Prediction of two-dimensional organic topological insulator bases in Metal-DCB lattices

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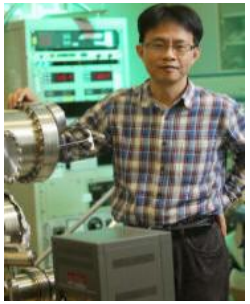
Collaborators

Computational calculation

Prof. Feng-Chuan Chuang (National Sun Yat-Sen University)
Dr. Zhi-Quan Huang (National Sun Yat-Sen University)
Gennevieve M. Macam (National Sun Yat-Sen University)

Prof. Li Huang's group (Southern University of Science and Technology, China)
I was a postdoc (2016.09-2018.09)

Experiment



Prof. Nian Lin's group (The Hong Kong University of Science and Technology, Hong Kong**)**

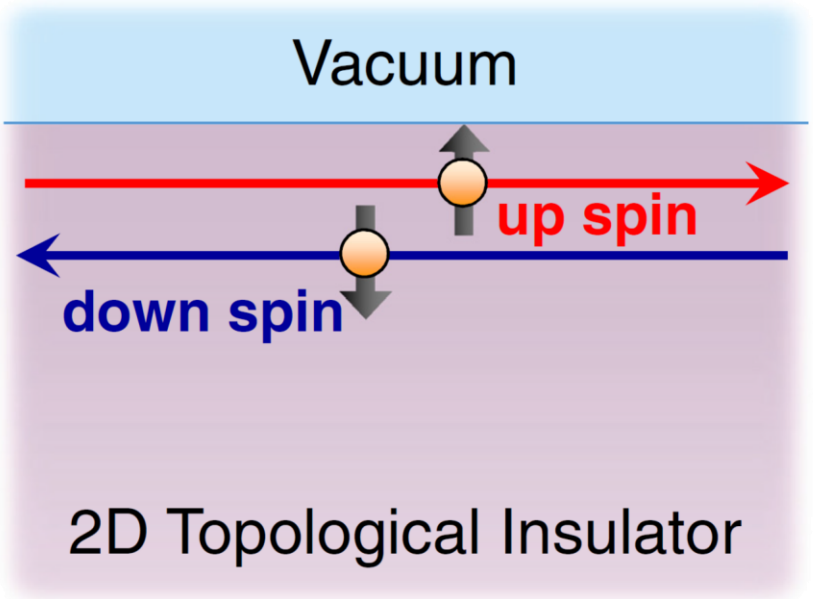
The growth of self-assembly metal-organic frameworks

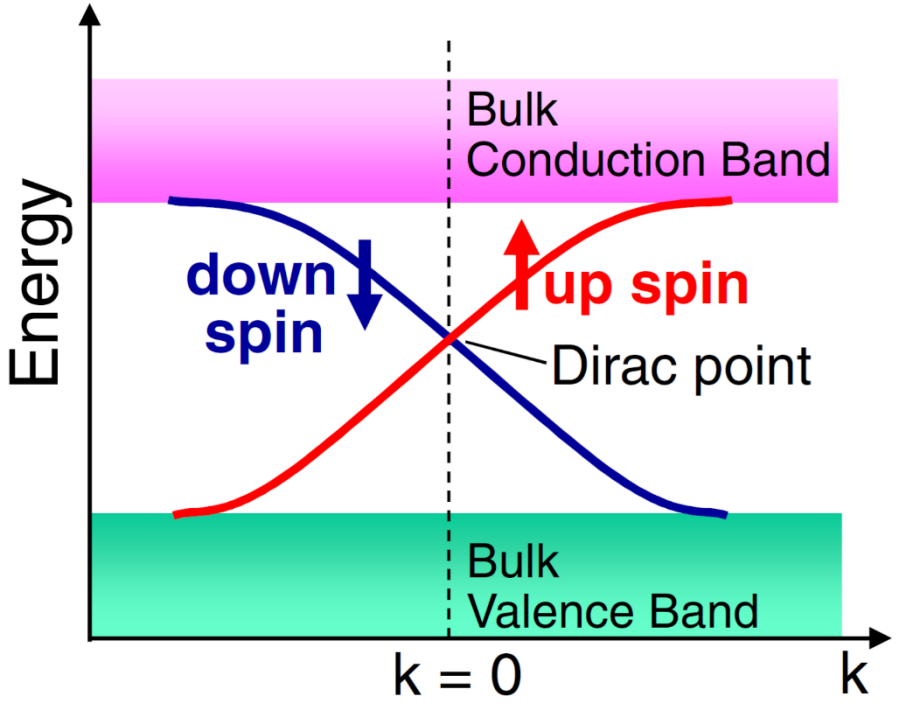
Outline

1. **Introduction**
2. **Prediction of two-dimensional organic topological insulator bases in Metal-DCB lattices**
3. **Synthesis and characterization of a single-layer conjugated metal–organic structure featuring a non-trivial topological gap**

2D Topological Insulator

A topological insulator is a material that behaves as an insulator in its interior but whose surface contains conducting states.





- Spin-orbit-coupling(SOC)

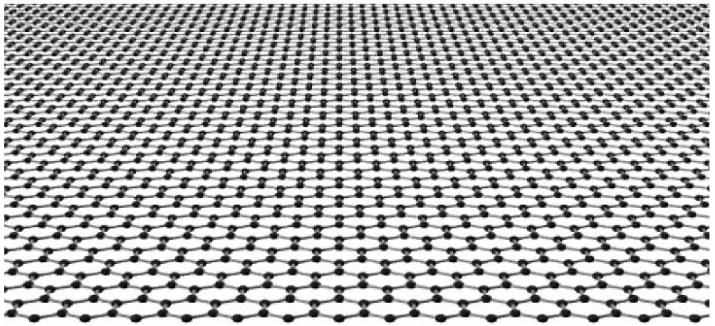
Topological insulator has two crucial features.

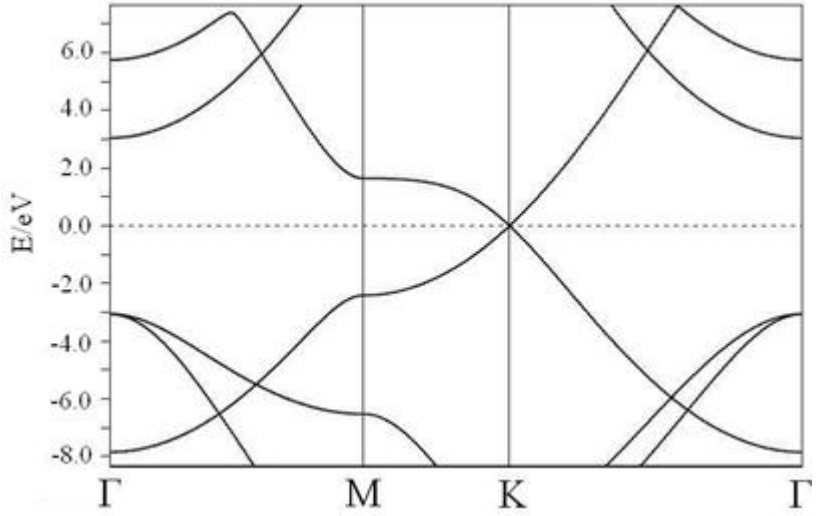
1. SOC→ edge state → **quantum spin Hall effect**
2. Time reversal symmetry → no back-scattering

