

# Manipulating the Topological Interface by Molecular Adsorbates: Adsorption of Co-Phthalocyanine on $\text{Bi}_2\text{Se}_3$

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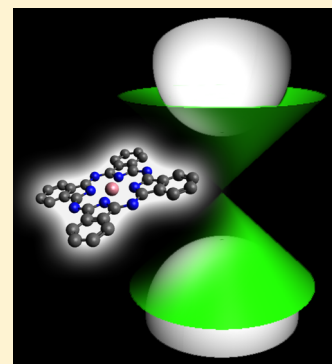
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## **S** Supporting Information

**ABSTRACT:** Topological insulators are a promising class of materials for applications in the field of spintronics. New perspectives in this field can arise from interfacing metal–organic molecules with the topological insulator spin-momentum locked surface states, which can be perturbed enhancing or suppressing spintronics-relevant properties such as spin coherence. Here we show results from an angle-resolved photoemission spectroscopy (ARPES) and scanning tunnelling microscopy (STM) study of the prototypical cobalt phthalocyanine (CoPc)/ $\text{Bi}_2\text{Se}_3$  interface. We demonstrate that the hybrid interface can act on the topological protection of the surface and bury the Dirac cone below the first quintuple layer.

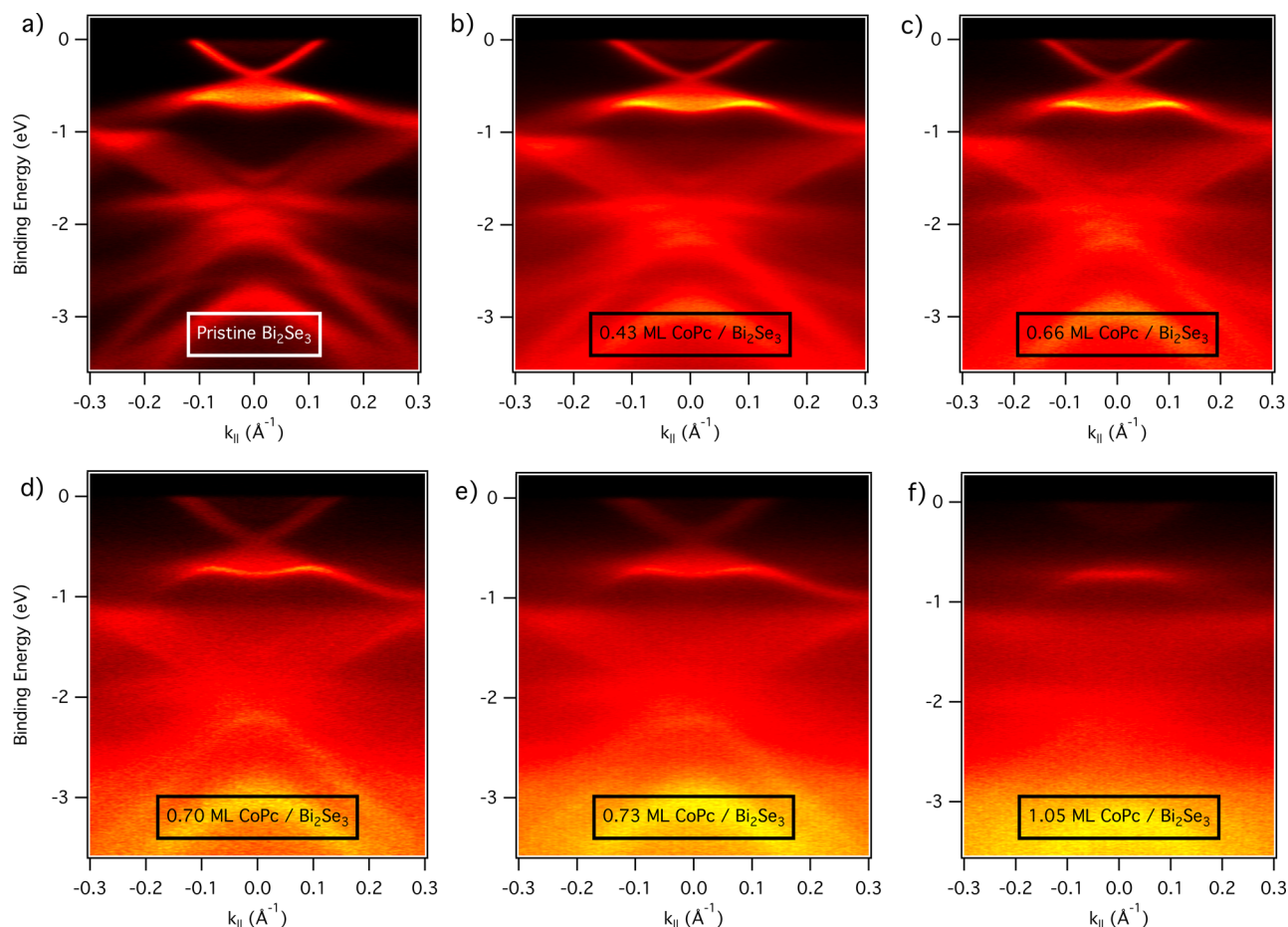
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**Figure 1.** ARPES spectra for CoPc/Bi<sub>2</sub>Se<sub>3</sub> at  $h\nu = 55$  eV. Intensity is coded in colors, from black (lowest) to red and to yellow (highest). CoPc coverage is as follows: (a) pristine surface, (b) 0.43 ML, (c) 0.66 ML, (d) 0.7 ML, (e) 0.73 ML, (f) 1.05 ML.

