TCNQ Physisorption on the Bi$_2$Se$_3$ Topological Insulator

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Table of Contents text (approx. 60-80 words)
The absorption of the prototypical molecular electron acceptor TCNQ has been studied on the Bi_2Se_3 topological insulator. Scanning tunneling microscopy, photoemission spectroscopy and density functional theory calculations reveal a negligible charge transfer and an essentially unperturbed electronic structure of the substrate, outlining an overall physisorption picture. The results reveal a significant potential of TCNQ for the realization of metal-organic coordination networks on topological insulator surfaces.

Abstract: Topological insulators are promising candidates for spintronic applications due to their topologically protected, spin-momentum locked and gapless surface states. The breaking of the time-reversal symmetry after the introduction of magnetic impurities, such as 3d transition metal atoms embedded in two-dimensional molecular networks, could lead to several phenomena interesting for device fabrication. The first step towards the fabrication of metal-organic coordination networks on the surface of a topological insulator is to investigate the adsorption of the pure molecular layer, which is the aim of this study. Here, the effect of the deposition of the electron acceptor 7,7,8,8-tetracyanoquinodimethane (TCNQ) molecules on the surface of a prototypical topological insulator, bismuth selenide (Bi_2Se_3), is investigated. Scanning tunneling microscope images at low-temperature reveal the formation of a highly ordered two-dimensional molecular network. The essentially unperturbed electronic structure of the topological insulator observed by photoemission spectroscopy measurements demonstrates a negligible charge transfer between the molecular layer and the substrate. Density functional theory calculations confirm the picture of a weakly interacting adsorbed molecular layer. These results reveal significant potential of TCNQ for the realization of metal-organic coordination networks on the topological insulator surface.

Introduction

Topological insulators (TIs) are a class of materials potentially interesting for applications in the field of optoelectronics and spintronics[1, 2], due to their uncommon electronic structure. TIs are characterized by an insulating bulk state and by a topological surface state (TSS) which presents a Dirac-cone-like dispersion located at the center of the Brillouin zone[3-5]. The spin and momentum degrees of freedom of the TSS are locked[3] and the electrons are topologically protected from elastic backscattering on defects by time-reversal symmetry[6]. This property leads to a variety of fascinating processes[7-12], such as nearly dissipationless currents[7, 8, 12]. The stability of these effects against local magnetic perturbations, which break time-reversal symmetry, is a prerequisite for the realization of spintronic devices based on TI material[6, 13]. On the other hand, the breaking of the time-reversal symmetry and the opening of an energy gap at the Dirac point of the TSS leads to a different class of phenomena[14, 15], such as the anomalous quantum Hall effect[16, 17], with a potential interest for the possible fabrication of low-power consumption electronics[18].

The effects of impurity doping on the electronic and magnetic properties of TIs have been under debate in the last years and seem to strongly depend on the presence of intrinsic defects of the pristine crystals[19], on the chemical nature of the magnetic impurities[20, 21], on the type of doping (surface or bulk)[11, 14, 20-25], on the possible clustering of impurities[20, 26-29], and, in the specific case of surface doping, on the adsorption sites[20, 21] and on the orientation of the magnetic easy axis with respect to the surface plane[14, 20, 21].

An interesting proposal to avoid clustering and obtain ordered and equivalent adsorption sites for surface magnetic impurities, is the use of highly-ordered two-dimensional (2D) metal-organic coordination networks (MOCNs), formed by co-depositing strong electron acceptor molecules

(such as tetracyanoethylene (TCNE, C_6H_4) or tetracyanoquinodimethane (TCNQ, $C_{12}H_4N_4$)) together with the magnetic impurities (e.g. Fe, Co, Ni) on the surface of TIs[26]. Interestingly, these MOCNs can even show ferromagnetic order in some cases, as reported on metal surfaces[30-37]. In particular, X-ray magnetic circular dichroism (XMCD) measurements[38] showed that Ni adatoms assume a spin-quenched configuration when deposited on their own on Ag(100) and Au(111) surfaces, whereas exhibit a ferromagnetic ordering when coordinated to TCNQ ligands into a MOCN. Similar networks may be also realized on TI surfaces and could be used to induce a magnetic perturbation of the TSS. Recent calculations[26] indicate that such MOCNs could display an out-of-plane magnetic anisotropy on Bi_2Se_3, break the time-reversal symmetry and induce the opening of an energy gap at the Dirac point of the TSS. The first step towards the fabrication of this type of networks is to investigate the adsorption of a pure layer of electron acceptor molecules and to verify that, on their own, they do not induce a significant modification or disruption of the TSS Dirac cone, as observed for other molecular species on TIs[39-44] or for similar molecular species on graphene[45].

