Tuning the topological states in metal-organic bilayers

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We have investigated the energetic stability and the electronic properties of metal-organic topological insulators bilayers (BLs), (MC₄S₄)₃-BL, with M=Ni and Pt, using first-principles calculations and tight-binding model. Our findings show that (MC₄S₄)₃-BL is an appealing platform to perform electronic band structure engineering, based on the topologically protected chiral edge states. The energetic stability of the BLs is ruled by van der Waals interactions; being the AA stacking the energetically most stable one. The electronic band structure is characterized by a combination of bonding and anti-bonding kagome band sets (KBSs), revealing that (NiC₄S₄)₃-BL presents a Z₂-metallic phase, whereas (PtC₄S₄)₃-BL may present both Z₂-metallic phase or quantum spin Hall phase. These non-trivial topological states were confirmed by the formation of chiral edge states in (MC₄S₄)₃-BL nanoribbons. We show that the localization of the edge states can be controlled with a normal external electric field, breaking the mirror symmetry. Hence, the sign of electric field selects in which layer each set of edge states are located. Such a control on the (layer) localization, of the topological edge states, bring us an additional and interesting degree of freedom to control the transport properties in layered metal-organic topological insulator.

I. INTRODUCTION

Two dimensional (2D) topological insulators, based on organic hosts, have been the subject of numerous studies addressing not only fundamental issues, but also future technological applications. In a seminal work, Wang et al. [1] predicted a non-trivial topological phase in an organic lattice composed by a monolayer (ML) of three benzene molecules bonded to metal atoms, Pb and Bi. Soon after the successful synthesis of 2D metal-organic ML lattices of nickel bis(dithiolene), (NiC₄S₄)₃ [2], theoretical studies based on first-principles calculations and single orbital tight-binding (TB) model, predicted a non-trivial topological phase in (NiC₄S₄)₃, characterized by the topological invariant Z₂ = 1 in (NiC₄S₄)₃, and the formation of spin-polarized chiral edge states at the time-reversal-invariant momenta (TRIM) [3].

By exploiting the large variety of (possible) combinations of metal-organic hosts, other metal-organic frameworks (MOFs), with non-trivial topological phase, have been proposed in the past few years. For instance, keeping the kagome lattice of (NiC₄S₄)₃, but substituting Ni with Mn atoms, Zhao et al. [4] verified the quantum anomalous Hall (QAH) state in (MnC₄S₄)₃. Here, the appearance of a ferromagnetic phase, mediated by the unpaired Mn-3d electrons, breaks the time-reversal symmetry of the original (NiC₄S₄)₃ system. Further QAH state has also been predicted in 2D lattices of (i) trans-Au-THTAP, where the ferromagnetism arise due to a half-filled flat band [5] ; and (ii) triphenil-manganese (MnC₄H₂)₃ [6], where ferromagnetically coupled Mn atoms are connected by benzene rings forming a honeycomb lattice. By keeping the same honeycomb structure of the benzene host, and substituting Mn with Pb atoms (triphenil-manganese→triphenil-lead), it has been predicted a non-magnetic ground state, where the spin-orbit coupling (SOC) promotes the QSH phase in (PbC₄H₂)₃ [1]. Further investigations [7] pointed out that, mediated by an external electric field, the (PbC₄H₂)₃ lattice presents an energetically stable ferrimagnetic QAH phase. Meanwhile, the recently synthesized Ni₃(C₁₈H₁₂N₂)₂ MOF [8] can be considered as the experimental realization of the so called topological Z₂-metallic phase [9] in MOFs. It is characterized by a kagome lattice, with a global energy gap at the edge of the Brillouin zone (K point), whereas the energy dispersion of the flat (kagome band) along the Γ–K direction gives rise to a local gap at the Γ point [10].

The design of 2D systems based on the MOFs is not limited by the metal→organic-host combinations. Based on the recent concept of van der Waals (vdW) heterostructures [11], we may access a set of new/interesting electronic properties by stacking 2D MOFs, as we have testified in inorganic layered materials [12]. Currently we are facing a suitable synergy between the experimental works addressing the successful synthesis of stacked 2D MOFs [8, 13–17], and theoretical studies aiming the understanding of their physical properties; and propose the design of new atomic structures [18, 19] focusing on a set of desired electronic properties. For instance, the control of the topological states in stacked MOFs.

In this paper we investigate the energetic stability and the electronic properties of (MC₄S₄)₃ (M=Ni and Pt) bilayers, (MC₄S₄)₃-BLs. The present study was carried out through a combination of first-principles calculations and TB model. The energetic stability of the (MC₄S₄)₃-BLs is ruled by vDW interactions; where (i) the electronic band structure of the most likely BL configuration (AA stacking) is characterized by a combination of bonding and anti-bonding kagome band sets (KBSs). The non-trivial nature of the energy gaps, induced by the SOC, was verified through the calculation of the edge states in (MC₄S₄)₃-BL nanoribbons (NRs). (ii) Turning on an external electric field normal to the BL, we find that the
electronic contributions from each ML are no longer symmetric; giving rise to an interlayer separation between the bonding and anti-bonding KBSSs. By mapping the localization of the edge states, we find that they follow the same spacial separation pattern, showing that the (layer) localization of the topologically protected edge states in (MC₄S₄)₃-BL NRs can be tuned by the external electric field. Based upon the first-principles calculations and a phenomenological model, we can infer that (i) and (ii), described above, will also take place in other vdW metal-organic BLs characterized by a superposition of kagome bands.

II. METHOD

The calculations were performed based on the DFT approach, as implemented in the VASP code[20]. The exchange correlation term was described using the GGA functional proposed by Perdew, Burke and Ernzerhof (PBE)[21]. The Kohn-Sham orbitals are expanded in a plane wave basis set with an energy cutoff of 400 eV. The 2D Brillouin Zone (BZ) is sampled according to the Monkhorst-Pack method[22], using a gamma-centered 4×4×1 mesh for atomic structure relaxation and 6×6×1 mesh to obtain the self-consistent total charge density. The electron-ion interactions are taken into account using the Projector Augmented Wave (PAW) method [23].

The real-space tight-binding (TB) Hamiltonian of kagome-hexagonal lattice [6, 25] in the presence of intrinsic spin-orbit coupling can be written as

\[ H_{TB} = H_0 + H_{SO} \]

where each term is given by

\[ H_0 = t_1 \sum_{\langle ij \rangle} c_{i\alpha}^{\dagger} c_{j\alpha} + t_2 \sum_{\langle \langle ij \rangle \rangle} c_{i\alpha}^{\dagger} c_{j\alpha} \]

\[ H_{SO} = i\lambda_1 \sum_{\langle ij \rangle} c_{i\alpha}^{\dagger} \sigma \cdot (d_{kj} + d_{jk}) c_{j\sigma} + i\lambda_2 \sum_{\langle \langle ij \rangle \rangle} c_{i\alpha}^{\dagger} \sigma \cdot (d_{kj} \times d_{jk}) c_{j\sigma} \]

Here, \( c_{i\alpha}^{\dagger} \) and \( c_{i\alpha} \) are the creation and annihilation operators for an electron with spin \( \alpha \) on site \( i \); \( \sigma \) are the spin Pauli matrices. As depicted in Figs. 1(d) and (e), \( d_{ik} \) and \( d_{kj} \) are the vectors connecting the \( i \)-th and \( j \)-th sites to the \( k \)-th nearest-neighbor in common; \( t_i \) and \( \lambda_i \) are the strength of hopping and spin-orbit terms. The \( \langle ij \rangle \) and \( \langle \langle ij \rangle \rangle \) refer to sums over nearest-neighbor and next-nearest-neighbor, respectively. See Sec. I of Supplemental Material (SM) [26] for more details.