**KEYWORDS:** *Topological insulator, phthalocyanine, ARPES, surface states, Dirac cone, charge transfer*

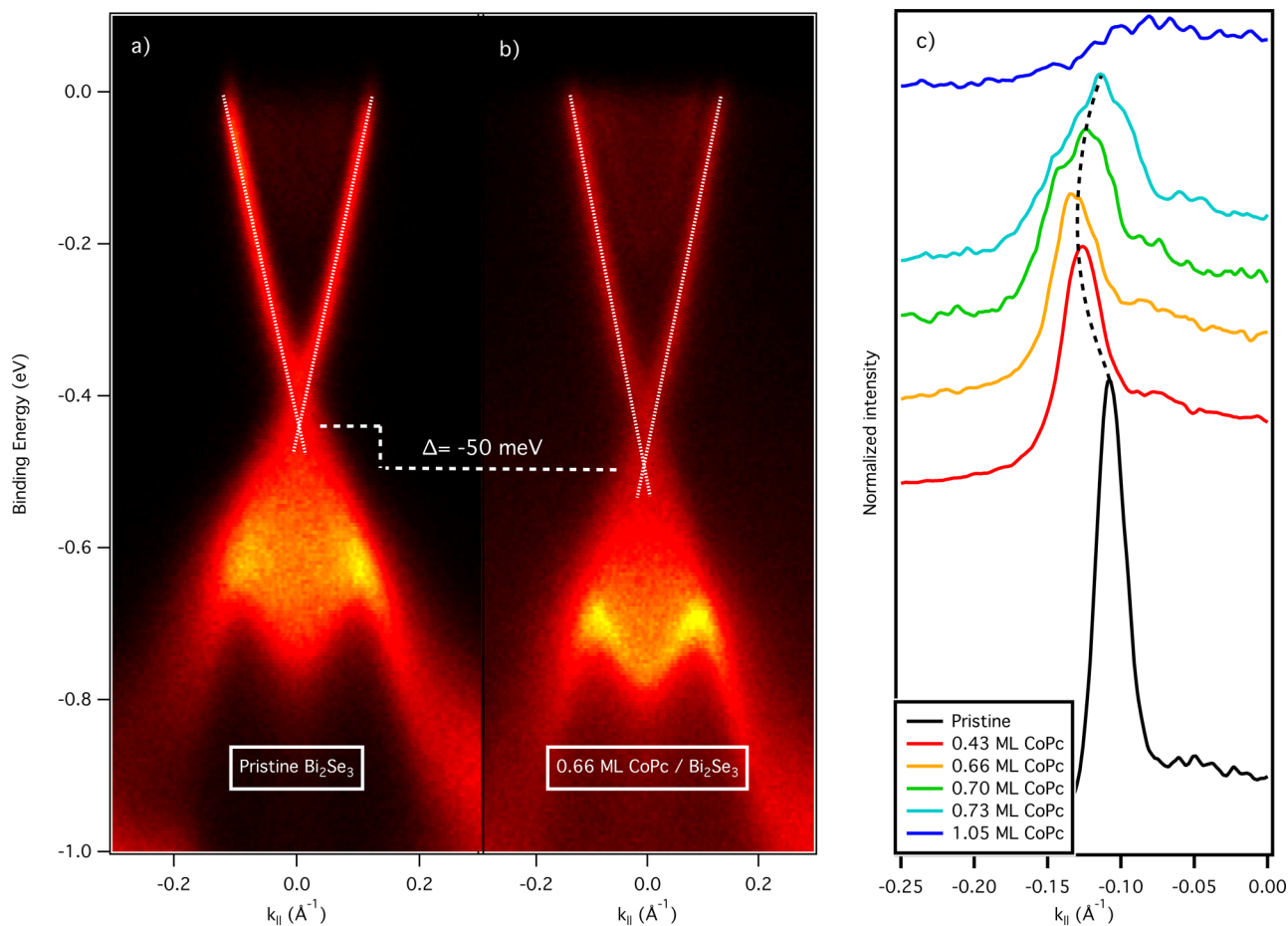
In these last years topological insulators received the attention of a large area of the scientific community thanks to their exotic properties. Topological insulators are semiconductors in the bulk, but they possess metallic surface states topologically protected by time-reversal symmetry. Moreover, these surface states are spin-momentum locked, meaning that for instance no backscattering is allowed for electrons occupying these states.<sup>1–3</sup> Thanks to these properties topological insulators are promising materials for the field of spintronics, where they can be exploited to implement spin generator, transport, or torque devices.<sup>4–8</sup>