Y. Ando, Journal of the Physical Society of Japan 82, 102001 (2013)

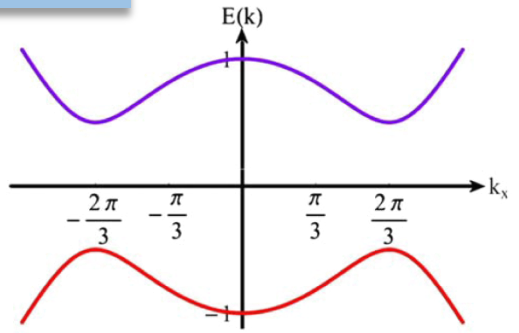
Quantum Spin Hall in graphene

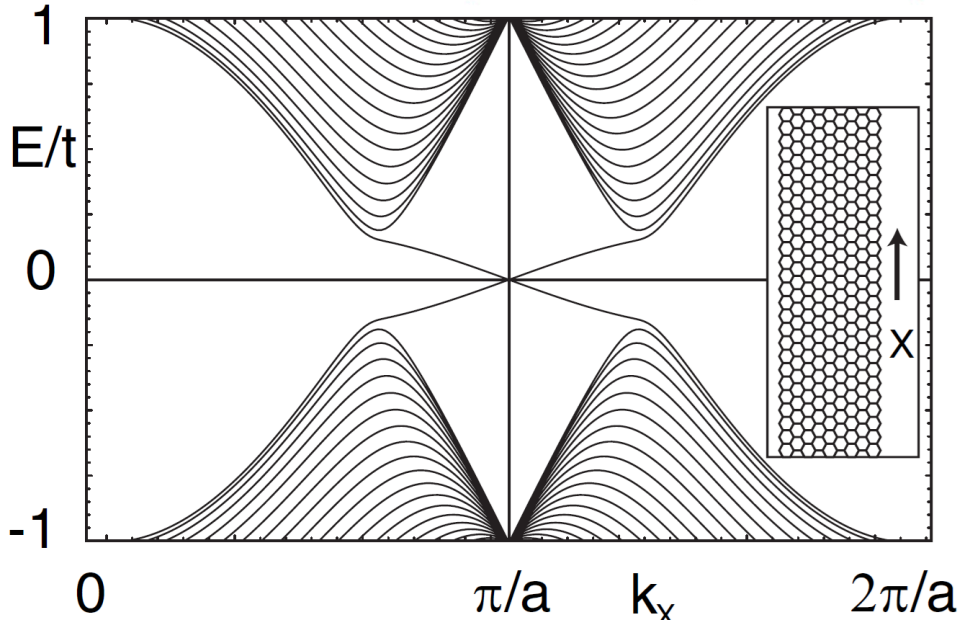
Graphene





Graphene ribbon



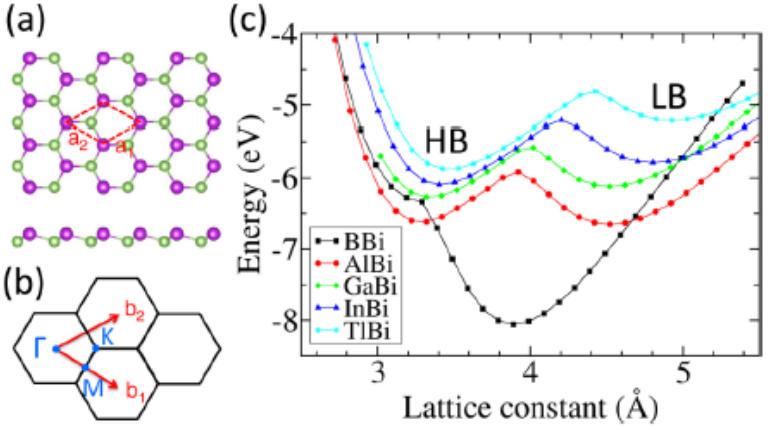


C. L. Kane and E. J. Mele Phys. Rev. Lett. 95, 226801 (2005)
Ralph van Gelderen and C. Morais Smith Phys. Rev. B .81.125435

Previous works

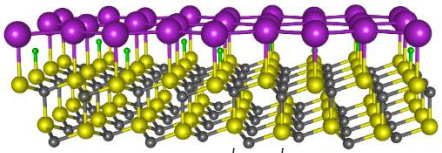
◆Free standing 2D topological material

- ➢ Honeycomb structure:
  - Ⅴ elements: Sb, Bi
  - Ⅲ-Ⅴ compounds: GaBi, TlBi, etc.
- ➢ Atomic adsorption:
  - Hydrogen and halogen atoms
  - Magnetic doping: Fe, Co, Ni, Mn

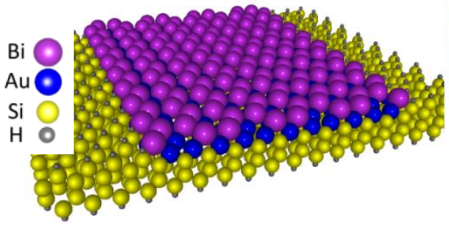


◆Substrate-supported 2D topological material

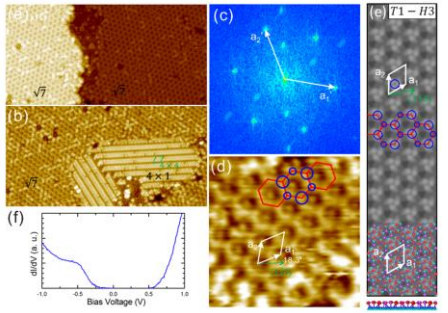
- ➢ Honeycomb structure:
  - Bismuthene on SiC(0001)
  - Stanene on Ge(111)
  - GaBi on Si(111)
- ➢ Surface alloys:
  - Group Ⅲ-Ⅵ elements on AuSi(111)
  - InBi alloy on Si(111)



1x1 Bi on √3x√3 SiC



2/3 ML Bi on Au/Si(111)



$\sqrt{7} \times \sqrt{7}$-InBi on Si(111)

Outline

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2. **Prediction of two-dimensional organic topological insulator bases in Metal-DCB lattices**
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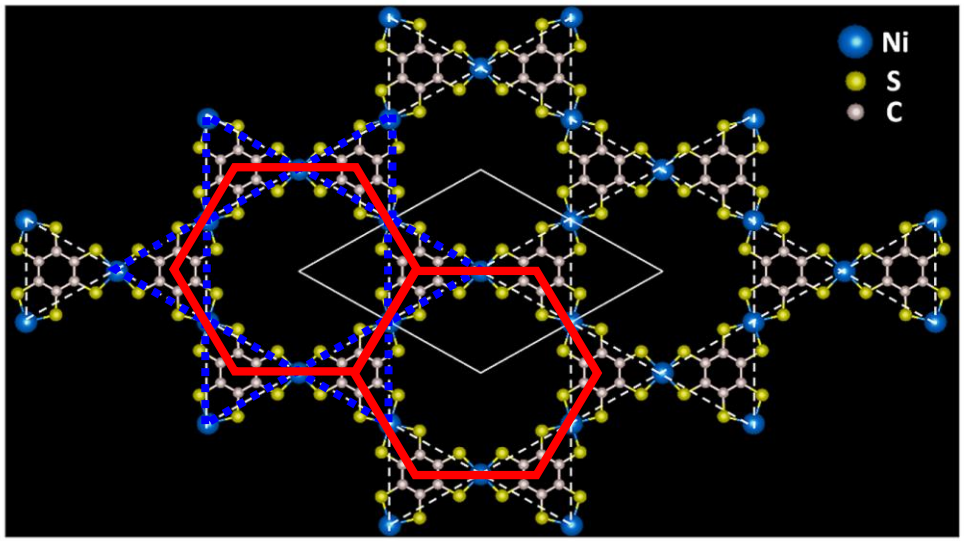
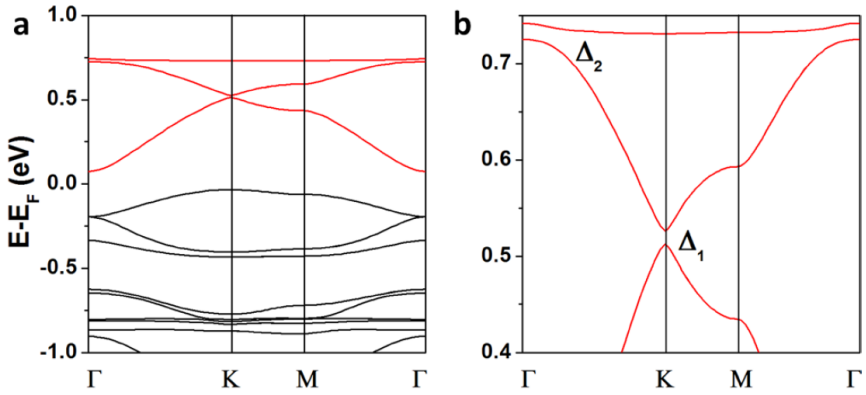
Prediction of a Two-Dimensional Organic Topological Insulator

Z. F. Wang, Ninghai Su, and Feng Liu*

$Ni3C12S12$: $\Delta 1 = 13.6\ meV, \Delta 2 = 5.8\ meV$

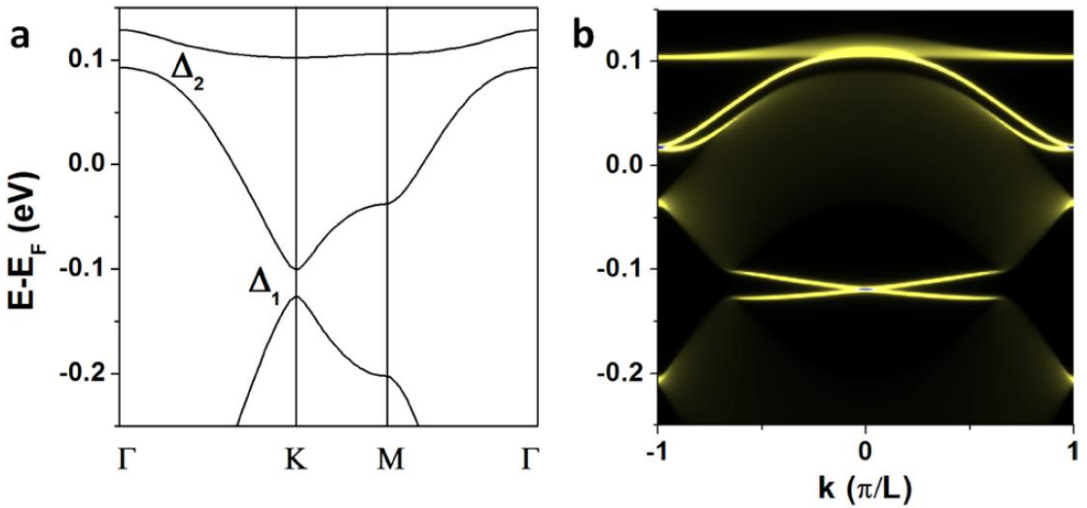




$Au3C12S12$: $\Delta 1 = 22.7\ meV, \Delta 2 = 9.5\ meV$

The Chern number and
spin Chern number are defined as

$$C = C_{\uparrow} + C_{\downarrow} \qquad C^s = \frac{1}{2}(C_{\uparrow} - C_{\downarrow})$$