III. RESULTS AND DISCUSSIONS

A. Monolayer

The metal organic framework of (MC₄S₄)₃ monolayer, (MC₄S₄)₃-ML, \( \text{M} = \text{Ni} \) and Pt, presents a hexagonal atomic structure [Fig. 1(a)], which can be viewed as a kagome lattice [Fig. 1(b)], where each site is occupied by a (MC₄S₄) molecule [Fig. 1(c)]. At the equilibrium geometry, we found that (NiC₄S₄)₃ presents a lattice parameter (\( a \)) of 14.70 Å, which is in good agreement with recent experimental measurements [2], and first-principles DFT results [3]. For (PtC₄S₄)₃ we obtained \( a = 15.06 \) Å, as the Pt covalent radius is greater than Ni, which is also in agreement with recent first-principles results [27].

The electronic band structures of both MOFs exhibit the typical kagome energy bands above the Fermi level (\( E_F \)), within \( E_F < E < E_F + 0.8 \) eV. These are graphene-like energy bands, with a Dirac cone at the K point, degenerated with a nearly flat band at the \( \Gamma \) point, as shown in Figs. 2(a1) and (b1). Such degeneracies are removed by the SOC. In (NiC₄S₄)₃-ML we find non-trivial global
Hybridization of C and S

The energy dispersion of c and 60 meV at K, as shown in Fig. 2(b2). Due to the energy dispersion of c in (PtC₄S₄)₃, the energy gap c2-c3 at the Γ point is a local gap, giving rise to the so-called Z₂-metallic state [10]. Further verification of the QSH phase can be done by mapping the edge states of (NiC₄S₄)₃- and (PtC₄S₄)₃-ML. Based on the TB approach, we calculated the energy bands of (NiC₄S₄)₃- and (PtC₄S₄)₃-ML NRs. As depicted in Figs. 2(a4) and (b4), the formation of chiral spin-polarized edge states, degenerated at the K point, confirms the non-trivial topological phases of the (NiC₄S₄)₃ and (PtC₄S₄)₃ MLs. We have examined the formation of edge states for other edge geometries as detailed in [26].

B. Bilayer

In this section, based on first-principles calculations, firstly we investigate the energetic stability, and the electronic properties of the (MC₄S₄)₃ BL systems; and next by combining first-principles calculations and the phenomenological model described below, we provide a comprehensive understanding of the interlayer-electronic tuning processes mediated by an external electric field and interlayer separation.

The energetic stability of (MC₄S₄)₃-BL was examined by considering a set of different (MC₄S₄)₃/(MC₄S₄)₃ interface geometries, aligning sites X and Y [for X, Y = A, B, G, H, and M, as indicated in Fig. 1(a)], i.e. the X site of one layer above the Y site of the other. In Table I we show the averaged interlayer equilibrium distance (δ₀), the root-mean-square deviation (⟨δz⟩) of the atomic position perpendicularly to the (MC₄S₄)₃ sheet, and the BL binding energy (E_b). Here, we define E_b as, E_b = 2E_{(ML)} - E_{(BL)}, where E_{(ML)} is the total energy of an isolated monolayer, and E_{(BL)} is the total energy of the (MC₄S₄)₃-BL for a given stacking configuration. We found that the AA stacking is the most stable one, with E_b of 9.99 and 8.46 meV/Å² (69 and 62 meV/atom) for (NiC₄S₄)₃-BL and (PtC₄S₄)₃-BL, respectively. Followed by the AG stacking by 0.70 and 0.36 meV/Å² (4.8 and 2.6 meV/atom). The energetic stability of those (MC₄S₄)₃-BLs is ruled by vdW interactions. It is worth noting that the binding strength of the (MC₄S₄)₃-BL is larger compared with other energetically stable 2D-vdW systems like graphene [29, 30] and boron-nitride [31, 32] bilayers. There are no chemical bonds at the (MC₄S₄)₃/(MC₄S₄)₃ interface region, where we found δ₀ of 3.64 and 3.66 Å for (NiC₄S₄)₃ and (PtC₄S₄)₃ BLs, and ⟨δz⟩ = 0.01 Å, thus indicating that the corrugations of the (MC₄S₄)₃ sheets are negligible in the AA stacking. In contrast, the other stacking geometries present ⟨δz⟩ between 0.1 and 0.2 Å.
TABLE I. Bilayer binding energy $E^b = 2E^{(ML)} - E^{(BL)}$ (in meV/Å²), mean equilibrium interlayer distance $d_0$ (Å) and root-mean-square deviation $\langle \delta z \rangle = \sqrt{(z^2) - \langle z \rangle^2}$ (Å).

| Stacking Geometry | $E^b$ (NiC$_4$S$_4$)$_3$ | $d_0$ | $\langle \delta z \rangle$ | $E^b$ (PtC$_4$S$_4$)$_3$ | $d_0$ | $\langle \delta z \rangle$ |
|-------------------|-------------------|------|----------------|-------------------|------|----------------|
| AA                | 9.99              | 3.64 | 0.01          | 8.46              | 3.66 | 0.01          |
| AB                | 8.51              | 3.37 | 0.22          | 6.92              | 3.37 | 0.23          |
| AM                | 9.26              | 3.64 | 0.08          | 7.97              | 3.60 | 0.15          |
| AG                | 9.29              | 3.57 | 0.12          | 8.10              | 3.51 | 0.13          |
| GH                | 8.56              | 3.35 | 0.11          | 6.92              | 3.37 | 0.13          |

FIG. 3. First-principles electronic band structure of (NiC$_4$S$_4$)$_3$-BLs (a) and (PtC$_4$S$_4$)$_3$-BLs. (a1) and (b1) bilayer structures without SOC, where $\Delta$ indicates the energy separation between the KBSs; (a2) and (b2) band structure with SOC, projected on the atomic orbitals of each (MC$_4$S$_4$)$_3$ ML; (a3) and (b3) SOC induced energy gaps near the Fermi level.

Next we discuss the electronic properties of the energetically most stable (NiC$_4$S$_4$)$_3$ and (PtC$_4$S$_4$)$_3$ BLs. Initially, we will examine the electronic band structure without the SOC. The electronic structure of the BLs can be described as a combination of anti-bonding (KBS$^+$) and bonding (KBS$^-$) kagome band sets, indicated by orange and green solid lines in Figs. 3(a1) and (b1). The Dirac bands of each KBS are preserved, where the KBS$^+$ and KBS$^-$ are separated (in energy) by $\Delta$; giving rise to one Dirac point at about $E_F + 0.6$ eV and another lying on the Fermi level. Here, $\Delta$ provide a measure of the interlayer coupling between the (MC$_4$S$_4$)$_3$ MLs [26]. Further projected energy bands [Figs. 3(a2) and (b2)] show that (i) each layer exhibits the same electronic contribution on the KBS$^+$ and KBS$^-$, where (ii) the energy bands are composed by $d_{xz}$ and $d_{yz}$ orbitals of the transition metals (Ni and Pt) hybridized with C and S $p_z$ orbitals of the organic host.

The SOC yields energy gaps at the Dirac points ($E^D$). For instance, in (NiC$_4$S$_4$)$_3$-BL [Fig. 3(a3)] we find a energy gap of 18 meV in KBS$^-$ ($E^{D-}_g$). This is a local energy gap, due to the presence of partially occupied metallic bands near the $\Gamma$ point. The SOC also induces energy gaps at the $\Gamma$ point. As shown in Fig. 3(a3), we find a small local gap of 4 meV in the KBS$^+$ ($E^{D+}_g$) near the Fermi level, and another local gap of 25 meV at $E_F + 0.2$ eV in the KBS$^-$ ($E^{D-}_g$). In contrast, (PtC$_4$S$_4$)$_3$ BL presents a global gap of 22 meV at the Fermi level ($E^D_g$), followed by $E^{D-}_g$ of 60 meV, and a local gap of 50 meV at the $\Gamma$ point ($E^{D-}_g$) [Fig.3(b3)]. As will be discussed below, those energy gaps induced by the SOC will dictate the formation of topologically protected edge states in the (MC$_4$S$_4$)$_3$-BLs.