Metal–organic molecules are another very promising material for spintronic applications. It has already been demonstrated that metal–organic molecules can be used as spin valves, molecular switches, and other devices.<sup>9–11</sup> Among all metal–organic complexes, porphyrines and phthalocyanines (Pc) are the most studied systems. These are simple molecules, composed of a macrocycle that can host a central metal atom. Replacing the central atom will result in changes in the molecular electronic structure, and in the case of half-filled d-orbital metals (i.e., Mn, Fe, and Co) interesting magnetic properties arise.<sup>12–15</sup>

A new class of spintronic devices could derive from the interplay between topological insulators and metal–organic molecules, and in this sense fundamental studies of this interface are highly desirable. Scanning tunnelling microscopy–spectros-

copy (STM–STS) studies of manganese phthalocyanine (MnPc), cobalt phthalocyanine (CoPc), and copper phthalocyanine (CuPc)/Bi<sub>2</sub>Te<sub>3</sub> show that a metal center-dependent interaction between molecule and substrate exists,<sup>16,17</sup> as already reported for transition metal phthalocyanine (TMPc)/Au(110) and (TMPc)/Ag(100).<sup>18,19</sup> An evidence of hybridization between unoccupied molecular orbitals and substrate states has been reported for MnPc/Bi<sub>2</sub>Te<sub>3</sub>, nevertheless in this case the substrate surface states are unaffected by the molecular adsorption.<sup>16</sup> A similar study has been also carried out by Song et al.,<sup>20</sup> where one monolayer (1 ML) of iron phthalocyanine (FePc) has been deposited on Bi<sub>2</sub>Te<sub>3</sub> surface. An in-plane easy magnetization axis for FePc has been observed; however, no signs of spontaneous magnetic ordering has been found for this system.