Nano Lett. 2013, 13, 2842−2845

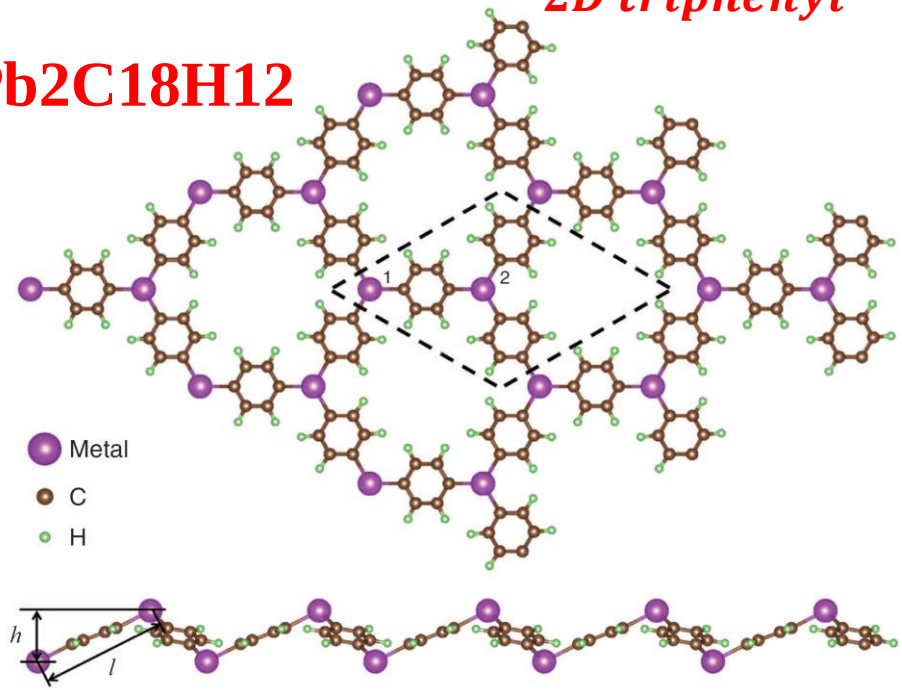
Organic topological insulators in organometallic lattices

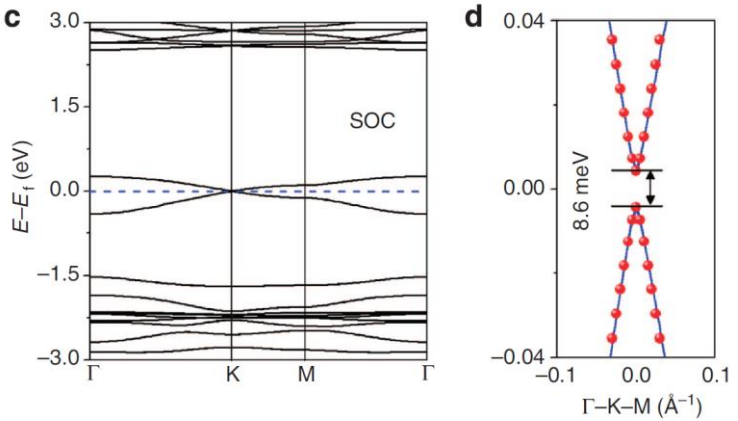
triphenyl-lead (TL) [Pb(C6H5)3]

Z.F. Wang[1], Zheng Liu[1] & Feng Liu[1]

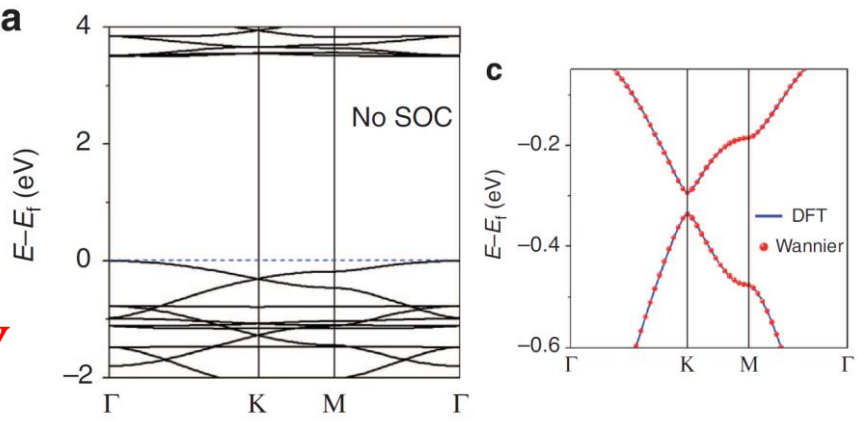
2D triphenyl − lead: gap = 8.6 meV within Fermi Level

Pb2C18H12





Buckled : Pb $6s^2 6p^2$ electronic configuration that favors the sp^3 hybridization

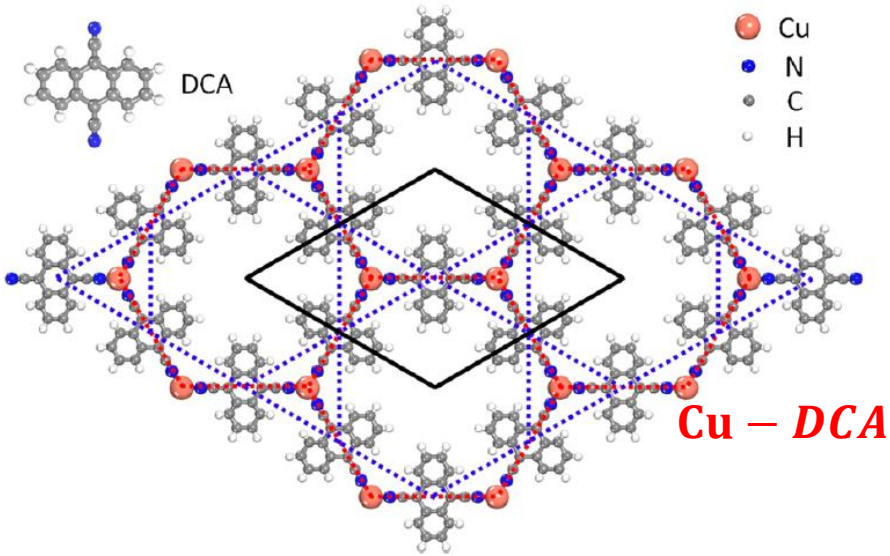


2D triphenyl − bismuth: gap = ~43 meV, but Fermi Level is shifted above ~0.31 eV

Nat. Commun. 2013, 4, 1471.

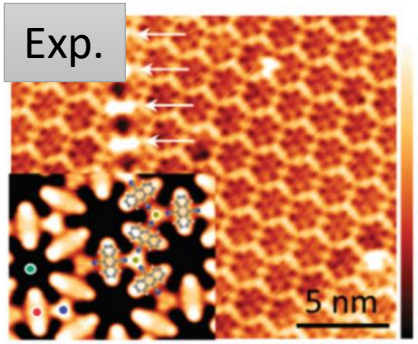
Intrinsic Two-Dimensional Organic Topological Insulators in Metal–Dicyanoanthracene Lattices

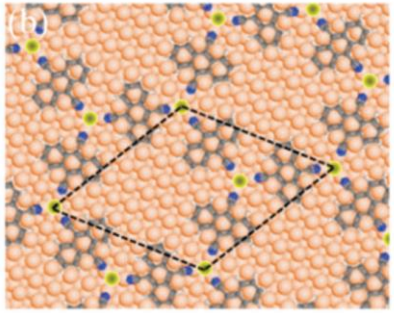
L. Z. Zhang,[†,‡,§] Z. F. Wang,[§,⊥] B. Huang,[§] B. Cui,[§] Zhiming Wang,[*,†] S. X. Du,[*,‡] H.-J. Gao,[‡] and Feng Liu[*,§,¶]



intrinsic 2D OTI without the need of doping

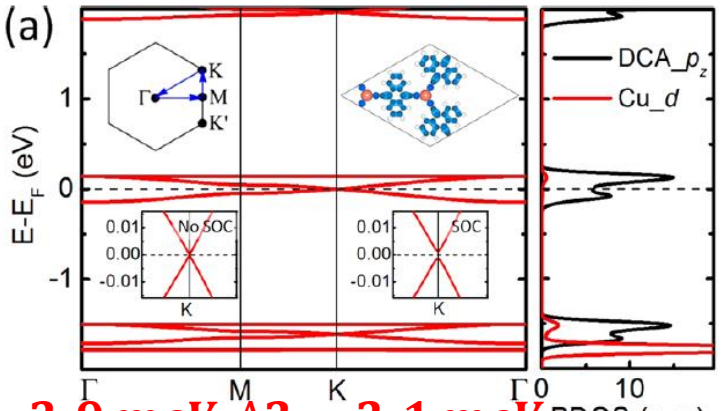
Exp.



