

Organic Monolayer Protected Topological Surface State

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(5) Supporting Information

ABSTRACT: Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA)/Bi₂Se₃ and Fe/PTCDA/Bi₂Se₃ heterointerfaces are investigated using scanning tunneling microscopy and spectroscopy. The close-packed self-assembled PTCDA monolayer possesses big molecular band gap and weak molecule–substrate interactions, which leaves the Bi₂Se₃ topological surface state intact under PTCDA. Formation of Fe-PTCDA hybrids removes interactions between the Fe dopant and the Bi₂Se₃ surface, such as doping effects and Coulomb scattering. Our findings reveal the functionality of PTCDA to prevent dopant disturbances in the TSS and provide an effective alternative for interface designs of realistic TI devices.



KEYWORDS: Scanning tunneling microscopy, scanning tunneling spectroscopy, topological insulator, self-assembled molecular layer, organic tunneling barrier, charge transfer

opological insulators (TIs) have attracted lots of interest from the science community due to their exotic physics and large potential for application in spintronics.¹⁻³ TIs possess unique topological surface states (TSSs) that exhibit a Diraccone-like dispersion similar to graphene. In contrast to spindegenerate Dirac cones of graphene, degrees of freedom of spin and momentum are locked with each other in the TSS.⁴ Therefore, electron transport through 3D TIs (in bulk band gaps) gives a fully spin-polarized current. In addition, time reversal symmetry (TRS) protected, the TSS are robust against surface disorder including magnetic and nonmagnetic surface adsorbates.^{5,6} However, doping effects and Coulomb scattering of the TSS due to adsorbates are also reported^{7,8} and may influence spin transport behaviors in the TSS. Previous researches demonstrate that TRS will be broken in the presence of long-range ferromagnetic ordering.^{9,10} In addition, Chang et al.¹¹ show breaking of the TRS in the Cr-doped Bi₂Se₃ system even without long-range ferromagnetic ordering. More importantly, under surface magnetic and charge doping from Fe atoms, the topological spin structure of the Bi₂Se₃ surface is significantly modified.¹² Furthermore, due to undesired surface and interface charge doping, the Fermi level could be moved to the bulk band edge that suppresses the contribution of the TSS in electrical detections of spin polarization.¹³⁻¹⁵ To harvest the exotic properties of TIs, it is necessary to reduce the disturbances from metal deposition.

Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) selfassembly exists on various substrates $^{16-20}$ even in the chemisorption cases^{17,19} because of carboxylic head groups that induce strong intermolecular hydrogen bonds.²¹ When the molecule–substrate interactions are weak, PTCDA prefers to form a close-packed herringbone structure and states on both sides are barely affected by each other.¹⁶ Thus, PTCDA remains gas-phaselike and the substrate states underneath can be detected by tunneling process. In addition, it has been reported that Fe dopant prefers to form Fe-PTCDA hybrids due to carboxylic oxygens bonded with the Fe atoms in which charge is transferred from Fe to PTCDA.²² According to the aforementioned properties, PTCDA molecules possess the potential to be dense and smooth tunneling barriers preventing disturbances from electrode deposition, for example, Fe, on the TI surfaces.

In this Letter, we use scanning tunnelling microscopy (STM) and scanning tunnelling spectroscopy (STS) measurements to demonstrate that the TSS is unaffected under the self-assembled PTCDA molecule layer. By analyzing the band gap of the PTCDA self-assembled monolayer and the characteristic feature of the DP in the tunneling spectra, as compared to the previous system of MePc (Me: Mn, Co, Cu) accompanying relatively strong hybridization with TI surfaces^{34,35} the weak molecule–substrate interaction in the PTCDA/Bi₂Se₃ hetero-

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structure is addressed. To evidence the protecting functionality of PTCDA layers, Fe has been deposited on to the PTCDA covered Bi_2Se_3 surfaces. Our results show the PTCDA layer further preventing disturbances of the TSS from doping and scattering effects under Fe deposition. The protecting mechanism is explained by the charge transfer phenomenon in the formation of Fe-PTCDA hybrids.