To this aim, here we investigate the deposition of the strong acceptor TCNQ molecules on a pristine Bi_2Se_3 surface by means of scanning tunneling microscopy (STM), angle-resolved photoemission spectroscopy (ARPES), X-ray photoemission spectroscopy (XPS) measurements and Density Functional Theory (DFT) calculations. Low-temperature STM measurements reveal the formation of a highly ordered H-bonded organic network of TCNQ molecules on the Bi_2Se_3 surface, while photoemission spectroscopy investigations evidence a nearly unperturbed electronic states of the topological insulator. These findings are supported by DFT calculations and strongly suggest a rather weak TCNQ-Bi_2Se_3 interaction.

Results and Discussion

Pristine Bi_2Se_3 surfaces were prepared by cleavage before every molecular deposition experiment resulting in atomically flat (0001) oriented substrates (Figure 1). These are characterized by terraces typically larger than 200 nm (Figure 1a) and by a number of defects whose type and random spatial distribution are similar to those previously reported and studied in the literature[46-48].

The deposition of TCNQ molecules resulted in the formation of extended and ordered 2D islands, as demonstrated by the STM image in Figure 2b. Molecules arrange in a characteristic brickwork pattern (Figure 2c) that is typical of H-bonded TCNQ, as also reported for the deposition of TCNQ on Au(111)[49, 50]. Within the H-bonded islands, each TCNQ binds to other four molecules, with the four hydrogens of the central ring of one molecule interacting with the electronegative nitrogen atoms of the neighboring molecules. This results in a rhombic unit cell for the supramolecular
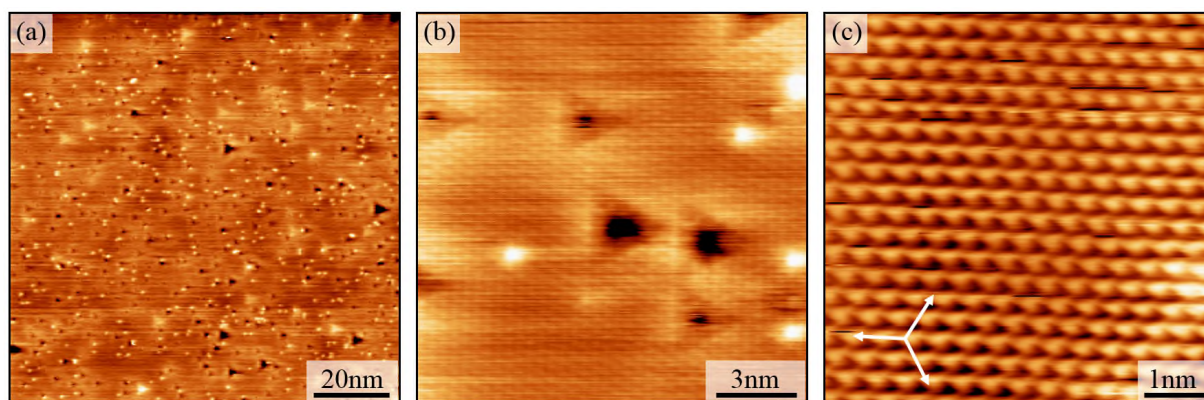

Figure 1: STM images showing a pristine cleaved Bi_2Se_3 surface at increasing magnification. Images (a) and (b) were acquired at 100K, image (c) at 77K. The principal crystallographic directions are indicated by white arrows in (c).
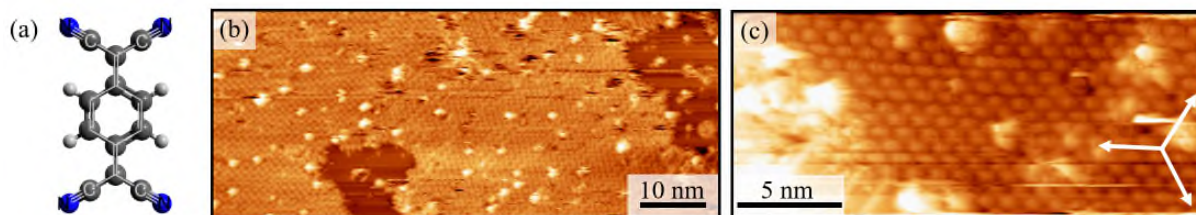
Figure 2: (a) Chemical structure of a TCNQ molecule. Black atoms correspond to carbon, dark blue to nitrogen and white to hydrogen. (b, c) STM images showing the supramolecular assembly resulting from the deposition of TCNQ on the Bi_2Se_3 surface. Images acquired at 77K. The principal crystallographic directions are indicated by white arrows in (c).