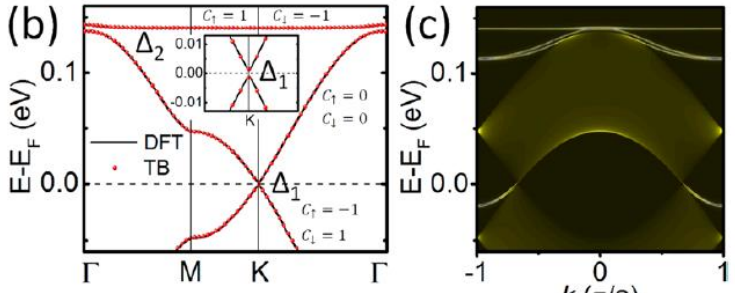


Chem. Commun., 2014, 50, 12289

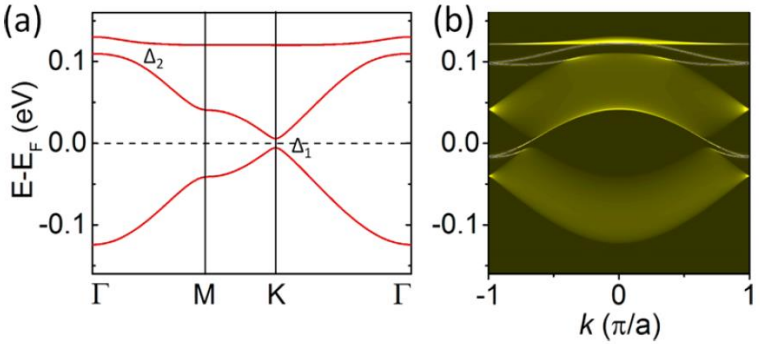
Nano Lett. 2016, 16, 2072−2075



Cu − *DCA*: Δ1 = 2.9 *meV*, Δ2 = 2.1 *meV*

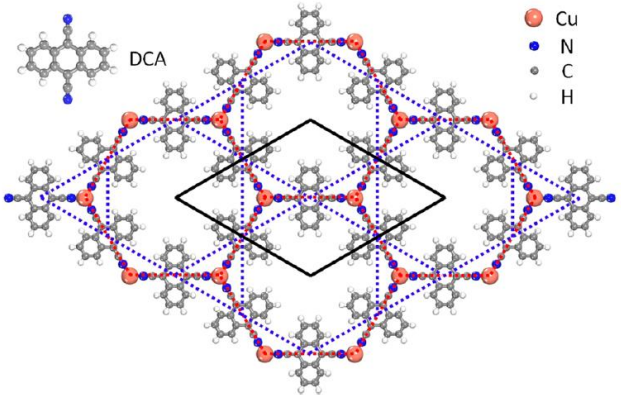


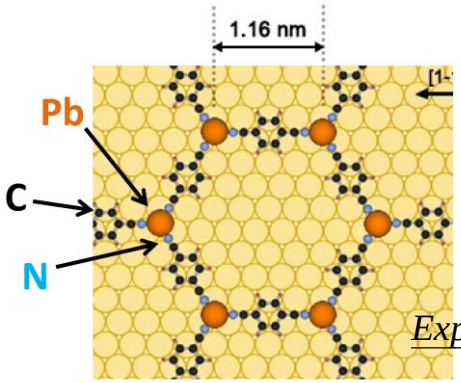
Au − DCA: Δ1 = 11.3 *meV*, Δ2 = 10.6 *meV*



Motivation

Nano Lett. 2016, 16, 2072−2075





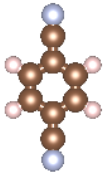
Pb-DCB

Experiment group at HKUST

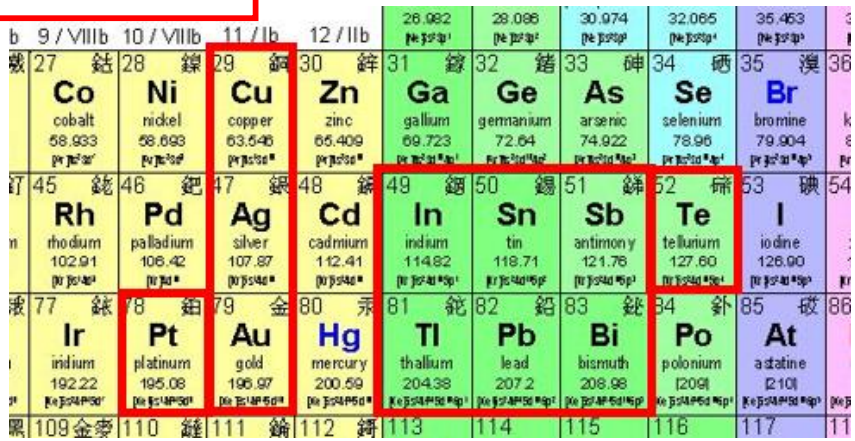
Au(111)

1. Di-cyano-anthracene (DCA) ⟹ Di-cyano-benzene (DCB)


DCA


DCB

2. Pb ⟹ group III-VI



Computation Packages and Method

◆Vienna Ab-Initio Simulation Package (VASP)

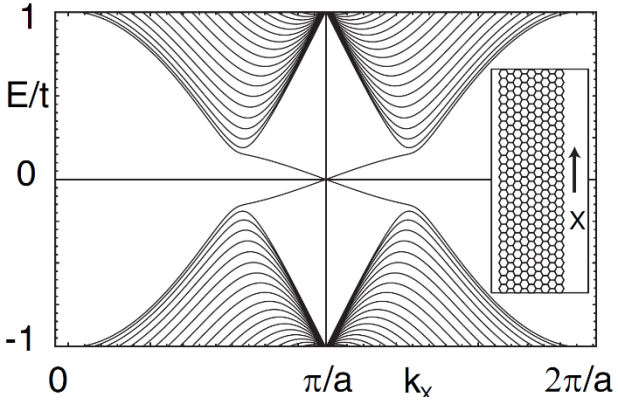
Our first-principles calculations were performed within the framework of the density functional theory (DFT) utilizing the generalized gradient approximation (GGA). Projector-augmented-wave (PAW) wave functions were used in VASP

◆Wannier90: A tool for obtaining maximally-localised Wannier functions

Berry curvature, Chern number and edge states were calculated with the Hamiltonian obtained from maximally-localized Wannier functions obtained via the WANNIER90 package

Find a topological insulator

Topologically protected Edge state



Phys. Rev. Lett. 95, 226801 (2005)

Parity analysis

$$(-1)^{\nu} = \prod_{i=1}^{4} \delta(K_i) = \delta(\Gamma)\delta(M)^3$$

TABLE I. The total parity at the Γ and M points and the Z_2 number of Bi (111) films with different thickness.

No. of BLs	1	2	3	4	5	6	7	8
$\delta(\Gamma)$	+	+	−	−	+	+	−	−
$3\delta(M)$	−	−	+	+	−	−	+	+
ν	1	1	1	1	1	1	1	1

Phys. Rev. Lett. 95, 226801 (2005)

Phys. Rev. Lett. 107. 136805 (2011)

Z_2 invariant

Z_2 is the topological number

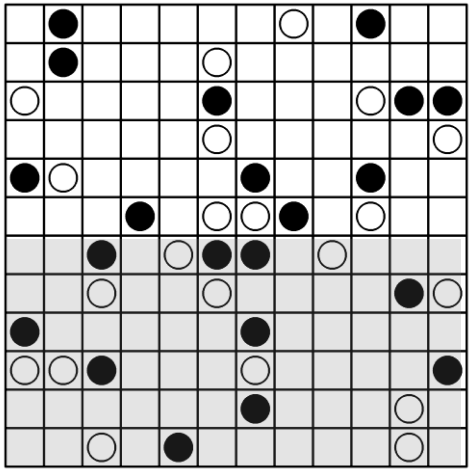
$Z_2 = 1$ The nontrivial topological phase

$Z_2 = 0$ The trivial topological phase

The white and black circles denote n =1 and -1, respectively, while the blank denotes 0. The Z_2 invariant is obtained by summing the n field over half of the tori.