These earlier experimental studies were focused on the molecular point of view, without the direct access to the effects of molecular adsorption on the topological insulator surface band structure that can be given by an angle resolved photoemission (ARPES) study. In a recent work Jakobs et al. dealt with this issue with a mixed theoretical and experimental approach:<sup>21</sup> they showed that depending on the molecule–surface interaction strength Rashba-split interface states can arise. Up to now, however, no such studies have been performed on metal–organic complexes. Adding metal atoms to the organic



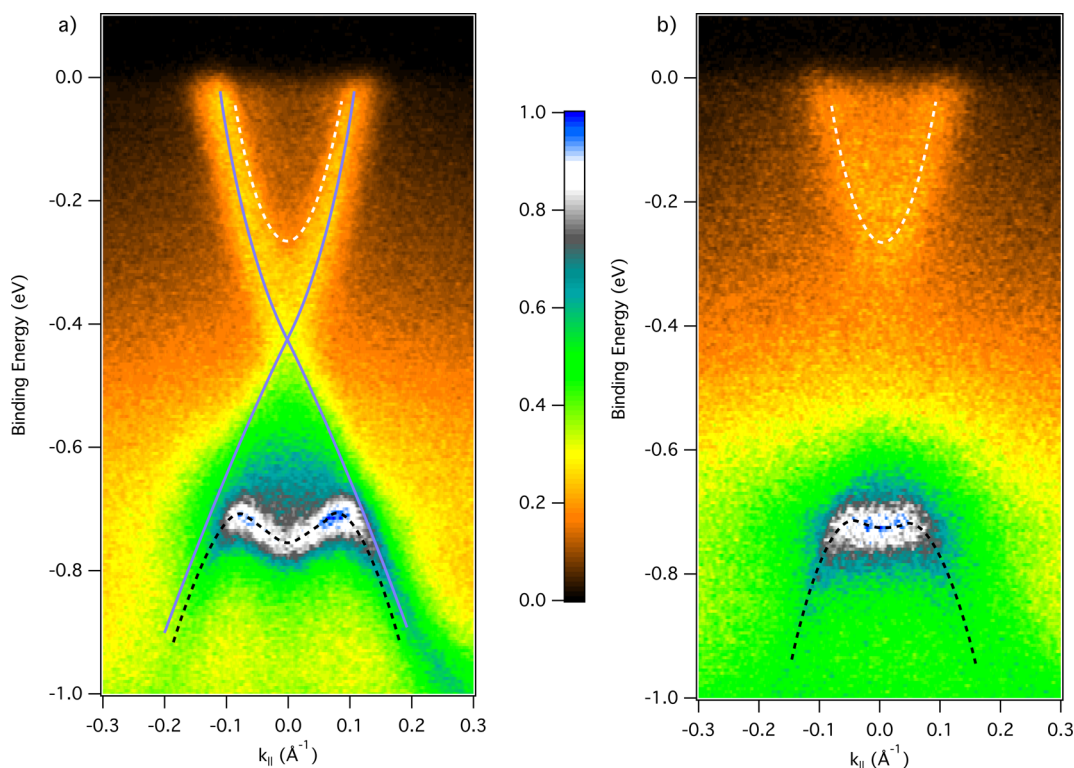
**Figure 2.** (a–b) Enlargement near the Dirac point for the pristine surface and for 0.66 ML CoPc/Bi<sub>2</sub>Se<sub>3</sub>. (c) MDC curves taken integrating the region 0–0.03 eV of binding energy and normalized to the bulk pocket intensity. Dashed lines are guides for eyes.

framework can introduce new effects: magnetic impurities and metal–organic complexes on the surface of a topological insulator are predicted to break the time reversal protection of the surface state;<sup>22–25</sup> however, previous investigations of the effect of metal adsorption on the surface states of Bi<sub>2</sub>Se<sub>3</sub> showed the opposite. Wray et al. claimed to have observed the breaking of time reversal symmetry and the consequent opening of a gap in the surface states upon Fe deposition,<sup>26</sup> but this interpretation was successively questioned explaining the observation by a simple band bending effect and simultaneous confinement of both valence and conduction bands.<sup>27</sup> Indeed, other experiments performed in similar conditions did not confirm any gap opening.<sup>28–31</sup>