To model the DFT results presented above, we propose a phenomenological Hamiltonian to describe the interaction between layers. Assuming the mirror symmetry of the AA stacking, the Hamiltonian reads

$$H_s = h_{3x3}(k) \otimes \tau_0 + \frac{\Delta}{2} \mathbb{I}_{3x3} \otimes \tau_z, \quad (2)$$

where, $h_{3x3}(k)$, represents the Hamiltonian of each monolayer separately, diagonal on the base $\{|#L; n, k\}$ ($n = 1, 2, 3$ bands, $# = 1, 2$ layers), which gives the kagome band dispersions; $\tau_j$ ($j = 0, x, y, z$) are the Pauli matrix in the layer space, and $\Delta/2$ the coupling term between the layers. In this model, each layer will interact forming the highest energy (anti-bonding, $|+\rangle$) and the lowest energy (bonding, $|-\rangle$) KBSs, energetically separated by $\Delta$. In this case, the Dirac bands at the Fermi level are given by the bonding KBSs, green solid lines in Fig.3(a1) and (b1). The mirror symmetry imposes that $\langle |#L| \rangle^2 = 1/2$, for $# = 1, 2$.

The mirror symmetry can be suppressed upon the interaction of the (MC$_4$S$_4$)$_3$-BLs with a solid surface, or due to the presence of an external electric field perpendicular to the (MC$_4$S$_4$)$_3$ layer. The latter can be expressed by adding a potential difference between the layers in $H_s$,

$$H = H_s - \varepsilon \mathbb{I}_{3x3} \otimes \tau_z. \quad (3)$$

Here, the potential difference due to only the external electric field ($E^{ext}$) will be $\varepsilon = (d/2)E^{ext}$, but the change rearrangement at the (MC$_4$S$_4$)$_3$(MC$_4$S$_4$)$_3$ interface can reduce this potential difference such that, $\varepsilon = \sigma E^{ext}$. Further discussion on the proposed model can be found in the Supplemental Material [26], Sec.II. Therefore, in this model the contribution of each layer to an given state is $E^{ext}$ dependent.

Initially, the effect of external electric field was studied based on the first-principles approach. In Figs. 4(a1) and (b1) we present the electronic band structures of the (PtC$_4$S$_4$)$_3$ and (NiC$_4$S$_4$)$_3$ BLs for $E^{ext} = 0$. The mirror
symmetry is fulfilled and both layer contributes equally for each state. The size of red circles is proportional to the layer contribution to each state, \(|\langle #L/n, k \rangle|^2\). By turning on the external electric field \(E^{\text{ext}} \neq 0\), there is an unbalance on the charge density distribution between the MLs, Figs. 4(a2) and (b2); followed by an increase on the energy separation between the kagome bands, \(\Delta = 0.63 \rightarrow 0.94\) eV as the electric field module increase from 0.0 \(\rightarrow\) 0.2 eV/Å in \((\text{NiC}_4\text{S}_3)_3\)-BL. In contrast, such an increase of \(\Delta\), as a function of the external field, is almost negligible in \((\text{PtC}_4\text{S}_3)_3\)-BL. For the electric field module increasing from 0.0 \(\rightarrow\) 0.5 eV/Å, the separation between the kagome bands changes by less than 0.03 eV (\(\Delta = 0.59 \rightarrow 0.61\) eV).

The dependence of \(\Delta\) with the external electric field can be understood by analyzing the changes on the total charge density \((\Delta \rho)\) as a function of \(E^{\text{ext}}\) and the interlayer distance \(d\). For a given value of \(d\), we can define \(\Delta \rho\) as,

\[
\Delta \rho = \rho(E^{\text{ext}}) - \rho(0),
\]

where \(\rho(E^{\text{ext}})\) and \(\rho(0)\) represent the total charge densities of the \((\text{MC}_4\text{S}_3)_3\) BL at \(E^{\text{ext}} \neq 0\) and \(E^{\text{ext}} = 0\), respectively. Our results of \(\Delta \rho\) for the \((\text{NiC}_4\text{S}_3)_3\) and \((\text{PtC}_4\text{S}_3)_3\) BLs show that, (i) at the equilibrium geometry \((d_0 = 3.6\) Å\), there is no charge transfer between the \((\text{NiC}_4\text{S}_3)_3\) MLs [Fig. 4(a3)]; in contrast (ii) a net charge transfer takes place between the \((\text{PtC}_4\text{S}_3)_3\) MLs [Fig. 4(b3)]. Such a net charge transfer gives rise to an intrinsic local electric field which can be written as, \(E^{\text{loc}} = -\alpha E^{\text{ext}}\); reducing the potential difference between the \((\text{PtC}_4\text{S}_3)_3\) MLs, in agreement with the small changes on the energy separation between the kagome bands. Increasing the interlayer distance, for instance \(d_0 \rightarrow d_1 = 3.9\) Å, we found that (i) the electronic interaction between the \((\text{MC}_4\text{S}_3)_3\) MLs reduces, as well as the coupling term \(\Delta\). We found \(\Delta = 0.41\) eV (first-principles calculations) for both \((\text{MC}_4\text{S}_3)_3\) BLs: and (ii) there is a reduction on the net charge transfer between the MLs due to the external electric field, as depicted in Figs. 4(a4) and (b4) for \((\text{NiC}_4\text{S}_3)_3\) and \((\text{PtC}_4\text{S}_3)_3\), respectively.

As shown in Figs. 4(a2) and (b2), the layer contribution on the KBS can be controlled by an external electric field. Here we will consider the electronic states around the Dirac point near the the Fermi level, indicated by (blue) rectangles in Figs. 4(a1)-(a2) and 4(b1)-(b2). The calculated partial charge densities within those rectangles, \(|\langle 1L|-\rangle|^2\) and \(|\langle 2L|-\rangle|^2\), are shown in Figs. 4(c) and (d) for \(E^{\text{ext}}\) from 0 to 0.5 eV/Å. Our first-principles results are indicated by colored circles, and solid lines indicate the ones obtained by using the phenomenological model. At \(E^{\text{ext}} = 0\) we have \(|\langle 1L|-\rangle|^2 = |\langle 2L|-\rangle|^2 = 0.5, i. e.\), both layers present the same electronic contribution as the mirror symmetry is fulfilled. For lower values of \(E^{\text{ext}}\), \(\varepsilon \ll \Delta/2\), the electronic contribution of each layer exhibits a linear behaviour, where the tangent modulus is \(\sigma/\Delta\) [20]. The separation of the particular charge densities between the MLs is strengthened for larger interlayer distances. For instance, at the equilibrium geometry, \(d_0 = 3.6\) Å, we find \(|\langle 1L|-\rangle|^2 = 0.27\) and \(|\langle 2L|-\rangle|^2 = 0.73\), which corresponds to a charge density separation ratio \(\eta\),

\[
\eta = \frac{|\langle 1L|-\rangle|^2}{|\langle 2L|-\rangle|^2}
\]

of 0.37 for \(E^{\text{ext}} = 0.1\) eV/Å in \((\text{NiC}_4\text{S}_3)_3\)-BL; increas-
ing $d$ to 3.9 Å, the charge density separation increases, \( \eta = 0.20 \) for the same value of \( E^\text{ext} \). On the other hand, the net charge transfers between the (PtC\(_4\)S\(_4\))\(_3\) MLs result in \( \varepsilon \ll \Delta/2 \) for a greater range of \( E^\text{ext} \), giving rise to a linear response of the layer contribution, even for \( E^\text{ext} = 0.5 \) eV/Å, black and red lines in Fig. 4(d). Indeed, for \( d_0 = 3.6 \) Å the charge density separation is very small, we find \( |\langle 1L| - \rangle|^2 = 0.40 \) and \( |\langle 2L| - \rangle|^2 = 0.60 \), \( \eta = 0.67 \) for \( E^\text{ext} = 0.50 \) eV/Å. On the other hand, increasing the interlayer distance to \( d = 3.9 \) Å, the charge transfer is suppressed [Fig. 4(b4)], and we find \( \eta = 0.19 \) for \( E^\text{ext} = 0.10 \) eV/Å, which is practically the result obtained in (NiC\(_4\)S\(_4\))\(_3\)-BL.