T. Fukui and Y. Hatsugai , J. Phys. Soc. Japan. 76, 053702 (2007)

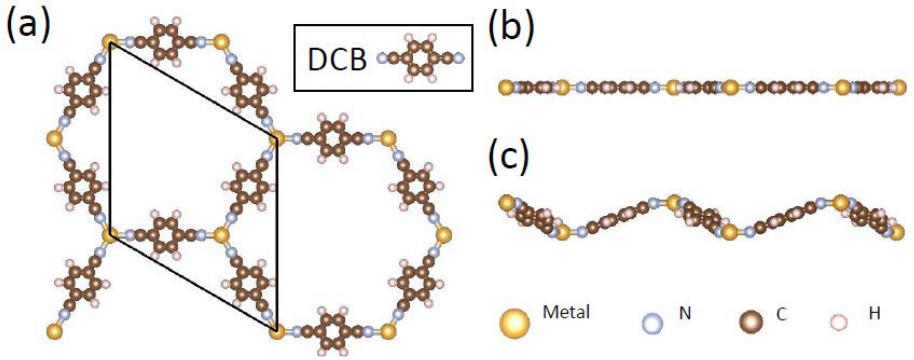
$Z_2 = 1$



Results and Discussion

APPLIED PHYSICS LETTERS 113, 233301 (2018)

Atomic structure of M-DCB



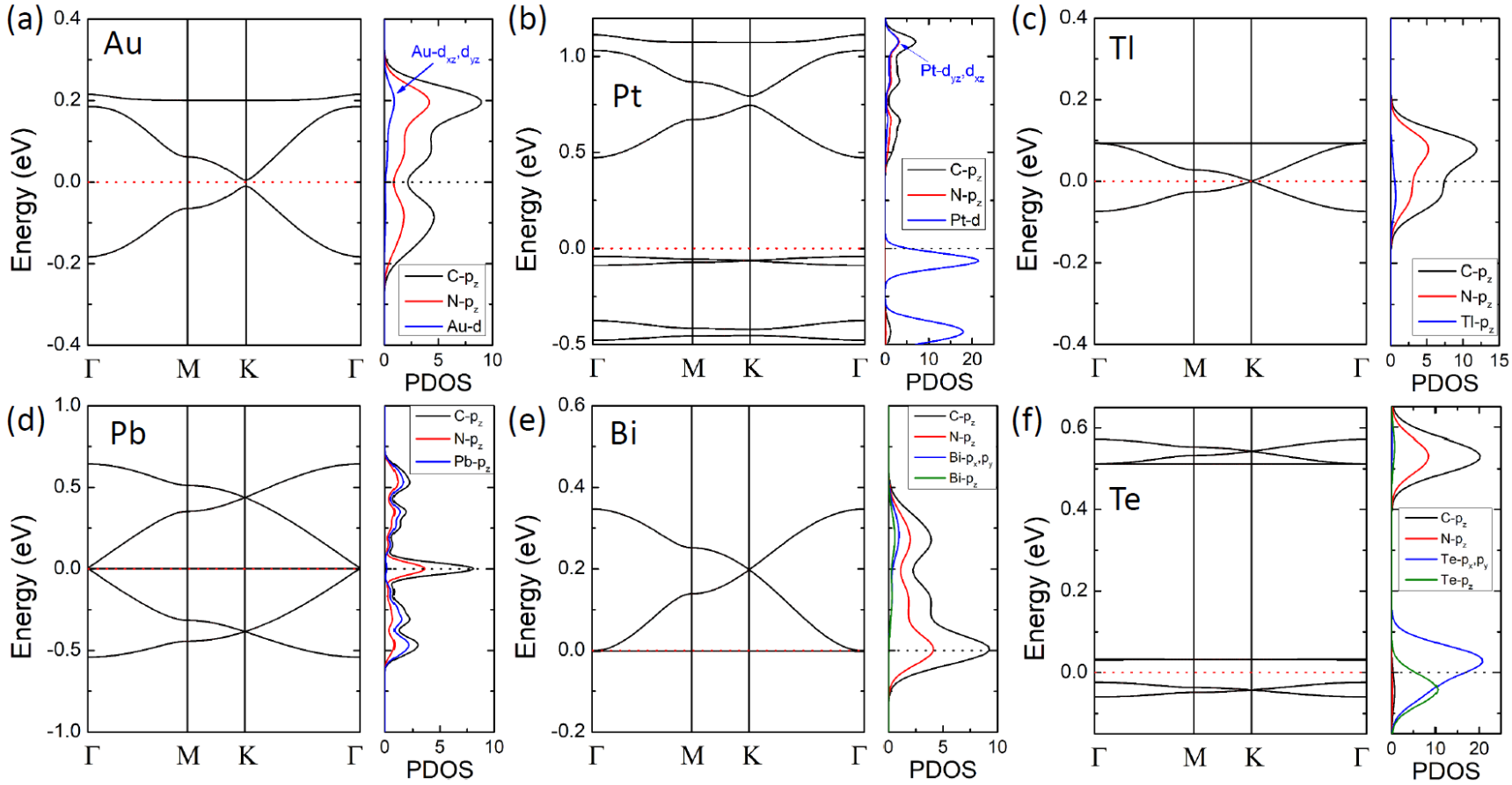
Stability of Atomic structure

$$\Delta E = E_{BK} - E_{PL}$$

	Planar Phase (PL)			Buckled Phase (BK)				
	Latt.	Gap (meV)	Z_2	Latt.	Gap (meV)	d_{BK} (Å)	Z_2	ΔE (eV)
Pt	20.72	514.5	0		NA			
Cu	20.29	3.3	1		NA			
Ag	21.21	3.0	1	20.10	0.8	1.298	1	-0.002
Au	20.99	14.3	1	19.70	14.6	3.575	1	-0.012
In	23.29	0.1	1		NA			
Tl	23.55	0.2	1		NA			
Sn	22.35	0.3	1		NA			
Pb	22.56	0.7	1		NA			
Sb	21.84	0.3	1	18.36	26.3	5.970	1	-0.229
Bi	22.07	1.0	1	18.55	46.4	6.019	1	-0.256
Te	24.93	54.9	0	16.84	175.6	6.586	1	-0.486

Representative band structures with SOC and PDOS

In planar phase



APPLIED PHYSICS LETTERS 113, 233301 (2018)

Strain and edge state of Au-DCB model

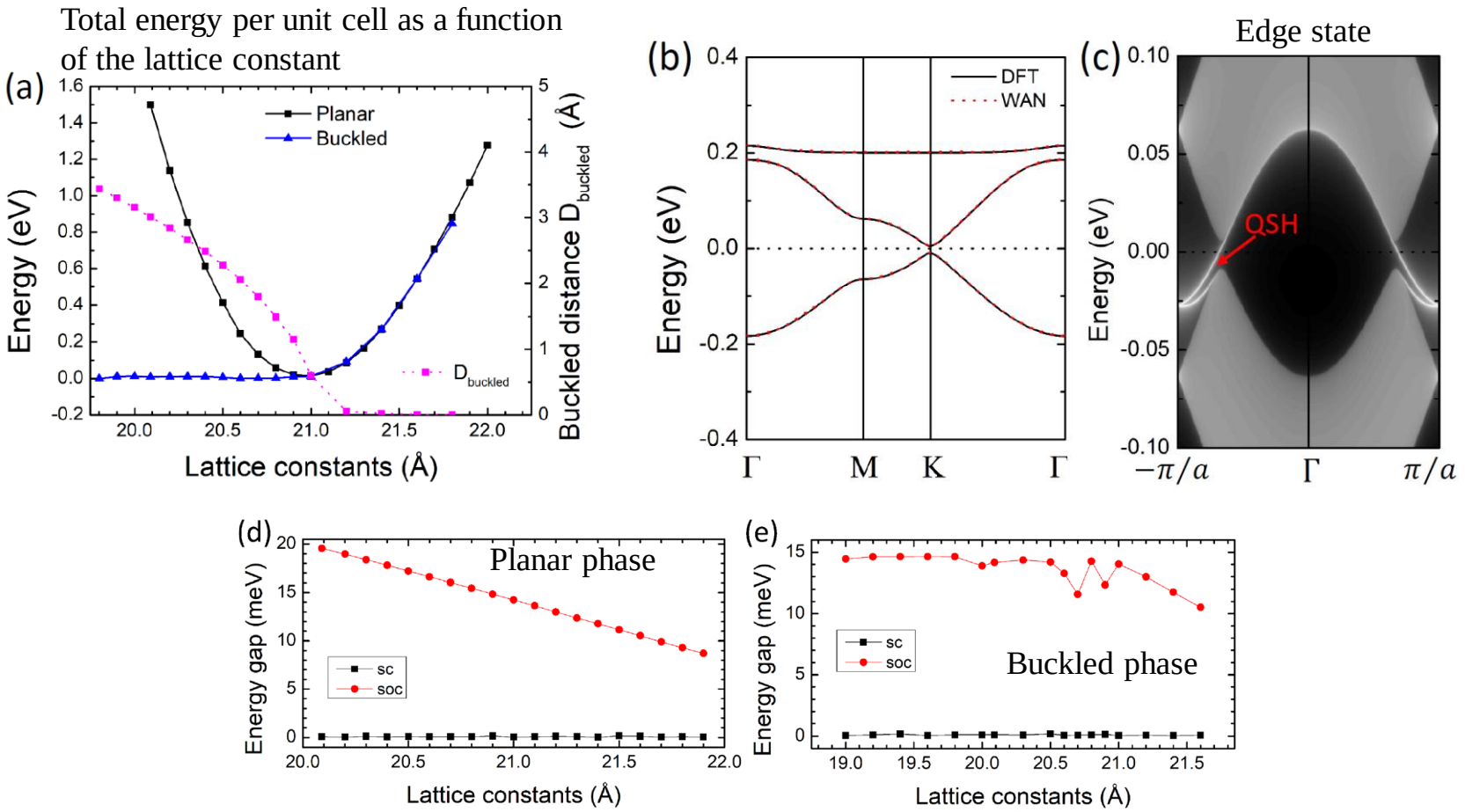


FIG. 3. (a) Total energy per unit cell as a function of the lattice constant for Au-DCB. The planar and buckled configurations are marked by black squares and blue triangles, respectively. The pink squares represent the buckling height d_{BK} between the adjacent Au atoms in a unit cell. (b) The first-principles band structure (black lines) is compared with the corresponding results obtained from a Wannier90-based tight-binding fit (red dashed lines) for the Au-DCB model. (c) is the LDOS of edge states in Au-DCB. The energy gap as a function of lattice constant for (d) PL and (e) BK phases. The red and black lines with markers are the gaps with and without the SOC, respectively.