In order to shed light on the effects of the adsorption of metal–organic molecules on the surface of a topological insulator, we performed a combined ARPES and STM investigation of cobalt phthalocyanine adsorbed on the prototypical topological insulator Bi<sub>2</sub>Se<sub>3</sub>. We chose Bi<sub>2</sub>Se<sub>3</sub> because its Dirac point is located in the bandgap, and this is a prerequisite for the realization of the anomalous quantum hall effect and other magnetoelectric phenomena. Furthermore, this surface is better suited for ARPES experiments on the Dirac point than Bi<sub>2</sub>Te<sub>3</sub> since it allows its direct visualization away from the bulk bands. The interface electronic structure upon CoPc adsorption was studied using ARPES with different photon energies, and so, probing depths. Our results indicate that the topological surface states (TSS) survive in the subsurface region, while it is disrupted in the first quintuple layer.

Figure 1 shows an overview of the evolution of the electronic structure of the interface upon CoPc adsorption (acquired with a photon energy of 55 eV). Increasing the coverage (from panel (a) to panel (f)) results initially in a blurring of the Bi<sub>2</sub>Se<sub>3</sub> bulk states that could be related to hybridization with molecular orbitals and/or scattering from the randomly distributed molecules on the surface. At higher coverage some almost dispersionless features appear at approximately 0.72 eV, 1.22 eV, 1.98 eV, 3.17 eV binding energy. These features can be assigned to the CoPc/Bi<sub>2</sub>Se<sub>3</sub> interface states: previous investigation on a monolayer of CoPc/Au(110) and CoPc/Au-poly reported analogous binding energy for these features.<sup>32,33</sup>

The case of one monolayer of CoPc/Cu(111) is different.<sup>34</sup> This interface shows the same emerging features, but they are shifted of about 0.15 eV toward higher binding energy. In this case a charge transfer from the substrate to the molecules has been observed as a shift toward lower binding energy of the Cu(111) surface Shockley state. In the case of CoPc/Bi<sub>2</sub>Se<sub>3</sub> we observed exactly the opposite occurrence: already from the lowest coverage a clear downshift of the Dirac cone due to a charge transfer from the molecule to the surface is evident. Figure 2a–b show the comparison between the clean surface and 0.66 ML CoPc/Bi<sub>2</sub>Se<sub>3</sub>: a clear downshift of 50 meV of the surface band structure is visible. Our measures show that when the coverage exceeds the value of 0.66 ML the charge transfer decreases. At higher coverage the increasingly blurry features prevent a reliable estimation of the actual Dirac point position; however, we can recall a qualitative trend from the momentum



**Figure 3.** Detail of the region 0–1 eV of binding energy for 0.73 ML CoPc/Bi<sub>2</sub>Se<sub>3</sub> (panel a, left) and 1 ML CoPc/Bi<sub>2</sub>Se<sub>3</sub> (panel b, right). Lines are guide for eyes indicating Bi<sub>2</sub>Se<sub>3</sub> surface states (blue continuous line), Bi<sub>2</sub>Se<sub>3</sub> bulk valence band (black dashed line), and Bi<sub>2</sub>Se<sub>3</sub> bulk conduction band (white dashed line).