Results. Self-Assembled PTCDA Layer on Bi₂Se₃ Surface and Undisturbed TSS. Figure 1b shows an STM image of self-



Figure 1. (a) PTCDA chemical structure (red, oxygen; blue, hydrogen; yellow, carbon). (b) STM image of self-assembled PTCDA layer on Bi₂Se₃. The PTCDA molecules are close-packed and adapt herringbone stacking. ($16 \times 8 \text{ nm}^2$, $V_{\text{bias}} = 1.0 \text{ V}$, $I_{\text{set point}} = 1.5 \text{ nA.}$) Color scale: left to right corresponds to 0.24–0 nm. Inset: enhanced color scale for the Bi₂Se₃ lattice. (c) STS curves on Bi₂Se₃ (black) and PTCDA (red). The HOMO–LUMO gap of PTCDA layer and the Bi₂Se₃ states are indicated by red and black dotted lines, respectively. ($V_{\text{bias}} = 1.5 \text{ V}$, $I_{\text{set point}} = 0.3 \text{ nA.}$) (d) Zoom-in STS curves on Bi₂Se₃ (black) and PTCDA (red). The black arrow refers to the energy position of the DP. The STS results of (c,d) are two different data sets measured by different parameters. Curves are shifted in *y*-axis for clarity. (To obtain the DP, set point is chosen to be $V_{\text{bias}} = -0.6 \text{ V}$, $I_{\text{set point}} = 0.1 \text{ nA.}$)

assembled PTCDA submonolayer on a clean Bi_2Se_3 surface. A well-ordered herringbone structure of PTCDA molecules as well as the Se-lattice are observed. Thanks to the weak interactions between PTCDA molecules and substrates, electronic structures of the substrate underneath the PTCDA monolayer are detectable by STS measurements. In the previous study of the self-assembled PTCDA layer on a Au(111) surface,¹⁶ which is an inert surface for PTCDA molecules, it is shown that the Au(111) surface state can be measured upon the PTCDA monolayer. Figure 1c shows STS

curves of the Bi₂Se₃ (black curve) and the PTCDA layer (red curve) in the bias range [-2.0, 2.0] V. Two pronounced Bi₂Se₃ states at around -1.06 and 1.16 V are acquired, indicated by black dotted lines, which are still detectable on the PTCDA layer. Such states are mainly contributed from the Bi₂Se₃ bulk states. Because the DOS is small in bulk band gap and near band edges,²³ it is difficult to obtain the Dirac point and the band edges with the set point of V_{bias} = 1.5 V, $I_{\text{set point}}$ = 0.3 nA. There is an energy gap of the PTCDA layer between the highest occupied molecular orbital (HOMO) at around -1.51V and the lowest unoccupied molecular orbital (LUMO) at around 1.70 V (indicated by red dotted lines). The big HOMO-LUMO gap and the sharp LUMO peak of the PTCDA layer result from the weak interaction between PTCDA molecules and Bi₂Se₃ surfaces. In order to reveal the Dirac point (DP), different set points and bias range are applied to acquire the STS results (Figure 1d, Bi₂Se₃ surface, black curve; PTCDA layer, red curve). The spectroscopy curve of the Bi_2Se_3 surface shows a characteristic v-shape dip at -0.32 V which originates from the Dirac point (indicated by a black arrow) of the Bi₂Se₃ surface state. For self-assembled PTCDA molecules, identical Dirac cone features at -0.32 V are acquired in STS, indicating a similarity of density of states (DOS) probed on the Bi₂Se₃ surface and on the PTCDA layer. Because the energy positions of both HOMO and LUMO of the PTCDA layer are far away from the DP of Bi₂Se₃, the influences from PTCDA molecular orbitals on the DP can be excluded. These indicate that the dI/dV signal with the characteristic DP dip acquired on the PTCDA layer comes from the Bi₂Se₃ surface underneath. The PTCDA monolayer therefore serve as a spacing layer for electrons tunneling between the tip and the Bi₂Se₃ surface.