It is worth noting that (i) by inverting the \( E^\text{ext} \) direction, the layer localization also inverts (1L \( \leftrightarrow \) 2L), and (ii) in the present scenario the charge density separation in (MC\(_4\)S\(_4\))\(_3\) BLs is ruled by the suppression of the mirror symmetry. Here we have considered the suppression of the mirror symmetry through an external electric field, but the same behavior is expected in other cases, e.g. the presence of a substrate. In the next section we discuss the bilayers ribbons and the location of the topologically protected edge states, by the breaking of the mirror symmetry.

Here, the electronic band structure of (NiC\(_4\)S\(_4\))\(_3\)- and (PtC\(_4\)S\(_4\))\(_3\)-BLs, obtained through first-principles calculations, was fitted within the TB approach considering the intralayer and interlayer hoppings, and two orbitals (A and B) per site of the kagome bilayer-lattice (details in Sec.1 of the SM). As shown in Figs. 5(a) and (b), the energy dispersions obtained through the TB Hamiltonian (red lines) present a reasonably well correspondence with the ones obtained by the first-principles calculations approach (blue circles), where the main features of the band structure are well described.

Similarly to the monolayers, the bilayers also have a \( Z_2 = 1 \) topological invariant. However, here it shows a \( Z_2 = 1 \) for each set of orthogonal subspaces. For the mirror symmetry case, these are the bonding (KBS\(^+\)) and anti-bonding (KBS\(^-\)) states. For a finite \( E^\text{ext} \) it is still possible to define two orthogonal sets [see Supplemental Material [26]], which are similar to the KBS\(^\pm\) states. Consequently, in the following we find two sets of edge states, one for each orthogonal subspace.

In order to identify these topologically protected edge states we have considered nanoribbon widths (W) of ~51 and ~52 nm for (NiC\(_4\)S\(_4\))\(_3\) and (PtC\(_4\)S\(_4\))\(_3\) BLs, Figs. 5(c) and (d).

In Figs. 6 and 7 we present the spin-polarized energy bands projected on the edge atoms indicated in Figs. 5(c) and (d). The formation of chiral edge states, degenerated at the TRIM, confirms the topological phases of the (NiC\(_4\)S\(_4\))\(_3\) and (PtC\(_4\)S\(_4\))\(_3\) BLs. Figures 6(a) and 7(a) show three sets of metallic edge states near the Fermi level, viz.: \( e_{-1}^\mathrm{D}, e_{+1}^\mathrm{D}, \) and \( e_D \), degenerated at the TRIM \( k = \pi/a \) and \(-\pi/a \). Those metallic bands come from the (non-trivial) energy gaps induced by the SOC, between (i) the kagome bands at the \( \Gamma \) point, \( E^\mathrm{g}_{-1} \), and \( E^\mathrm{g}_{+1} \), and (ii) the Dirac states at the K point, \( E^\mathrm{D}_{-1} \). In (NiC\(_4\)S\(_4\))\(_3\)-BL, the energy gaps (i) and (ii) [Fig. 3(a3)] are not global, however, the formation of spin polarized chiral edge states supports the so called \( Z_2 \)-metallic phase. In contrast, (PtC\(_4\)S\(_4\))\(_3\)-BL presents a (large) global energy gap of 22 meV (\( E^\text{D}_{-1} \)) at the Fermi level, Fig. 3(b3). Thus, in order to access the QSH phase in (PtC\(_4\)S\(_4\))\(_3\)-BL, it is not necessary any external doping to place the Fermi level in the non trivial energy gap.

Edge states localized at opposite sides of the same (MC\(_4\)S\(_4\))\(_3\) ML present opposite chiralities; while edge states of different MLs present the same chirality and the same electronic density of states. The latter is a consequence of the mirror symmetry in the BL systems. As we have shown in the previous section, the mirror symmetry can be removed by turning on an external electric field perpendicularly to the (MC\(_4\)S\(_4\))\(_3\) layers. Here we will focus on the interlayer separation of the topological edge states mediated by an external electric field.

The effect of \( E^\text{ext} \) on the localization of the edge states are depicted in Figs. 6(b) and 7(b). In the former diagram we present the localization of the edge states in the (NiC\(_4\)S\(_4\))\(_3\)-BL NR upon an external field of 0.1 eV/Å. The edge states \( e_{-1}^\mathrm{D} \) and \( e_{+1}^\mathrm{D} \) are mostly localized on one

FIG. 5. Electronic band structure of (NiC\(_4\)S\(_4\))\(_3\)-(a), and (PtC\(_4\)S\(_4\))\(_3\)-(b) bilayers, obtained through first-principles calculations (blue circle), and TB (red line) calculations for \( d_{1L} = 3.6 \) Å and including the SOC. Bilayer nanoribbon geometry, top-view (c) and side-view (d).

C. Bilayer Nanoribbon

In this section we will discuss the edge states of BL nanoribbons, in order to provide a more complete picture of the electronic properties of the (MC\(_4\)S\(_4\))\(_3\)-BLs.
FIG. 6. Spin polarized electronic band structure of the (NiC$_4$S$_4$)$_3$-BL NR, projected on the edge atoms [Edge 1 and Edge 2 indicated in Figs.5(c) and (d)] for $E^\text{ext} = 0$ (a), and $E^\text{ext} = 0.1 \text{eV/Å}$ (b). The color map are the $\langle S_z \rangle$, and the size of projection is proportional to $|\langle #L, \text{Edge}|n,k \rangle|^2$.

ML (1L), while $e^+_1$ lies on the other (2L).

Similarly to what we have done in the BL systems, we can define a separation ratio for the edge states ($\eta_e$). In order to compare with the $\eta$ calculated for (MC$_4$S$_4$)$_3$-BLs, we will consider the (layer) projection of the edge states $e^{-}_{D}$,

$$\eta_e = \frac{|\langle 1L|e^{-}_{D} \rangle|^2}{|\langle 2L|e^{-}_{D} \rangle|^2}.$$  

We find $\eta_e = 0.39$ for ($E^\text{ext} = 0.1 \text{eV/Å}$), which is practically the same result obtained in (NiC$_4$S$_4$)$_3$-BL, at the same external field. As shown in Fig. 7(b), such a charge density separation also takes place in the (PtC$_4$S$_4$)$_3$-BL NR, however is not so effective. This is a consequence of the net charge transfer verified in (PtC$_4$S$_4$)$_3$-BL, as discussed above. Indeed, here we find $|\langle 1L|e^{-}_{D} \rangle|^2 = 0.39$, and $|\langle 2L|e^{-}_{D} \rangle|^2 = 0.61$, giving rise to $\eta_e = 0.64$, for $E^\text{ext} = 0.5 \text{eV/Å}$; which is practically the same value obtained in (PtC$_4$S$_4$)$_3$-BL, $\eta = 0.67$.

