = 3 \mu_B$ per Ta atom. From Fig. 4(a), the strong magnetic exchange field in Ta$_3$(C$_{18}$H$_{12}$O$_6$)$_2$ results in a large separation between the up-spin (purple solid curves) and down-spin (green dashed curves) states of a given electronic band, pushing the down-spin electronic bands far away from $E_f$. Without considering SOC, the $|d^1_{xy}, \uparrow\rangle$ bands are degenerate at the $\Gamma$ point, and the $|d^3_{z^2}, \uparrow\rangle$ bands are degenerate at the $K$ point, leaving a Dirac cone. When SOC is turned on, such band degeneracies at the $\Gamma$ and $K$ points are broken, with two small band gap openings between $|d^1_{xy}, \uparrow\rangle$ (24 meV) and between $|d^3_{z^2}, \uparrow\rangle$ (23 meV), respectively. Similar phenomena occur in the $|d^1_{yz}, \uparrow\rangle$ bands, with band gap openings between $|d^1_{yz}, \uparrow\rangle$ and between $|d^3_{z^2}, \uparrow\rangle$ (14 and 21 meV, respectively).

To further verify the capability of monolayer Ta$_3$(C$_{18}$H$_{12}$O$_6$)$_2$ for hosting a QAH phase, we look into
its QAH conductivity $\sigma_{xy}$, expressed as $\sigma_{xy} = C \cdot e^2 / h$, where $C$ is the Chern number, $e$ is the elementary charge, and $h$ is the Planck constant. $C$ is the summation of the Chern numbers of electronic bands ($C_n$) that are occupied. (See the Supplemental Material for the calculation of $C_n$ [29]). The calculated $C_n$ values for $|d_{yz}^{1,2,3}, \uparrow\rangle$, $|d_{yz}^{1,2,3}, \uparrow\rangle$, and $|d_{yz}^{1,2,3}, \uparrow\rangle$ in Ta$_3$(C$_{18}$H$_{12}$N$_3$O$_6$)$_2$ are $-1$, 0, and 1, respectively, and those for $|d_{yz}^{1,2,3}, \uparrow\rangle$, $|d_{yz}^{1,2,3}, \downarrow\rangle$, and $|d_{yz}^{1,2,3}, \downarrow\rangle$ are 0, 1, and $-1$, respectively (Fig. 4). Since $E_f$ in Ta$_3$(C$_{18}$H$_{12}$N$_3$O$_6$)$_2$ falls between the $|d_{yz}^{1,2,3}, \uparrow\rangle$ bands, the sum of $C_n$ for all occupied bands is $-1$, the same as $C_n$ for $|d_{yz}^{1,2,3}, \uparrow\rangle$, leading to a finite $\sigma_{xy}$ in the system [Fig. 4(c)], implying the capability of hosting the QAH phase.

Chemical modification is also applied to Ir$_3$(HITP)$_2$, but with half of the N atoms replaced by O atoms while preserving the inversion symmetry around the central Ir atom [Fig. 3(b)]. The new COF structure —Ir$_3$(C$_{18}$H$_{12}$N$_3$O$_3$)$_2$—has two more electrons in the vicinity of each Ir atom than the original structure. The added electrons change the highest half-filled bands from the $d_{yz}^{1,2,3}$ orbitals to the $d_{yz}^{1,2,3}$ orbitals, but do not alter $\mu$ of the system ($1 \mu_B$ per Ir atom). At equilibrium, the Ir$_3$(C$_{18}$H$_{12}$N$_3$O$_3$)$_2$ monolayer is a semiconductor with a band gap around 0.53 eV without considering SOC, which results from the energy splitting between the $|d_{yz}^{1,2,3}, \uparrow\rangle$ and $|d_{yz}^{1,2,3}, \downarrow\rangle$ states [Fig. 5(a)]. Among the valence bands, the $|d_{yz}^{1,2,3}, \uparrow\rangle$ bands are degenerate at the $K$ point and the $|d_{yz}^{1,2,3}, \uparrow\rangle$ bands are degenerate at the $\Gamma$ point, while at the conduction band edge, the $|d_{yz}^{1,2,3}, \downarrow\rangle$ bands are degenerate at the $\Gamma$ point and the $|d_{yz}^{1,2,3}, \downarrow\rangle$ bands are degenerate at the $K$ point. These degeneracies are broken by SOC [Fig. 5(b)]. The SOC-induced band gaps between $|d_{yz}^{1,2,3}, \uparrow\rangle$ and between $|d_{yz}^{1,2,3}, \downarrow\rangle$ are each $\approx$8–9 meV; however, those between $|d_{yz}^{1,2,3}, \uparrow\rangle$ and between $|d_{yz}^{1,2,3}, \downarrow\rangle$ are 0 meV or even negative. The Chern numbers of $|d_{yz}^{1,2,3}, \uparrow\rangle$ are 0, 1, and $-1$, respectively, and those of $|d_{yz}^{1,2,3}, \downarrow\rangle$ are 1, 0, and $-1$, respectively. From Fig. 5(b), the sum of $C_n$ for all occupied bands and thus the Hall conductivity in the system is 0, since $E_f$ is between the $|d_{yz}^{1,2,3}, \uparrow\rangle$ and $|d_{yz}^{1,2,3}, \downarrow\rangle$ bands, meaning a topologically trivial state. However, if $E_f$ of the Ir$_3$(C$_{18}$H$_{12}$N$_3$O$_3$)$_2$ monolayer is lowered to between the $|d_{yz}^{1,2,3}, \uparrow\rangle$ bands or raised to between the $|d_{yz}^{1,2,3}, \downarrow\rangle$ bands [yellow areas in Figs. 5(b) and 5(c)], $C$ of the system will become 1, indicating a finite $\sigma_{xy}$ [Figs. 5(d) and 5(e)]. Such Fermi-level tuning could be achieved by a gating voltage that injects electrons or holes into the system. The requisite injected charge carrier density in Ir$_3$(C$_{18}$H$_{12}$N$_3$O$_3$)$_2$ is estimated to be $2.3 \times 10^{13}$ cm$^{-2}$. This should be viable, since higher carrier densities ($>10^{14}$ cm$^{-2}$) have been experimentally demonstrated in monolayer graphene samples by electric gating technologies [40,41].