Effects on TSS due to Fe Deposition. For the design of TI devices in spintronics,² Fe is one of the commonly used ingredients for the fabrication of magnetic detectors. However, the electronic structures of the TSS would be modified under the Fe deposition due to a large Coulomb charge and significant magnetic moment.¹² Thereby, to investigate interactions between Fe and the Bi₂Se₃ surface, Fe adatom/ Bi_2Se_3 is prepared. Figure 2a shows the STM image of ~1% monolayer Fe deposited on the Bi₂Se₃ surface. Single Fe atoms (pointed by arrows) that differ in apparent height and shapes are observed at -0.6 V. These differences result from different absorption sites, labeled α and β , with respect to the underlying Se-lattice.⁸ Spectra taken on top of the Fe atoms [blue (red) curve for α (β) site] and the pristine Bi₂Se₃ surface (black curve) are presented in Figure 2b. Because of Coulomb scattering of the TSS by impurities,^{24,25} in the case of this report by the Fe atoms a resonance state appears on the Fe atoms at both sites. The α and β sites possess a different resonance spectrum in the STS results.⁸ By comparing the characteristic resonance spectrum, we are able to assign the adsorption sites for the Fe adatoms. Therefore, in agreement with the report by Honolka et al.,8 the pristine TI DP (indicated by a black arrow) is overwritten and cannot be measured. Figure 2c shows STS curves of the pristine Bi₂Se₃ (black curve) surface and the Fe-deposited Bi₂Se₃ surface (named as doped Bi₂Se₃, purple curve, taken at the position marked by the purple cross in Figure 2a). After Fe deposition, DP is shifted downward by around 80 mV. In our measurements, this shifting amount is much bigger than the energy variation of the pristine DP and is uniform with respect to the Fe atom location (see Supporting Information). Such



Figure 2. (a) STM image of Fe adatom on Bi₂Se₃; 10 ×10 nm², $V_{\text{bias}} = -0.6 \text{ V}$, $I_{\text{set point}} = 0.3 \text{ nA}$. α and β represent two different Fe atom adsorption sites. (b) STS curves at Fe atom with adsorption site α (blue) and β (red). $V_{\text{bias}} = -0.6 \text{ V}$, $I_{\text{set point}} = 0.3 \text{ nA}$. Resonance states are observed at both adsorption sites. The black curve corresponds to the STS of the pristine Bi₂Se₃ surface. The black arrow indicates the energy position of the pristine DP. (c) STS curves of pristine Bi₂Se₃ (black) and doped Bi₂Se₃ (purple). $V_{\text{bias}} = -0.6 \text{ V}$, $I_{\text{set point}} = 0.1 \text{ nA}$. The purple cross in panel a represents the location where the STS of doped Bi₂Se₃ was taken.

electron doping moves the Fermi level toward the bulk band edge. As a result, near the Fermi level contribution of the DOS from the spin-degenerate bulk bands is increased and suppresses contributions of the TSS in spin transport measurements.¹³ In short, consequences of Fe deposition can be summarized into two effects: (i) resonance states that originate from Coulomb scattering between the Fe atoms and the TSS and (ii) electron doping effects due to charge transfer from the Fe atoms to the Bi₂Se₃ surface, which causes the shift of the DP energy position.

PTCDA Monolayer Protect TSS from Fe Deposition. As a result of the interactions and hybridizations between Fe atoms and Bi2Se3 states, Coulomb scattering and doping effect are found. In order to save the Bi₂Se₃ surface from such effects, an additional hybridization, Fe-PTCDA, is introduced to replace the interactions between Fe atoms and the Bi₂Se₃ surface. To demonstrate the ability of the PTCDA layer to be protecting layers for preventing interactions between the Fe atoms and the Bi₂Se₃ surface, ~1% Fe/1.5 ML PTCDA/Bi₂Se₃ is prepared. Figure 3a presents the STM image of 1.5 ML PTCDA on Bi₂Se₃ in which well-ordered first and second layer of PTCDA are observed. Upon ~1% Fe depositing on a 1.5 ML PTCDA/ Bi_2Se_3 surface at ~5 K (Figure 3b), the Fe atoms constitute cluster-like features on both the first and second PTCDA layer (marked by arrows). Figure 3c shows the zoom-in STM image of the first layer of Fe/1.5 ML PTCDA/Bi₂Se₃. The purple spots indicate the locations where STS curves are taken and the averaged result, denoted by on_Fe_PTCDA, is displayed as the purple curve in Figure 3d. Spectra taken away from the Fe atoms are named as off_Fe_PTCDA (black curve in Figure 3d). It is intriguing that both on Fe PTCDA and off -Fe PTCDA exhibit the same bias voltage of -0.32 V for the DP (indicated by a black arrow), which coincides with the one of pristine Bi₂Se₃. The identical DP energy acquired before and