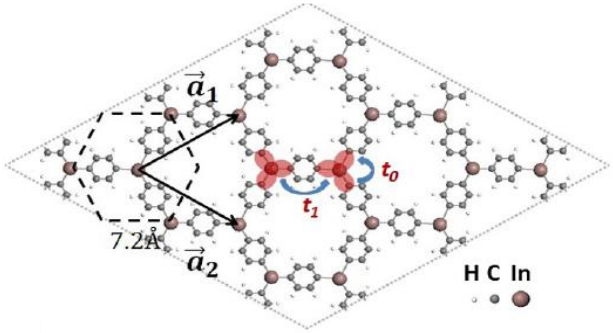
APPLIED PHYSICS LETTERS 113, 233301 (2018)

Flat Chern Band in a Two-Dimensional Organometallic Framework

Zheng Liu,[1] Zheng-Fei Wang,[1] Jia-Wei Mei,[2] Yong-Shi Wu,[3,4] and Feng Liu[1,*]

PRL 110, 106804 (2013)

2D indium-phenylene organometallic framework (IPOF)



$$H_{\text{eff},\sigma_z=\pm1}(k) = H_{\text{hop}}(k) + H^0_{\text{SOC},\sigma_z} + H_{\text{Zeeman}}$$

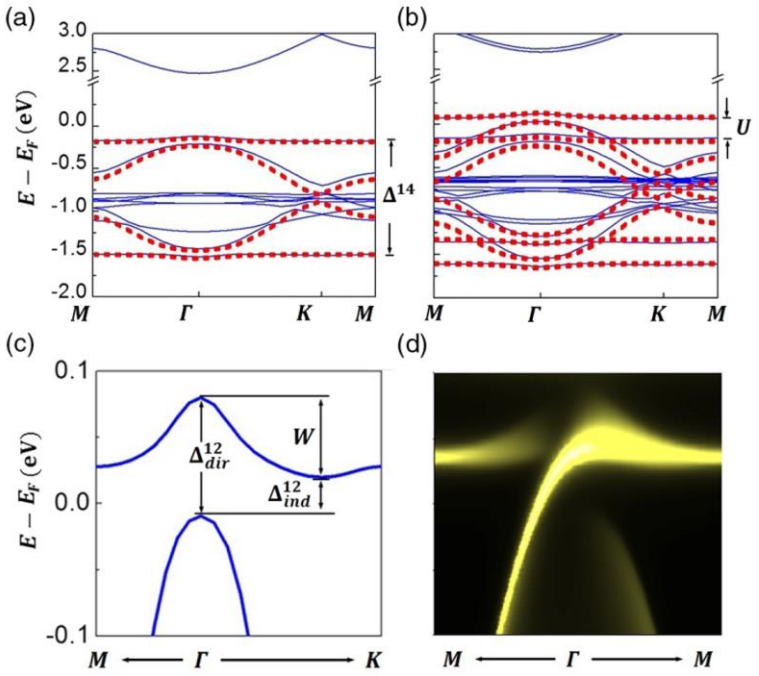
Eq. (8)

$$= -t_1 \begin{pmatrix} 0 & 0 & V_{xx} & V_{xy} \\ 0 & 0 & V_{xy} & V_{yy} \\ V^*_{xx} & V^*_{xy} & 0 & 0 \\ V^*_{xy} & V^*_{yy} & 0 & 0 \end{pmatrix} + \sigma_z \lambda \begin{pmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{pmatrix} + \sigma_z M.$$

TABLE I. Energy scales associated with the FCB in the IPOF.

Property	Symbol	Value	Reference
Bandwidth	W	60 meV	Figure 2(c)
Spin splitting	U	100 meV	Figure 2(b)
Debye temperature	ω_d	300 meV	Figure S1 [14]
Energy gap	Δ^{12}_{dir}	90 meV	Figure 2(c)
	Δ^{12}_{ind}	30 meV	Figure 2(c)
	Δ^{14}	1.4 eV	Figure 2(a)

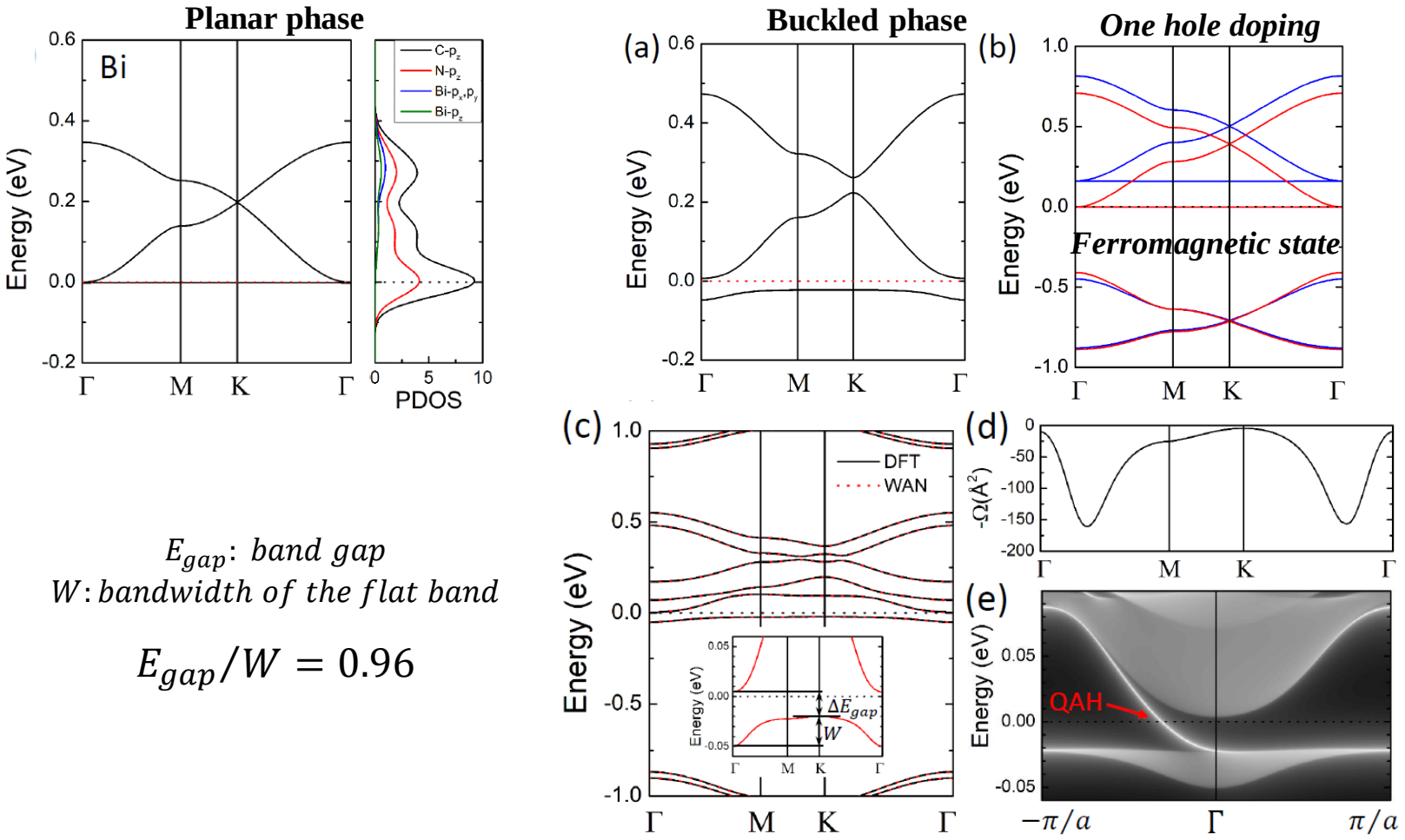
$\Delta^{12}_{ind}/W = 0.50$



(a) Band structure with SOC. (b) Band structure with SOC when doping one hole into the unit cell. The solid (blue) curves are DFT results. The dashed (red) curves are from model Hamiltonian Eq. (8) with parameters (a) $t_1 = 0.7\ eV$, $\lambda = 0.05\ eV$, M = 0 (b)) $t_1 = 0.7\ eV$, $\lambda = 0.05 eV$, M = $0.1\ eV$. (c) Zoomed-in band plot around the Fermi level. (d) Momentum-resolved edge density of states of a semi-infinite IPOF with SOC and doping.