On the other hand, as shown in Fig. 4, the separation of the partial charge densities in (MC$_4$S$_4$)$_3$-BLs can be tuned by changing the vertical distance between the (MC$_4$S$_4$)$_3$ sheets. For instance, $\eta$ reduces from 0.67 to 0.19 by increasing the interlayer distance from 3.6 to 3.9 Å in (PtC$_4$S$_4$)$_3$-BL. Edge states in (PtC$_4$S$_4$)$_3$-BL NR present the same behavior. By increasing the interlayer distance to $d_1 = 3.9 \text{Å}$, the layer separation of the edge states is strengthened, where we find $|\langle 1L|e^{-}_{D} \rangle|^2 = 0.18$, and $|\langle 2L|e^{-}_{D} \rangle|^2 = 0.82$, $\eta_e = 0.22$, for $E^\text{ext} = 0.1 \text{eV/Å}$. That is, in addition to the external electric field, the interlayer distance is another degree of freedom which allow us to control the localization of the topologically
protected edge states in (MC\textsubscript{4}S\textsubscript{4})\textsubscript{3} BL nanoribbons. It is worth to mention that such a control on the interlayer distance, between the organic layers, can be done through the current pillaring processes in MOFs [33, 34].

**IV. CONCLUSION**

Based on first-principles calculations and tight-binding model, we show that the energetic stability of the (MC\textsubscript{4}S\textsubscript{4})\textsubscript{3}-BLs, M = Ni and Pt, is ruled by vdW interactions, being the AA stacking the most stable one. The electronic structure of the (MC\textsubscript{4}S\textsubscript{4})\textsubscript{3}-BLs is characterized by the formation of bonding and anti-bonding KBSs; where the energy gaps in the KBSs, induced by the SOC, give rise to QSH or Z\textsubscript{2}-metallic state in (MC\textsubscript{4}S\textsubscript{4})\textsubscript{3}-BLs. Their topologically non-trivial nature was identified through the formation of chiral spin-polarized edge states. By considering a phenomenological model, combined with first-principles calculations, we present a very comprehensive picture of the electronic properties upon the presence of an external electric field. In this case, the electronic contributions from each ML, to the formation of the bonding and anti-bonding KBSs, are no longer symmetric, with the bonding and anti-bonding KBSs localized in different MLs. We find that the chiral edge states follow the same pattern, and thus the localization of the topologically protected edge states in (MC\textsubscript{4}S\textsubscript{4})\textsubscript{3}-BLs can be tuned by an external electric field. Our findings are not restricted to the (NiC\textsubscript{4}S\textsubscript{4})\textsubscript{3} and (PtC\textsubscript{4}S\textsubscript{4})\textsubscript{3} BLs. We can infer that such a tuning process will also take place in other mirror symmetric vdW metal-organic BLs characterized by a superposition of the kagome bands.

**V. ACKNOWLEDGMENTS**

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[1] Z. F. Wang, Z. Liu, and F. Liu, Nat. Commun. **4**, 1471 (2013).
[2] T. Kambe, R. Sakamoto, K. Hoshiko, K. Takada, M. Miyachi, J.-H. Ryu, S. Sasaki, J. Kim, K. Nakazato, M. Takata, and H. Nishihara, J. Am. Chem. Soc. **135**, 2462 (2013).
[3] Z. F. Wang, N. Su, and F. Liu, Nano Lett. **13**, 2842 (2013).
[4] M. Zhao, A. Wang, and X. Zhang, Nanoscale **5**, 10404 (2013).
[5] M. G. Yamada, T. Soejima, N. Tsuji, D. Hirai, M. Dincă, and H. Aoki, Phys. Rev. B **94**, 081102 (2016).
[6] Z. Wang, Z. Liu, and F. Liu, Phys. Rev. Lett. **110**, 196801 (2013).
[7] H.-J. Kim, C. Li, J. Feng, J.-H. Cho, and Z. Zhang, Phys. Rev. B **93**, 041404 (2016).
[8] D. Sheberla, L. Sun, M. A. Blood-Forsythe, and T. T. Tan, Phys. Rev. Lett. **110**, 041404 (2013).
[9] H. Pan, X. Li, Z. Qiao, C.-C. Liu, Y. Yao, and S. A. Yang, New J. Phys. **16**, 123015 (2014).
[10] B. Zhao, J. Zhang, W. Feng, Y. Yao, and Z. Yang, Phys. Rev. B **90**, 201403 (2014).
[11] A. K. Geim and I. V. Grigorieva, Nature **499**, 419 (2013).
[12] B. Radisavljevic, A. Radenovic, J. Brivio, and A. Kis, Nat. Nanotech. **6**, 147 (2011).
[13] S. Kitagawa, R. Kitaura, and S.-i. Noro, Angew. Chem. Int. Ed. **43**, 2334 (2004).
[14] J. W. Colson and W. R. Dichtel, Nat. Chem. **5**, 453 (2013).
[15] M. Zhang, G. Feng, Z. Song, Y.-P. Zhou, H.-Y. Chao, D. Yuan, T. T. Tan, Z. Guo, Z. Hu, B. Z. Tang, et al., J. Am. Chem. Soc. **136**, 7241 (2014).
[16] D. Rodriguez-San-Miguel, P. Amo-Ochoa, and F. Zamora, Chem. Commun **52**, 4113 (2016).
[17] R. Sakamoto, K. Takada, X. Sun, T. Pal, T. Tsukamoto, E. J. H. Phua, A. Rapakousiou, K. Hoshiko, and H. Nishihara, Coord. Chem. Rev. **320**, 118 (2016).
[18] J.-J. Adjizian, P. Briddon, B. Humbert, J.-L. Duvail, P. Wagner, C. Adda, and C. Ewels, Nat. Commun. **5**, 5842 (2014).
[19] J. Zhou, RSC Adv. **4**, 13361 (2014).
[20] G. Kresse and H. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
[21] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[22] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[23] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
[24] K. Lee, E. D. Murray, L. Kong, B. I. Lundqvist, and D. C. Langreth, Phys. Rev. B **82**, 081101 (2010).
[25] E. Tang, J.-W. Mei, and X.-G. Wen, Phys. Rev. Lett. **106**, 236802 (2011).
[26] See supplemental materials for more details of the methodology.
[27] T.-Y. L, H. Feng, S.-W. Yang, and J.-C. Zheng, Comput. Mater. Sci. **126**, 170 (2017).
[28] M. Zhou, Z. Liu, W. Ming, Z. Wang, and F. Liu, Phys. Rev. Lett. **113**, 236802 (2014).
[29] I. V. Lebedeva, A. A. Knizhnik, A. M. Popov, Y. E. Lozovik, and B. V. Potapkin, Phys. Chem. Chem. Phys. **13**, 5687 (2011).
[30] E. Mostaani, N. Drummond, and V. Falko, Phys. Rev. Lett. **115**, 115501 (2015).
[31] N. Marom, J. Bernstein, J. Garel, A. Tkatchenko, E. J. H. Phua, K. Hoshiko, and H. Nishihara, Coord. Chem. Rev. **320**, 118 (2016).
[32] W. Gao and A. Tkatchenko, Phys. Rev. Lett. **114**, 096101 (2015).
[33] J. F. Eubank, L. Wojtas, M. R. Hight, T. Bousquet, V. C. Kravtsov, and M. Eddaoudi, J. Am. Chem. Soc. **133**, 5842 (2014).
[34] H. Sun, D. Lin, and Z. Gao, J. Porous Mater. 24, 291 (2017).
Supplemental Materials: Tuning the topological states in metal-organic bilayers

In the present Supplemental Material, we provide details of the TB model applied for the $(MC_4S_4)_3$-ML/BL systems, Section I; describe the phenomenological Hamiltonian for mirror symmetric bilayers and the effect of breaking this mirror symmetry, Section II; and analyse the Rashba spin-orbit contribution to the topological phases of the $(MC_4S_4)_3$-ML and BL, Section III. In this latter section, based on the TB model and first-principles calculations, we show that the Rashba spin-orbit contribution can be safely neglected in the present study.