Figure 3. (a) STM image of 1.5 ML PTCDA on Bi₂Se₃; 50 × 50 nm², $V_{\rm bias} = 1.5$ V, $I_{\rm set \ point} = 0.15$ nA. The right region of the image shows the first PTCDA layer with the herringbone stacking and the left region of the image presents the second PTCDA layer. (b) STM image of 1% Fe on 1.5 ML PTCDA on Bi₂Se₃; 50 × 50 nm², $V_{\rm bias} = 1.5$ V, $I_{\rm set \ point} = 0.1$ nA. Fe atoms constitute cluster-like features on both the first and second PTCDA layer (marked by arrows). Color scale: left to right corresponds to 0–0.57 nm. (c) STM image of 1% Fe on the first layer of PTCDA. 30 × 20 nm², $V_{\rm bias} = 1.5$ V, $I_{\rm set \ point} = 0.1$ nA. Purple spots indicates the positions where STS curves are taken. Color scale: left to right corresponds to 0–0.19 nm. (d) STS curves at the position with Fe (purple) and without Fe (black). To obtain the DP, set point is chosen tobe $V_{\rm bias} = 0.4$ V, $I_{\rm set \ point} = 0.1$ nA.

after Fe deposition indicates that the electron doping effect due to the Fe atoms is removed by the PTCDA layer. Moreover, in the case of on_Fe_PTCDA, the characteristic DP feature is recovered from the resonance state, which points out that Coulomb scattering between the TSS and the Fe atom is prevented. On the basis of the absence of doping effects and resonance states, we conclude that by introducing PTCDA molecules interactions between the Fe atoms and the TSS of Bi₂Se₃ are tremendously reduced and therefore the desired TSS can be conserved in this.

Discussion. To gain deeper insight into the protecting mechanism of the PTCDA layer in the Fe/PTCDA/Bi₂Se₃ system, spatially resolved STS measurement is performed. This measurement provides spatial distributed DOS that allows us to locally analyze the charge states of PTCDA molecules after coordinating with the Fe atoms. Figure 4a displays the STS results of PTCDA molecules with and without Fe coordinated. The inset of Figure 4a shows the STM topography of the spatially resolved STS data set in which the color-coded squares represent the averaged area for the STS curves of molecule A to E respectively. Without the Fe atom bounded, molecule A shows a pronounced LUMO peak at around 1.70 V. In the case

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Figure 4. (a) STS curves at the Fe position on the PTCDA layer (indicated by the color squares in the inset image, scale bar: 1 nm). $V_{\text{bias}} = 1.5 \text{ V}$, $I_{\text{set point}} = 0.3 \text{ nA}$. (b) STM image at $V_{\text{bias}} = 0.8 \text{ V}$, $I_{\text{set point}} = 0.1 \text{ nA}$; $5 \times 5 \text{ nm}^2$. Inset displays the density functional theory simulated LUMO charge density of a gas-phase PTCDA that shows mirror symmetry along both short and long axis of the molecule, revealing two lobes for the outer and three for the inner part. (c–e) STM images at the same area and $I_{\text{set point}}$ as (b) with different bias voltage of 1.1, 1.55, and 1.65 V.