The emergence of the fractional quantum Hall state requires further enlarging the energy gap Δ^{12} and reducing the bandwidth W to satisfy the condition $\Delta \gg U > W$

Bi-DCB model with one hole doping



E_{gap}: band gap

W: bandwidth of the flat band

$$E_{gap}/W = 0.96$$

(a) Band structure of Bi-DCB in the BK phase at the lattice constant of 21.08Å with SOC interaction. Band structures of Bi-DCB with one hole doping for (b) spin-polarized calculation. Further inclusion of SOC is shown in (c). The inset figure in (c) is a zoom-in near the Fermi level. The black solid and red dashed lines represent the results of the first-principles calculation and Wannier90-based tight-binding fit, respectively. (d) is the Berry curvature computed using Wannier90-based tight-binding Hamiltonian. (e) is LDOS of the edge state for a semi-infinite Bi-DCB with SOC and doping

APPLIED PHYSICS LETTERS 113, 233301 (2018)

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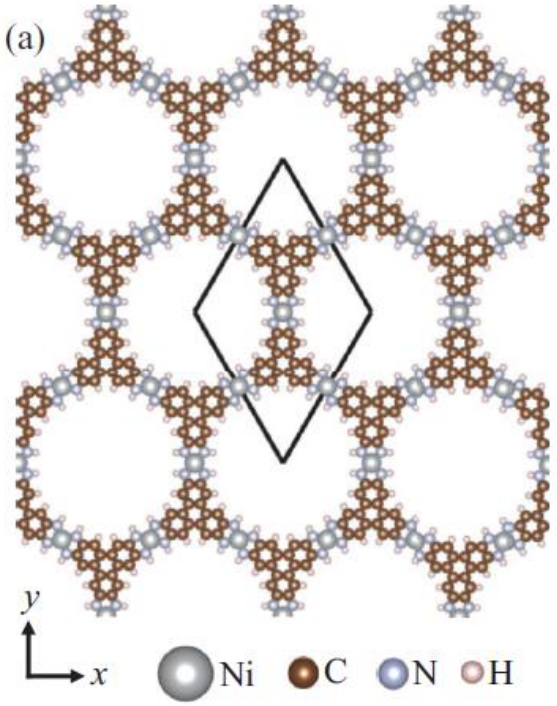
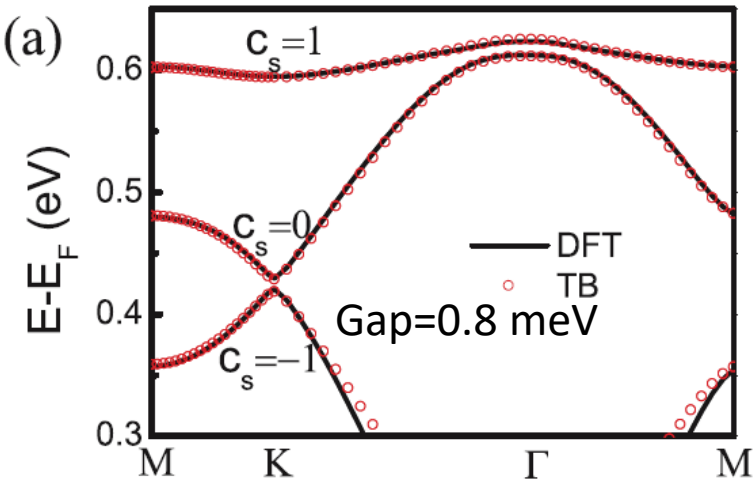
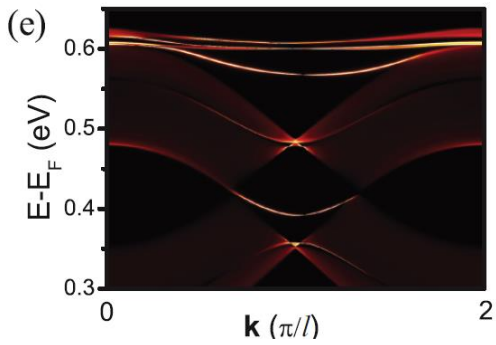
Quantum spin Hall and Z_2 metallic states in an organic material

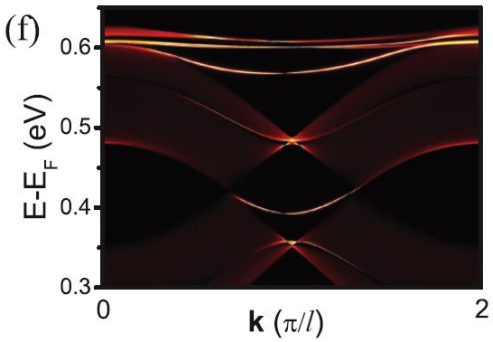
Bao Zhao,[1] Jiayong Zhang,[1] Wanxiang Feng,[2] Yugui Yao,[2] and Zhongqin Yang[1,*]

$Ni_3(C_{18}H_{12}N_6)_2$=Ni_3(HITP)$_2$









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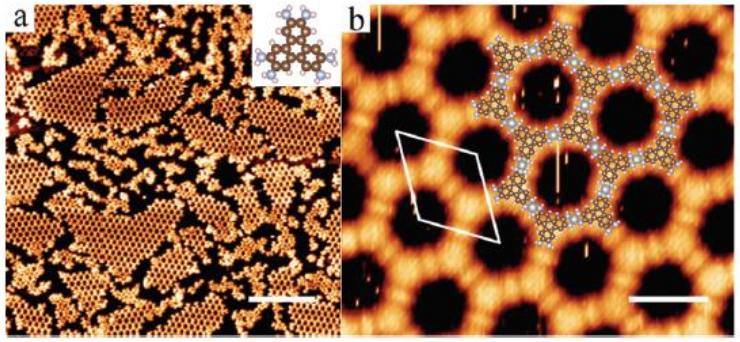
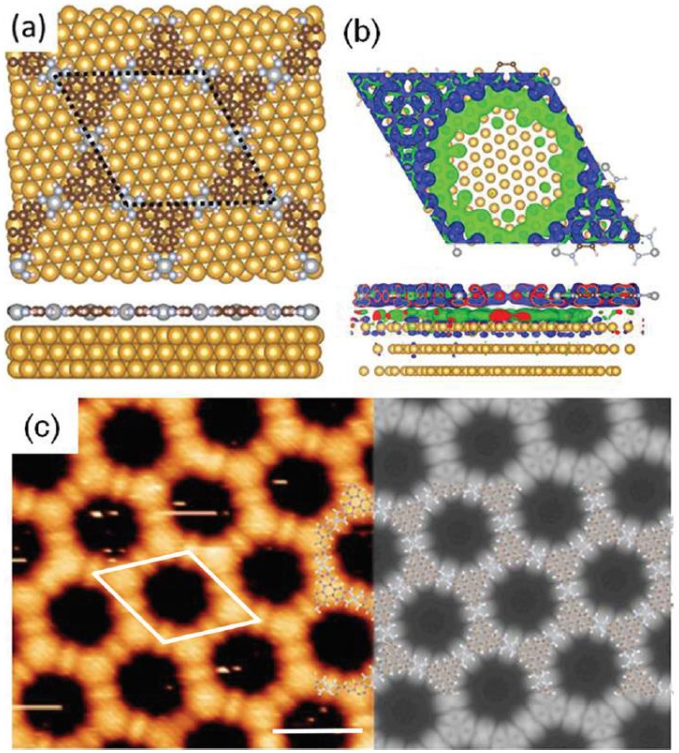
Results and Discussion

STM image



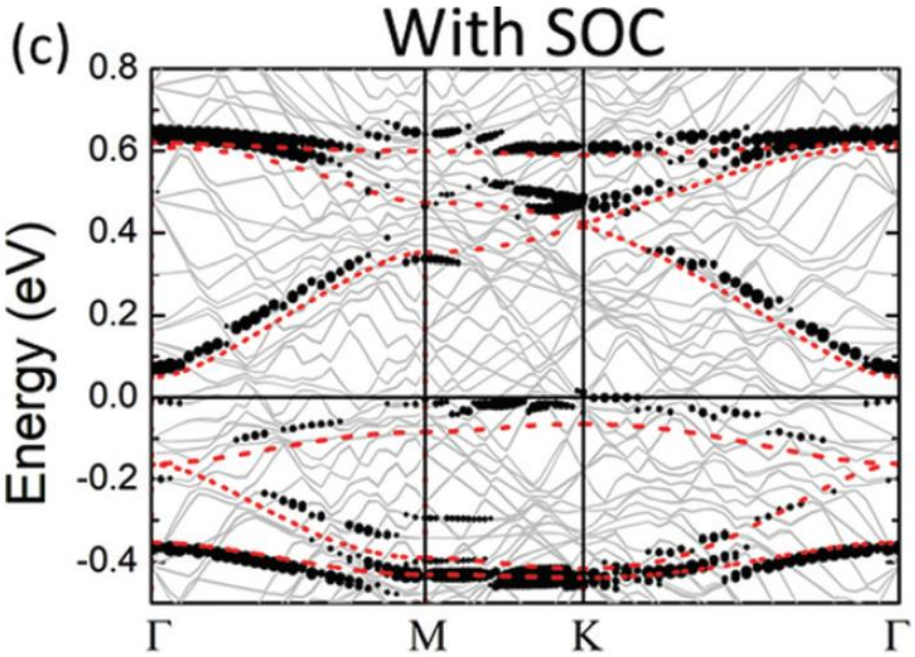
Single-layer $Ni_3(HITP)_2$ network self-assembled on Au(111). (a) An overview STM image (inset: a molecular model of the HATP molecule, C: brown, N: blue, H: pink). Scale bar: 20 nm. (b) A high-resolution STM image overlaid with a molecular model (Ni: large blue balls). Scale bar: 2 nm.