VI. KAGOME LATTICE TIGHT-BINDING MODEL

The real-space tight-binding Hamiltonian of kagome-hexagonal lattice in the presence of intrinsic spin-orbit coupling (SOC) [S1, S2] can be written as

$$H_{TB} = H_0 + H_{SO}$$

where each term is given by

$$H_0 = \sum_{\langle ij \rangle; \alpha} c_{i\alpha}^\dagger c_{j\alpha} + \sum_{\langle\langle ij \rangle \rangle; \alpha} c_{i\alpha}^\dagger c_{j\alpha};$$

$$H_{SO} = i \lambda_1 \sum_{\langle ij \rangle} c_{i\alpha}^\dagger \sigma \cdot (d_{kj} \times d_{ik}) c_{j\alpha} + i \lambda_2 \sum_{\langle(ij) \rangle} c_{i\alpha}^\dagger \sigma \cdot (d_{kj} \times d_{ik}) c_{j\alpha};$$

here, $c_{i\alpha}^\dagger$ and $c_{i\alpha}$ are the creation and annihilation operators for an electron with spin $\alpha$ on site $i$; $\sigma$ the spin Pauli matrices, $d_{ik}$ and $d_{kj}$ the unity vector connecting the $i$-th and $j$-th sites to the $k$-th nearest-neighbor in common [Fig. S1(a)], such that $d_{kj} \times d_{ik} = \pm (\sqrt{3}/2) \hat{e}_z$ (where the proportionality constant $\sqrt{3}/2$ is absorbed in $\lambda_1$), and $t_i, \lambda_i$ the strength of hopping and spin-orbit terms. The $\langle ij \rangle$ and $\langle(ij) \rangle$ refer to nearest-neighbor and next nearest-neighbor summation, respectively. It worth to mention that we have done DFT first-principles calculation on the $(MC_4S_4)_3$ monolayers (ML) with perpendicular external electric field up to $0.5 \text{ eV/Å}$, in which we do not observe any Rashba SOC effect on the band structure. Therefore in our TB model we have taken the Rashba SOC as null [more details on the Rashba SOC term in the last section].

The kagome lattice is given by a hexagonal lattice with 3 atoms as base [see main text, Fig.1]. For this lattice we can identify the nearest ($t_1$) and next nearest ($t_2$) neighbors in plane hopping, as represented in Fig.S1(a). By the formation of bilayer systems in addition to the in plane hopping, interlayer hopping are considered as represented in Fig.S1(b).

![FIG. S1. (a) In plane hopping and SOC parameter for nearest ($t_1, \lambda_1$) and next nearest ($t_2, \lambda_2$) neighbors; (b) Interlayer hopping parameter $t_0, t_{1\perp}, t_{2\perp}$. Blue lines indicate the coupling between two sites ($t_i, \lambda_i$) and green lines the $d_{ik}$, unity vectors of SOC term.](image)

For $(MC_4S_4)_3$-ML (M= Ni, Pt) we find a good TB description of the system by fitting the first-principles band structure with the parameters show in TABLE S1, considering a single orbital per kagome site. We can see that the
TABLE SI. Monolayer TB parameters in meV.

| Parameter | (NiC₄S₄)₃ | (PtC₄S₄)₃ |
|-----------|-----------|-----------|
| $E₀$      | 550.0     | 575.0     |
| $t₁$      | -38.0     | -40.0     |
| $t₂$      | -2.0      | -3.0      |
| $λ₁$      | -1.8      | -4.7      |
| $λ₂$      | -0.2      | -1.7      |

single orbital TB Hamiltonian describe well the kagome band set (KBS) dispersion [Fig. S2(a1) and (b1)] obtained by DFT first-principles calculations [see main file methodology to DFT description].

Within the TB hamiltonian we can track the evolution of Wannier Charge Center (WCC) of an effective 1D system. Where the $Z₂$ topological invariant number is given by WCC evolution through half pumping cycle

$$Z₂ = \sum_α [\vec{x}^{I}_α(π) - \vec{x}^{II}_α(π)] - \sum_α [\vec{x}^{I}_α(0) - \vec{x}^{II}_α(0)] \mod 2,$$

where $I, II$ are for Kramers pairs, and $α$ are the index of occupied states in terms of pairs [S3, S4]. One graphical way to visualize the $Z₂$, is to draw a reference arbitrary vertical line from $k_y = 0$ to $k_y = π$ on the WCC evolution, where even (odd) number of crossing with the reference line determine the topological trivial (non-trivial) characteristic of the system [S4].

![FIG. S2. (NiC₄S₄)₃ (a) and (PtC₄S₄)₃ (b) band structure and Wannier Charge Center (WCC) evolution. TB (red solid line) and DFT (blue circle) band structure (a1) and (b1); WCC for the occupation up to $E_D^g$ gap (a2) and (b2); WCC for the occupation up to $E^g$ gap (a3) and (b3).](image)

By considering the occupation of (MC₄S₄)₃-ML up to $E_D^g$, namely band $c1$ fully occupied and $c2, c3$ unoccupied [Fig. S2(a1) and (b1)], we can calculate the WCC of the system. As show in Fig. S2(a2) and (b2) for (NiC₄S₄)₃ and (PtC₄S₄)₃, respectively, the reference line (blue solid line) cross the evolution line one time, therefore $Z₂ = 1$ which characterizes this gap as topologically non-trivial. In a same way, for the occupation up to $E^g$, namely $c1$ and $c2$ band fully occupied [Fig. S2(a1) and (b1)], the reference line cross the evolution line one time as show in Fig. S2(a3) and (b3) for (NiC₄S₄)₃ and (PtC₄S₄)₃, respectively. We can conclude that both gaps $E_D^g$ and $E^g$ are topologically non-trivial, and making a lateral interface with a trivial material is expected a chiral edge state.

Next we have constructed nanoribbons of (MC₄S₄)₃ with width (W) of $\sim 50$ nm, with three different edge geometries, Fig. S3(a), (b) and (c). Here are observed the formation of chiral edge states within the bulk SOC induced gap energy $E_D^g$ ($\sim 0.5$ eV) and $E^g$ ($\sim 0.7$). From Fig. S3(a) we can see that the ribbon geometry does not have inversion symmetry...
as we have two different type of edges, i.e., one terminated with a chain of atoms (Edge 1) and other by triangles (Edge 2). Within this asymmetric nanoribbon, each edge has a chiral momentum-spin locked states, degenerated at the time reversal invariant momenta (TRIM) in $k = \pm \pi/a$, but with different Fermi velocities. On the other hand, for the inversion symmetric nanoribbons, Fig. S3(b) and (c), the chiral states of opposite edges has the same Fermi velocity.

FIG. S3. (MC$_4$S$_4$)$_3$-ML nanoribbon with three different edge geometries (a), (b), (c). Edge projected band structure, with the color scale indicating $\langle S_z \rangle$; (NiC$_4$S$_4$)$_3$/Edge 1 in (a1), (b1), (c1); (NiC$_4$S$_4$)$_3$/Edge 2 in (a2), (b2), (c2); (PtC$_4$S$_4$)$_3$/Edge 1 in (a3), (b3), (c3); (PtC$_4$S$_4$)$_3$/Edge 2 in (a4), (b4), (c4).