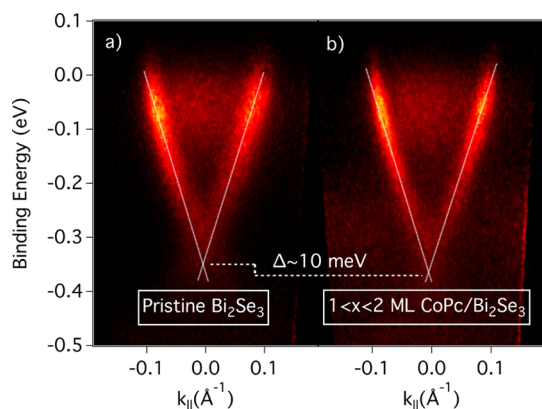
distribution curves (MDC) acquired at the Fermi level shown in panel c of Figure 2: Fermi momentum increases up to the coverage of 0.66 ML, when it reaches its maximum, while with further deposition it decreases. The Fermi momentum is clearly related to the energy position of the Dirac point: a downshift of the latter causes the Dirac cone to be cut by the Fermi level further with respect to its vertex, where the distance between the two branches, and thus the Fermi momentum, is higher. On the contrary, we can clearly see that for coverages higher than 0.66 ML the Fermi momentum moves toward lower values: this is an indication that the substrate energy levels are shifting now to lower binding energy. This could be an indication of a coverage-dependent interaction between surface and molecules. Different studies on MPc on Au and Ag showed that molecule–substrate distance changes depending on the molecular coverage, increasing for coverages approaching 1 ML.<sup>35–37</sup> An increase in the molecule–substrate distance turns in a decoupling between the two that in this case can be observed as a reduction of the charge transfer. Furthermore, this behavior allows us to rule out spurious effects related to surface contamination: in this case the electron doping varies continuously up to a saturation value, where it remains.<sup>38</sup>

Once the monolayer has been completed, the topologically protected surface states seem to vanish from the surface sensitive ARPES signal. Figure 3 shows a detail of the region 0–1 eV of binding energy for the last two depositions: 0.73 ML CoPc/Bi<sub>2</sub>Se<sub>3</sub> and 1 ML CoPc/Bi<sub>2</sub>Se<sub>3</sub>. In panel a (corresponding to 0.73 ML CoPc/Bi<sub>2</sub>Se<sub>3</sub>) surface states, although blurry, are still clearly discernible, along with the bulk valence and conduction band. Adding more molecules, up to complete one monolayer, results in an abrupt change in the band structure. Panel b of Figure 3 shows that, while bulk conduction and valence bands of Bi<sub>2</sub>Se<sub>3</sub>

are still visible, the Dirac cone between the two disappeared. Of course the presence of both Bi<sub>2</sub>Se<sub>3</sub> bulk valence and conduction bands ensures that the electron inelastic mean free path is sufficient to make outgoing electrons overcome the molecular layer and reach the vacuum.

It is worth noting that also the shape of the bulk valence band seems to undergo a drastic change: this is due to the superposition of the nondispersing interface state at 0.72 eV with the bulk valence band, which hides the dispersion of the latter.

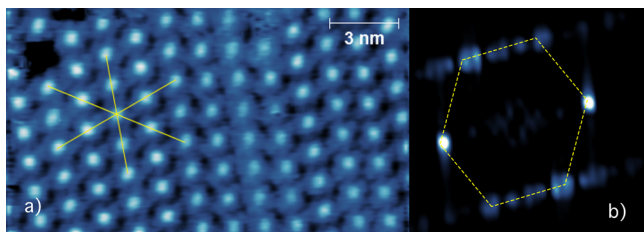
Of course the disappearance of the ARPES signal coming from the topologically protected surface states does not imply that these do not exist anymore. One of the options to be considered is that their wave function is perturbed by the hybridization between molecular orbitals and surface states so that they disappear from the first quintuple layer. However, the surface states in 3D topological insulators is known to penetrate in the bulk for at least two quintuple layers,<sup>39,40,45</sup> so, due to the robust topological protection, the tail of the surface states extending into the second quintuple layer can remain unperturbed. The images shown up to now were acquired with a photon energy of 55 eV, where the electron inelastic mean free path (IMFP) can be estimated between 3 Å and 6 Å,<sup>41</sup> less than the height of one quintuple layer (approximately 1 nm<sup>42</sup>). By changing the photon energy it is possible to increase the probing depth of our experiment. Figure 4 shows a comparison of a pristine Bi<sub>2</sub>Se<sub>3</sub> surface (panel a) and a CoPc/Bi<sub>2</sub>Se<sub>3</sub> interface (panel b) acquired with a photon energy of 6.28 eV. At this energy the estimated IMFP approaches 20 Å,<sup>43</sup> enough to access the first and the second quintuple layer, and Figure 4 shows clearly that in this condition the Dirac cone is still clearly discernible. Well-resolved surface states enable us also to estimate in 10 meV their energy