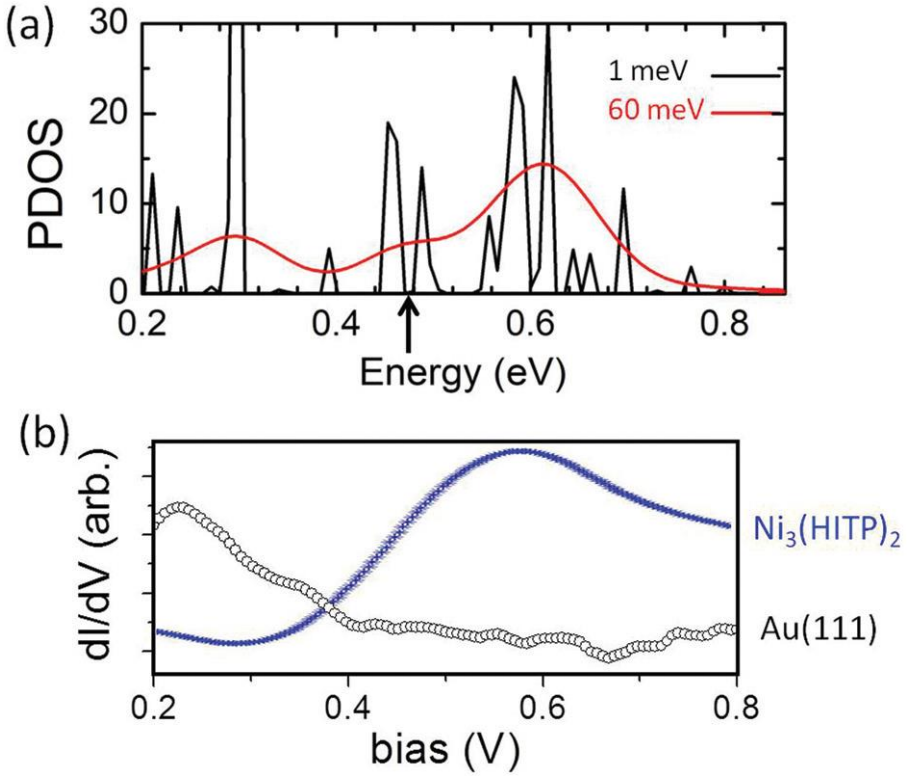
(a) DFT optimized structure of the $Ni_3(HITP)_2$ single layer adsorbed on a Au(111)-$\sqrt{57} \times \sqrt{57}$ substrate. (b) Top and side views of charge transfer at an isosurface level of 2.87×10^{-4} e a^{-3} (a stands for Bohr radius). Green (blue) color represents charge accumulation (depletion), respectively. (c) Experimental (left) and simulated (right) STM images. Scale bar: 2 nm.

Results and Discussion

Electronic properties



DFT-calculated band structures of the $Ni_3(HITP)_2$ layer adsorbed on a Au(111)-$\sqrt{57} \times \sqrt{57}$ substrate with SOC. The black solid circles indicate the contribution (more than 60%) of the $Ni_3(HITP)_2$ network. The red dotted lines are the bands of a free-standing $Ni_3(HITP)_2$ network.



(a) DFT-calculated projected density of states (PDOS) of the $Ni_3(HITP)_2$ monolayer (black: 1 meV smearing; red: 60 meV smearing). (b) Differential tunneling spectrum acquired at the $Ni_3(HITP)_2$ network (blue) and Au(111) surface (open dots).

Summary

1. **Prediction of two-dimensional organic topological insulator bases in Metal-DCB lattices**

   - An intrinsic organic topological insulator in Au-DCB lattice
   - A flat Chern band in Bi-DCB with one hole doping.

2. **Synthesis and characterization of a single-layer conjugated metal–organic structure featuring a non-trivial topological gap**

   - To conduct quantum transport measurements and to explore the functionality of this system, future work of growing or transferring the single layer to an insulating substrate is highly desirable.

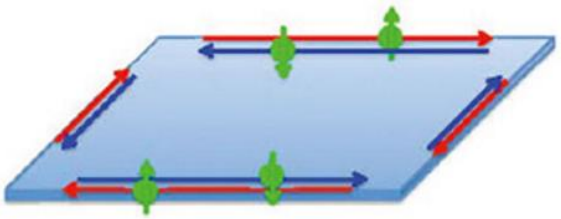
Thank you for your attention

成果

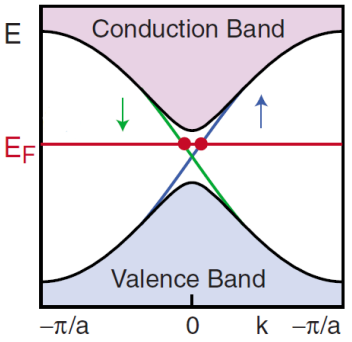
1. **Chia-Hsiu Hsu**, et al.,” Prediction of two-dimensional organic topological insulator bases in Metal-DCB lattices”.(Preparing)
2. **Chia-Hsiu Hsu**, et al.,”Growth of a predicted two-dimensional topological insulator based on InBi-Si(111)- $\sqrt{7}\times\sqrt{7}$”, Phys. Rev. B **98**, 121404 (2018).
3. **Chia-Hsiu Hsu**, et al., ”*Quantum anomalous Hall insulator phase in asymmetrically functionalized germanene*”, Phys. Rev. B **96**, 165426 (2017).
4. Xiao-Bo Wang, Xiao-Ming Ma, Eve Emmanouilidou, Bing Shen, **Chia-Hsiu Hsu**, et al., ” *Topological surface electronic states in candidate nodal-line semimetal CaAgAs*”, Phys. Rev. B **96**, 161112(R) (2017).
5. Christian P. Crisostomo1, Zhi-Quan Huang1, **Chia-Hsiu Hsu**, et al., “Chemically induced large-gap quantum anomalous Hall insulator states in III-Bi honeycombs”, npj Computational Materials 3, 39 (2017).

Quantum spin and Quantum anomalous Hall Effect

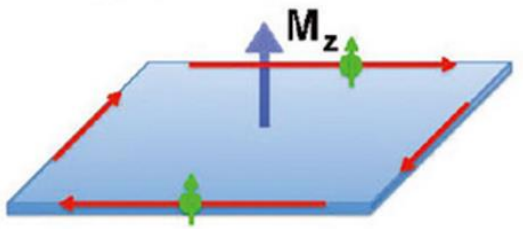
- 2D Topological insulator (QSH)
  - Time-reversal symmetry
  - Characterized by the Z_2 invariant
    if $Z_2 = 0$, trivial phase
    if $Z_2 = 1$, non-trivial phase



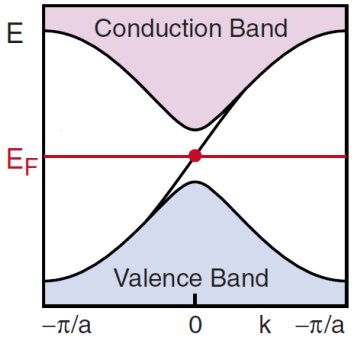
Quantum Spin Hall effect



- QAH insulator
  - Breaking of TRS.
  - Characterized by the *Chern* number, requires $C \neq 0$,



Quantum Anomalous Hall effect



M. Z. Hasan and C. L. Kane Rev. Mod. Phys. 82, 3045 (2010)

A way to realize QAH effect in a viable material:

1. it must be ferromagnetic insulating materials,
2. and has topologically non-trivial electronic band structures.

QAH search: A good start is a known QSH material

Chern number

We identify the topological properties of each structure, by following the similar method in Ref[1] by calculating the **Chern number**[2,3]

$$C = \frac{1}{2\pi} \sum_n \int_{BZ} d^2k \Omega_n,$$

The Hall conductance is the sum of Chern numbers of all occupied bands in unit of e^2/h.

where $\boldsymbol{\Omega_n}$ is *n*th band **Berry curvature** in *k*-space[2,4].The Berry curvature $\boldsymbol{\Omega(k)}$, is calculated using the Kubo formula[2,5] by using the maximally-localized Wannier functions as provided by the **WANNIER90** package[6].

The edge state of nanoribbons were calculated using the tight-binding method with parameterizations from the **WANNIER90** package.

[1] *Phys. Rev. B* **82**, 161414(R) (2010)
[2] *Phys. Rev. Lett.* **49**, 405 (1982)
[3] A*nn. Phys. N.Y.* **160**, 343 (1985)
[4] *Phys. Rev. B* **53**, 7010 (1996)
[5] *Phys. Rev. Lett.* **92**, 037204 (2004)
[6] *Comput. Phys. Commun.* **178**, 685–699 (2008)