For the mirror symmetric (MC$_4$S$_4$)$_3$-BL Hamiltonian, one can break the mirror symmetry by adding a potential difference between the layers through the on site energy of each layer orbital, i.e., making $E_0 \rightarrow E_0 \pm \varepsilon/2$, with + (−) sign for the upper (lower) layer. This potential difference can be due to an external electric field ($E^{\text{ext}}$). Taking (NiC$_4$S$_4$)$_3$-BL as an example, we can see that in the absence of external electric field [Fig. S4(a)] the system is mirror symmetric and each layer contribute equally to each state. On the other hand, by breaking the mirror symmetry the contribution of each layer to an given state are $E^{\text{ext}}$ dependent, as show the color map fin Fig. S4(b) and (c). We

| Parameter | (NiC$_4$S$_4$)$_3$ | (PtC$_4$S$_4$)$_3$ | Parameter | (NiC$_4$S$_4$)$_3$ | (PtC$_4$S$_4$)$_3$ |
|-----------|------------------|------------------|-----------|------------------|------------------|
| $E_0^{(A)}$ | 360.0 | 369.0 | $E_0^{(B)}$ | -506.0 | -488.0 |
| $t_0$ | 291.0 | 291.0 | $t_0^{(AA)}$ | -46.7 | -47.5 |
| $t_0^{(AB)}$ | -1.0 | -5.0 | $t_0^{(BB)}$ | -45.6 | -45.6 |
| $t_0^{(AA)}$ | 7.6 | 14.0 | $t_0^{(AB)}$ | 0.0 | 0.0 |
| $t_0^{(AB)}$ | 0.0 | 0.0 | $\lambda_1^{(AA)}$ | -1.8 | -4.7 |
| $t_0^{(BB)}$ | -0.2 | -1.7 | $\lambda_1^{(BB)}$ | -1.9 | -6.0 |
| $\lambda_2^{(AA)}$ | -1.8 | -4.5 | $\lambda_2^{(AB)}$ | 0.0 | 0.0 |
| $\lambda_2^{(BB)}$ | 0.0 | 0.0 | $\lambda_2^{(AA)}$ | -9.0 | -7.0 |
| $t_2^{(AA)}$ | 0.0 | 0.0 | $t_2^{(AB)}$ | -20.0 | -20.0 |
| $t_2^{(AB)}$ | 0.0 | 0.0 | $t_2^{(BB)}$ | 2.0 | 8.0 |
| $t_2^{(AA)}$ | 0.0 | 0.0 | $t_2^{(AB)}$ | 0.0 | 0.0 |
| $t_2^{(AB)}$ | -2.0 | -2.0 | $t_2^{(BB)}$ | 0.0 | 0.0 |

For the mirror symmetric (MC$_4$S$_4$)$_3$-BL Hamiltonian, one can break the mirror symmetry by adding a potential difference between the layers through the on site energy of each layer orbital, i.e., making $E_0 \rightarrow E_0 \pm \varepsilon/2$, with + (−) sign for the upper (lower) layer. This potential difference can be due to an external electric field ($E^{\text{ext}}$). Taking (NiC$_4$S$_4$)$_3$-BL as an example, we can see that in the absence of external electric field [Fig. S4(a)] the system is mirror symmetric and each layer contribute equally to each state. On the other hand, by breaking the mirror symmetry the contribution of each layer to an given state are $E^{\text{ext}}$ dependent, as show the color map fin Fig. S4(b) and (c). We
introduce a phenomenological model to explain the effects of this mirror symmetry breaking, as discussed in the next section.

**FIG. S4.** (NiC$_4$S$_4$)$_3$-BL band structure with external electric field of 0.0 (a), 0.1 (b) and 0.25 eV/Å (c). The color map indicates $|\langle 2L|n,k\rangle|^2 - |\langle 1L|n,k\rangle|^2$

**VII. PHENOMENOLOGICAL MODEL: (MC$_4$S$_4$)$_3$-BL**

Here we propose a phenomenological model to describe the interaction between the layers for the AA staking configuration. Firstly, knowing the Hamiltonian of each monolayer separately $h_{3\times3}(k)$, diagonal on the base $\{\#L;n,k\}$ ($n=1,2,3$ bands, $\# = 1,2$ layers), which gives each kagome band set (KBS) dispersions. Therefore, the general Hamiltonian for the two identical layers in the AA staking interacting with each other, and with an external electric field perpendicular to the layers is

$$H = h_{3\times3}(k) \otimes \tau_0 + \frac{\Delta}{2} \mathbb{I}_{3\times3} \otimes \tau_x - \varepsilon \mathbb{I}_{3\times3} \otimes \tau_z,$$

where $\tau_j$ ($j = x,y,z$) are the Pauli matrix in the layers space, $\Delta/2$ is the coupling between the layers and $\varepsilon$ the potential energy associated with the electric field. Here we omit the spin degree of freedom, since time-reversal is preserved. Also $\varepsilon$ describe the asymmetry of the two layers upon presence of external electric field. If, on the presence of external electric field, the two layers does not exchange electrons, the potential energy between the layers is just $V = d_{LL} E^{\text{ext}}$ (for $E^{\text{ext}}$ in eV/Å), and defining $\varepsilon = \sigma E^{\text{ext}}$, we have $\sigma = d_{LL}/2$. On the other hand, if the presence of external electric field make the layers exchange electrons, the potential energy between the layers is weakened by the presence of a induced local electric field $E^{\text{loc}} = -\alpha E^{\text{ext}}$, therefore in this case $V = d_{LL}(1 - \alpha) E^{\text{ext}}$, and for $\varepsilon = \sigma E^{\text{ext}} \rightarrow \sigma = d_{LL}(1 - \alpha)/2$. The eigenvalues and eigenstates of this interacting layer model are given by

$$E^{(n)}_{\pm} = h^{(n)}(k) \pm \sqrt{\varepsilon^2 + \left(\frac{\Delta}{2}\right)^2},$$

$$|\pm; n,k\rangle = A_\pm \{ |1L;n,k\rangle \pm B_\pm |2L;n,k\rangle \}$$

with

$$A_\pm = \left(1 + B_\pm^2\right)^{-1/2} ;$$

$$B_\pm = \left[\frac{\sqrt{\varepsilon^2 + (\Delta/2)^2} \pm \varepsilon}{(\Delta/2)}\right],$$

and the band index $n = 1,2,3$. Therefore we can write the energy separation between each KBS as $E_{+} - E_{-} = 2\sqrt{\varepsilon^2 + (\Delta/2)^2}$.

If the electric field is absent ($\varepsilon = 0$) the Hamiltonian commutes with the mirror symmetry, such that the eigenvalues and eigenstates are

$$E^{(n)}_{\pm} = h^{(n)}(k) \pm \frac{\Delta}{2},$$

(S6)
$|\pm; n, k\rangle = \frac{1}{\sqrt{2}} (|1L; n, k\rangle \pm |2L; n, k\rangle). \quad (S7)$

These solutions show us that: (i) for $\Delta \neq 0$ the band structure is composed by two KBS (symmetric $|+\rangle$ and anti-symmetric $|-\rangle$) separated in energy by $\Delta (= E_+ - E_-)$, and as long as the mirror symmetry is present, each state is an equal linear combination of the state from each layer ($|\langle #L|\pm\rangle|^2 = 1/2$); on the other hand (ii) for $\Delta = 0$ the system present two fold degenerated KBS (regardless of spin).

In contrast, for $\varepsilon \neq 0$ the contribution of each layer to a given band is $E^{ext}$ dependent, been $|A_\pm|^2$ and $1 - |A_\pm|^2$ for the layer $1L$ and $2L$, respectively. For $\varepsilon \ll \Delta/2$ these contributions are linear with $E^{ext}$,

$$
|\langle 1L|\pm\rangle|^2 \approx \frac{1}{2} \pm \frac{\sigma}{\Delta} E^{ext};
$$

$$
|\langle 2L|\pm\rangle|^2 \approx \frac{1}{2} \mp \frac{\sigma}{\Delta} E^{ext}. \quad (S8)
$$

In Section I we have seen that each monolayer returns the topological invariant $Z_2 = 1$. Interestingly, the bilayer system also has $Z_2 = 1$. As shown above, for a mirror symmetric bilayer ($\varepsilon = 0$), we find KBS states formed by bonding and anti-bonding orthogonal subspaces, which are energy split by $\Delta$ [see Eqs. (S6)-(S7)]. These are eigenstates of the mirror symmetry with eigenvalues $m_z = \pm 1$. Within each subspace, the topological invariant is $Z_{m_z} = 1$. For a finite $\varepsilon$ the mirror symmetry is broken. Nonetheless, it is still possible to label the KBS states by the orthogonal subspaces defined by the eigenstates of $\tilde{M} = (\Delta/2 \tau_x - \varepsilon \tau_z)/\sqrt{\varepsilon^2 + (\Delta/2)^2}$ [see Eq. (S5)], with eigenvalues $\tilde{m}_z = \pm 1$. This simply generalizes the mirror symmetry and yields $Z_{2m_z} = 1$ for each subspace. Notice that for $\varepsilon \ll \Delta$, $\tilde{M}$ reduces to the mirror symmetry operator, while for $\varepsilon \gg \Delta$ it labels the top and bottom layers, as shown in Fig. S4.