of the Fe atom coordinated molecules, the discrepancy in the LUMO peak position is addressed (1.03, 1.19, 1.49, and 1.55 V for molecule B–E, respectively). In addition, we found that the HOMO is under -1.0 V in any case (see Supporting Information). Figure 4b-e shows STM images with intramolecular resolution at various bias voltage. The inset of Figure 4b presents the density functional theory simulated LUMO of a gas-phase PTCDA molecule.²² After hybridizing with the Fe atom, molecule B shows at 0.8 V the LUMO feature that coincides with the simulated LUMO (Figure 4b). Molecules C-E exhibit the LUMO feature in sequence with increasing bias voltage (Figure 4c-e). The LUMO feature obtained by STM further confirms the corresponding LUMO peak in the STS curve. The decreased LUMO energies are attributed to charge transfer from Fe to PTCDA and the disparities of the shifting amount are ascribed to the different charge transfer magnitudes. The amount of transferred charge is proportional to the amount of the frontier orbital shifting.²⁶ The measured LUMO shift for molecule B to E is -0.67, -0.51, -0.21, -0.15 V, respectively. Such spatial charge transfer distribution indicates hybridization strength between the molecules and the Fe atom. Among these molecules, molecule B exhibits the largest amount of LUMO shifting as well as the broadest LUMO peak thus possessing the strongest hybridization.^{27,28} Accordingly, the Fe atom might couple with molecule B and the transferred charge could spread to adjacent molecules (C-E) through intermolecular bonds.²⁹ In the previous study on

the Fe-PTCDA hybrid system,²² it was found that the LUMO would shift -0.68 V per electron accepted. This suggests that molecule B accepts approximately 1 electron after forming Fe-PTCDA complex and Fe gives more than 2 electrons to its environment. In previous reports,^{22,30,31} such Fe-PTCDA bonds are found stable up to 450 K. Therefore, the above-mentioned charge transfer phenomenon is expected at room temperature. The formation of the robust Fe-PTCDA bonds is one of the advantages of using PTCDA molecules as a protecting layer. Our results evidence charge transfer from the Fe atom to PTCDA molecules, and concentration of the Coulomb charge, which affects the TSS, is dramatically reduced. As a result, the resonance states (Figure 2b) and the doping effect (Figure 2c) are eliminated (Figure 3d).

In conclusion, we have grown self-assembled PTCDA layers on a topological insulator Bi_2Se_3 surface. A weak interaction between PTCDA molecules and the Bi_2Se_3 surface is identified. The Fe atoms play roles of electron donors and scattering potentials. The effects due to the Fe atoms on the Bi_2Se_3 surface are tremendously suppressed after introducing a PTCDA layer in between. Our findings demonstrate that the PTCDA monolayer not only provide a smooth organic/TI interface but also serves as a buffer layer which protects Bi_2Se_3 surfaces from Fe deposition. By using organic molecules as spacers in the future TI devices, undesirable doping and scattering effects at the interfaces can be prevented. This new approach by using organic molecules for tunneling barriers sheds light on the fabrication of high efficiency TI devices.

Methods. *Experimental Setup.* Measurements are performed in an Omicron ultrahigh vacuum low-temperature (~4.5 K) scanning tunneling microscopy with constant current mode using electrochemically etched tungsten tips. For scanning tunneling spectroscopy, a modulation voltage (ΔU = 30 mV, f = 5.9 kHz) is added to the bias voltage and the induced current modulation is recorded via lock-in techniques. All images are processed using Nanotech WSxM.³²

Sample Preparation. $PTCDA/Bi_2Se_3$ is prepared by depositing PTCDA (rate, ~ 0.01 ML/s, sublimation temperature, ~550 K) (ML, monolayer, refer to the surface fully covered by self-assembled PTCDA molecules) onto in situ cleaved Bi_2Se_3 (Bridgman-growth)³³ surfaces at room temperature. Subsequently deposition of Fe at ~5 K is performed for fabrication of Fe/PTCDA/Bi₂Se₃ samples.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano-lett.5b02811.

Spatially resolved STS measurement with respect to the Fe adatom location. STS results on the molecular orbital with the larger energy range. Spatially resolved STS on the pristine Bi_2Se_3 surface. (PDF)

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Author Contributions

H.-H.Y. and M.-T.L. designed and prepared the experiment. H.-H.Y. performed STM and STS measurements with assistance from Y.-H.C. and support in instrument maintenance from C.-I.L. and C.J.B. Crystal growth and characterization were performed by R.S. under the supervision of F.-C.C. The manuscript is prepared by H.-H.Y. and M.-T.L. with input from Y.-H.C. The project is conceived and led by M.-T.L.

Notes

The authors declare no competing financial interest.

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