We also perform GGA + $U$ calculations to verify that the QAH phases in Ta$_3$(C$_{18}$H$_{12}$O$_6$)$_2$ and Ir$_3$(C$_{18}$H$_{12}$N$_3$O$_3$)$_2$ are preserved, and the on-site Coulomb interactions for the 5$d$ elements only influence the SOC induced band gaps to some degrees. Detailed information is given in the Supplemental Material [29]. The band gap is 8–23 meV in Ta$_3$(C$_{18}$H$_{12}$O$_6$)$_2$ monolayer and 8–18 meV in Ir$_3$(C$_{18}$H$_{12}$N$_3$O$_3$)$_2$ monolayer, depending on the choice of the Coulomb term. Using 26 meV equivalent to 300 K as a rough estimate, the QAH phase in Ta$_3$(C$_{18}$H$_{12}$O$_6$)$_2$ is expected to be robust at temperatures between 81 and 277 K, and that in Ir$_3$(C$_{18}$H$_{12}$N$_3$O$_3$)$_2$ is expected to be robust at temperatures between 104 and 208 K. This is much higher than the temperature (<100 mK) at which current QAH experiments are conducted [8–10]. Furthermore, the FM ordering temperature in Ta$_3$(C$_{18}$H$_{12}$O$_6$)$_2$ and Ir$_3$(C$_{18}$H$_{12}$N$_3$O$_3$)$_2$ is large enough to retain the QAH phases in the above-mentioned temperature ranges (see the Supplemental Material [29]). Finally, the viability of synthesizing similar COF structures [Ni$_3$(HITP)$_2$ and Cu$_3$(HITP)$_2$] has been experimentally...
demonstrated [24,25]. Taken together, these three points make Ta$_3$(C$_{18}H$_{12}O$_6$)$_2$ and Ir$_3$(C$_{18}H$_{12}N$_3$O$_3$)$_2$ monolayers very promising in practical QAH applications.

This work is supported by the Grants No. EFMA-542879, No. CMMI-1363203, and No. CBET-1235870 from the U.S. National Science Foundation. Y. K. acknowledges support from NSF Grant No. DMR–1120901 and computational support from the HPCMO of the U.S. DOD and the NERSC of the U.S. DOE. A. M. R. acknowledges support from the U.S. Office of Naval Research, under Grant No. N00014-14-1-0761. The authors acknowledge useful discussions with Professor Charles Kane.

*Corresponding author.
vshenoy@seas.upenn.edu

29] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.110.096601, which includes Refs. [30–37], for (I) Computational details, (II) the lattice parameter of $X_3$(HTTP)$_2$, (III) the electronic band structure of $X_3$(HTTP)$_2$, (IV) relative stability of Ta$_3$(C$_{18}H$_{12}O$_6$)$_2$ and Ir$_3$(C$_{18}H$_{12}N$_3$O$_3$)$_2$ monolayers, (V) the detailed derivation of the Chern number, (VI) the effect of local Coulomb interactions in Ir$_3$(C$_{18}H$_{12}N$_3$O$_3$)$_2$ and Ta$_3$(C$_{18}H$_{12}O$_6$)$_2$, (VII) FM ordering temperature in Ta$_3$(C$_{18}H$_{12}O$_6$)$_2$ and Ir$_3$(C$_{18}H$_{12}N$_3$O$_3$)$_2$, and (VIII) comparison of Ta$_3$(C$_{18}H$_{12}O$_6$)$_2$ and Ir$_3$(C$_{18}H$_{12}N$_3$O$_3$)$_2$ with previously proposed organic structures.