![FIG. S5. Electronic band structures, obtained by the TB approach for the kagome (MC$_4$S$_4$)$_3$-ML [Eq. (S10)], for different Rashba SOC strength ($\lambda_R$); bulk states (a1)-(d1), and nanoribbon edge states (a2)-(d2) projected on the $\langle S_z \rangle$ component of the spin-polarization.](image)

**VIII. RASHBA SPIN-ORBIT COUPLING**

The contribution of the Rashba SOC on the electronic band structure of the (MC$_4$S$_4$)$_3$-ML and -BL systems is defined by the term $H_R$ added to the tight-binding Hamiltonian

$$
H_{TB} = H_0 + H_{SO} + H_R, \quad (S10)
$$

where $H_0$ and $H_{SO}$ are given in Eq.(S1), and

$$
H_R = i\lambda_R \sum_{\langle ij \rangle} c_{i}^\dagger \hat{e}_z \cdot (\boldsymbol{\sigma} \times \mathbf{d}_{ij}) c_{j},
$$
with $d_{ij}$ the unitary vector connecting the $i$-th to the $j$-th site. The effect of Rashba SOC in the low energy Dirac dispersion of graphene is well known: the energy gap induced by intrinsic spin-orbit coupling vanishes for large Rashba SOC contribution, characterized by a spin-splitting of the energy bands [S5, S6]. Here, we find a somewhat similar picture in the (MC$_4$S$_4$)$_3$-ML and -BL. In Figs. S5(a1)-(d1) we present the energy bands of (MC$_4$S$_4$)$_3$-ML as a function of the strength of the Rashba SOC ($\lambda_R$) in $H_{RB}$, $\lambda_R = 0 \rightarrow 3\lambda_1$, where we can identify the spin-splitting due to the Rashba SOC for $\lambda_R \geq \lambda_1$. Further consequences on the edges states of (MC$_4$S$_4$)$_3$ nanoribbons, upon the inclusion of $H_R$, are shown in Figs. S5(a2)-(d2). The edge states are preserved, however, their chiral spin polarizations fade out by increasing the Rashba SOC contribution ($\lambda_R = 0 \rightarrow 3\lambda_1$). It is interesting to note that even for large Rashba contribution, e.g. $\lambda_R = 2\lambda_1$ in Fig. S5(c), the (spin) chirality of the edge states has been preserved. In the sequence, based on first-principles calculations, we will show that the contributions of the Rashba SOC are quite small in the present (MC$_4$S$_4$)$_3$-ML and BL systems.

An external electric field perpendicular to the (MC$_4$S$_4$)$_3$ layers suppresses the mirror of the system, and thus promoting the Rashba SOC effects. In order to provide a quantitative measure of such a contribution on the (MC$_4$S$_4$)$_3$ and (PtC$_4$S$_4$)$_3$-ML and -BL systems, we perform a set of first-principles calculations of the electronic band structures of those (MC$_4$S$_4$)$_3$ systems upon the presence of an external electric field ($E^{ext}$). In Figs. S6(a1)-(c1) and S6(a2)-(c2) we present the electronic band structure of (NiC$_4$S$_4$)$_3$- and (PtC$_4$S$_4$)$_3$-MLs for $E^{ext} = 0 \rightarrow 0.5$ eV/Å; where we find that the effect of Rashba SOC is much smaller compared with the one of the intrinsic SOC, up to $E^{ext} = 0.5$ eV/Å. For instance, the (NiC$_4$S$_4$)$_3$-ML exhibits a spin-splitting of about 0.5 meV for $E^{ext} = 0.5$ eV/Å, which is small in comparison with the (intrinsic SOC) energy gap of 14 meV (less than 4%), Fig. S6(d1). Similarly, in (PtC$_4$S$_4$)$_3$-ML, we found a spin-splitting of $\sim$5 meV and an energy gap of 60 meV due to the intrinsic SOC, Fig. S6(d2).

Following the same scheme, based on the TB model [Eq. (S10)], in Figs. S7(a1)-(d1) we present the electronic band structures of the (MC$_4$S$_4$)$_3$-BL, as a function of the strength of the $H_R$ contribution ($\lambda_R$), and the respective spin-polarized edge states, Figs. S7(a2)-(d2). Similarly to what we found in the single layer systems, (i) the spin-chirality of the edges fades out for larger values of $\lambda_R$ in comparison with $\lambda_1$, however (ii) even for $\lambda_R = 2\lambda_1$, the chiral character of the (edge) energy bands has been maintained. In the sequence, we performed first-principles calculations of the electronic band structures of (NiC$_4$S$_4$)$_3$-BL and (PtC$_4$S$_4$)$_3$-BLs as a function of the external electric field. Our results are summarized in Fig. S8, where we show the evolution of the electronic band structures of (NiC$_4$S$_4$)$_3$-BL (a1)-(c1) and (PtC$_4$S$_4$)$_3$-BL (a2)-(c2). For both systems, we found that the spin-splitting due to the Rashba SOC about ten times smaller than the energy gap induced by the intrinsic SOC, Figs. S8(d1) and (d2).

Therefore, we can infer that the effect of Rashba SOC is small, compared with the other contributions, and can be dismissed in the (present) (MC$_4$S$_4$)$_3$ monolayer and bilayer systems for $E^{ext}$ within the studied range.

**FIG. S6.** First-principles electronic band structure as a function of the external electric field $E^{ext}$. (a1)-(c1) (NiC$_4$S$_4$)$_3$-ML and (a2)-(c2) (PtC$_4$S$_4$)$_3$-ML. In (d1) and (d2) we evidenciate the blue dashed rectanges of (c1) and (c2) respectively.
FIG. S7. Electronic band structures, obtained by the TB approach for the kagome (MC\textsubscript{4}S\textsubscript{4})\textsubscript{3}-BL [Eq. (S10)], for different Rashba SOC strength ($\lambda_R$); bulk states (a1)-(d1), and nanoribbon edge states (a2)-(d2) projected on the $\langle S_i \rangle$ component of the spin-polarization. $i, j = A, B$.

FIG. S8. First-principles electronic band structure as a function of the external electric field $E^{ext}$. (a1)-(c1) (NiC\textsubscript{4}S\textsubscript{4})\textsubscript{3}-BL and (a2)-(c2) (PtC\textsubscript{4}S\textsubscript{4})\textsubscript{3}-BL. In (d1) and (d2) we evidenciate the blue dashed retangles of (c1) and (c2) respectively.

[S1] E. Tang, J.-W. Mei, and X.-G. Wen, Phys. Rev. Lett. 106, 236802 (2011).
[S2] Z. Wang, Z. Liu, and F. Liu, Phys. Rev. Lett. 110, 196801 (2013).
[S3] A. A. Soluyanov and D. Vanderbilt, Phys. Rev. B 83, 235401 (2011).
[S4] R. Yu, X. L. Qi, A. Bernevig, Z. Fang, and X. Dai, Phys. Rev. B 84, 075119 (2011).
[S5] M. Gmitra, S. Konschuh, C. Ertler, C. Ambrosch-Draxl, and J. Fabian, Phys. Rev. B 80, 235431 (2009).
[S6] C. L. Kane and E. J. Mele, Phys. Rev. Lett. 95, 146802 (2005).