**Figure 4.** Comparison between a pristine  $\text{Bi}_2\text{Se}_3$  surface (panel a) and a  $\text{CoPc}/\text{Bi}_2\text{Se}_3$  interface (panel b) acquired with a photon energy of 6.28 eV. Overlayer thickness is estimated to be in the range between one and two ML. White dashed lines are guide for eyes.

shift once a complete monolayer of CoPc is formed, much less than the 50 meV observed in the case of 0.66 ML. This is consistent with the qualitative trend showed in Figure 2 and also with the data presented by Bathon et al.,<sup>17</sup> where a negligible charge transfer is reported.

The effect of CoPc adsorption is dramatically different with respect to the effect of metal-free phthalocyanine<sup>21</sup> (see also Supporting Information) and of metal atom deposition. Other attempts under similar conditions, with coverages ranging from a few percent to some tenths of a monolayer of iron<sup>29,31</sup> and cobalt<sup>28</sup> did not lead to anything similar to what is shown here: surface metallic doping seems to have no effects on the topologically protected states. However, for a direct comparison between our experiment and previous surface doping studies, the equivalent coverage of Co atoms has to be known. STM topography in Figure 5 shows that the molecules are arranged in



**Figure 5.** (a) STM image of a monolayer of CoPc acquired at a  $V_{\text{bias}} = 2.78$  V and  $I_t = 14$  pA. (b) Fourier transform of the panel a. Yellow lines indicate the overlayer symmetry.

a self-assembled monolayer with a similar hexagonal herringbone-distorted geometry previously observed for  $\text{CoPc}/\text{Bi}_2\text{Te}_3$ .<sup>17</sup> The intermetallic distance in this case is 1.28 nm, and assuming 0.25 nm as lattice constant for a Co film grown on the  $\text{Bi}_2\text{Se}_3$  surface (the same lattice constant of bulk Co crystal with also the same hexagonal symmetry), a nominal coverage of 0.04 ML of cobalt atoms is obtained, comparable to the previous surface doping experiments.

The different behavior observed for  $\text{CoPc}/\text{Bi}_2\text{Se}_3$  in contrast with all other surface-doped systems underlines once again the flexibility inherent of metal–organic networks. These are capable of avoiding clustering of metal atoms, induce a different crystal field splitting, and in general modify the metal–surface interaction. All of these factors may lead to very different

interfacial interactions and corresponding perturbation of the TSS as compared to metallic impurity doped surfaces, as observed in the present work.

In conclusion, we studied the electronic structure modification induced by the adsorption of different coverage of cobalt phthalocyanine on  $\text{Bi}_2\text{Se}_3$  surface. First ARPES results point toward the existence of a relevant interaction between the molecule and the surface underneath, with the effect of burying the wave function of the TSS below the first quintuple layer. Future studies are required to understand the mechanism of this occurrence. One possibility is that the metal–organic network is capable of triggering a surface-mediated interaction between the metal centers of the molecules as proposed by some theoretical works,<sup>22–24</sup> which could be elucidated by X-ray magnetic circular dichroism experiments. Our results show the potential of metal–organic molecules for the control of Dirac Fermions in topologically protected states through the metal–metal as well as the metal–substrate interaction, which could be further tuned by adding different functional groups to the ligand.<sup>44</sup>

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.5b02635.

Experimental method, XPS deposition calibration, ARPES data on freshly prepared 1 ML  $\text{CoPc}/\text{Bi}_2\text{Se}_3$  sample, and an analogous experiment on 2H-Pc (PDF)

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### Notes

The authors declare no competing financial interest.

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