structure (see Figure 3b), with dimension: $a_1 = a_2 = (8.7 \pm 0.4)$ Å, $\alpha = (97 \pm 2)°$. These values of the lattice parameters are compatible with those obtained from DFT calculations for the TCNQ free-standing monolayer ($a_1 = a_2 = 9.064$ Å and $\alpha = 96°$), see Figure S4 in the supporting information, SI), representing a first indication of the weak interaction between the TCNQ molecules and the Bi_2Se_3 substrate. This is further supported by the fact that the measured unit cell parameters identify a supramolecular layer that is not commensurate with the substrate lattice. It should however be noted that the main molecular axes of the TCNQ molecules align closely to the main crystallographic directions of the $Bi_2Se_3(0001)$ surface. A similar situation has been reported for the 2D self-assembly of other organic molecules on low-interacting substrates such as graphite[51] or graphene[52] and is sometimes indicated as van der Waals epitaxy[53].

The bias voltage dependence STM imaging of TCNQ molecules on Bi_2Se_3 is reported in Figures 3a and 3b. At negative voltage (occupied sample states imaging), TCNQ molecules appear as elliptic protrusions. Instead, at positive voltage (empty sample states), the images of the molecules show a close similarity to the shape of the DFT-calculated isosurface for the lowest unoccupied

molecular orbital (LUMO) of the free-standing TCNQ monolayer. In fact, the characteristic nodal central plane separates two symmetric U-like protrusions and circular protrusions appear in the middle of the dicyanomethylene groups.
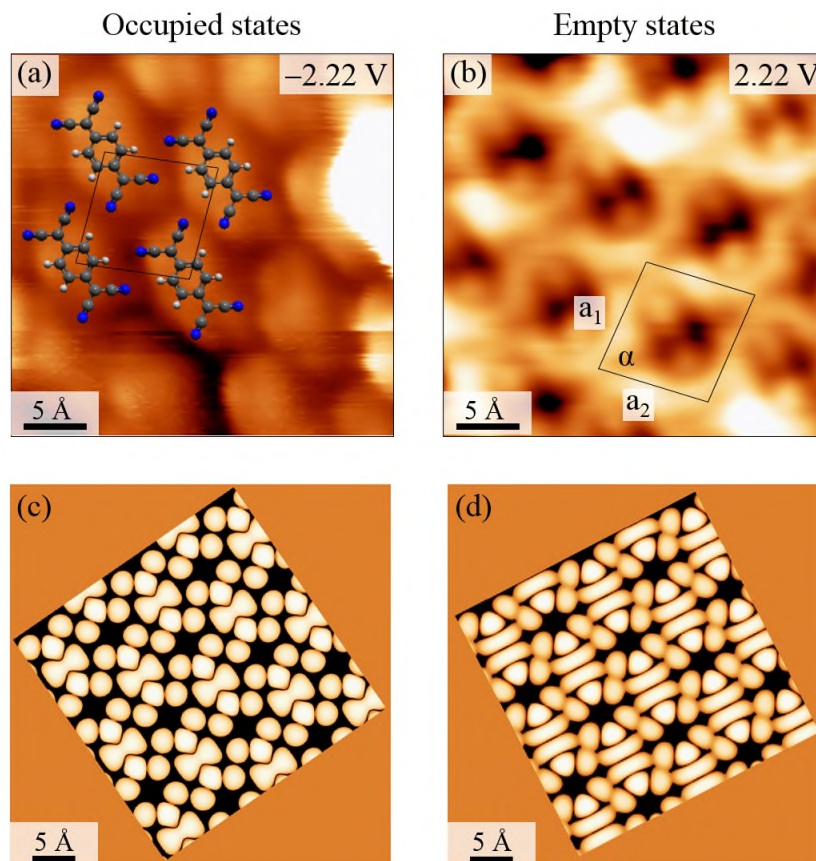

Figure 3: (a) and (b) high magnification STM images acquired on a TCNQ island at negative (occupied sample states) and positive (empty sample states) bias voltages, respectively. Structural models are superposed in (a) as a guide for the eye. Images acquired at 77K. (c) and (d) DFT calculated isosurfaces of the HOMO and LUMO for a free standing TCNQ monolayer, respectively.

The resemblance of the empty sample states STM images of TCNQ with the DTF-calculated LUMO strongly suggests negligible charge transfer, similarly to what reported for TCNQ on Au(111)[49, 50] and on graphene on Ir(111)[54]. This assumption is further supported by the observed H-bond brickwork assembly of TCNQ that has been reported only for TCNQ interacting weakly with the underneath substrate and in the absence of charge transfer[49, 50, 54]. On the contrary, negatively charged TCNQ molecules would probably show a LUMO-like appearance for negative bias voltages (occupied states), similarly to what reported in the literature in cases when charge transfer occurred[50, 55].
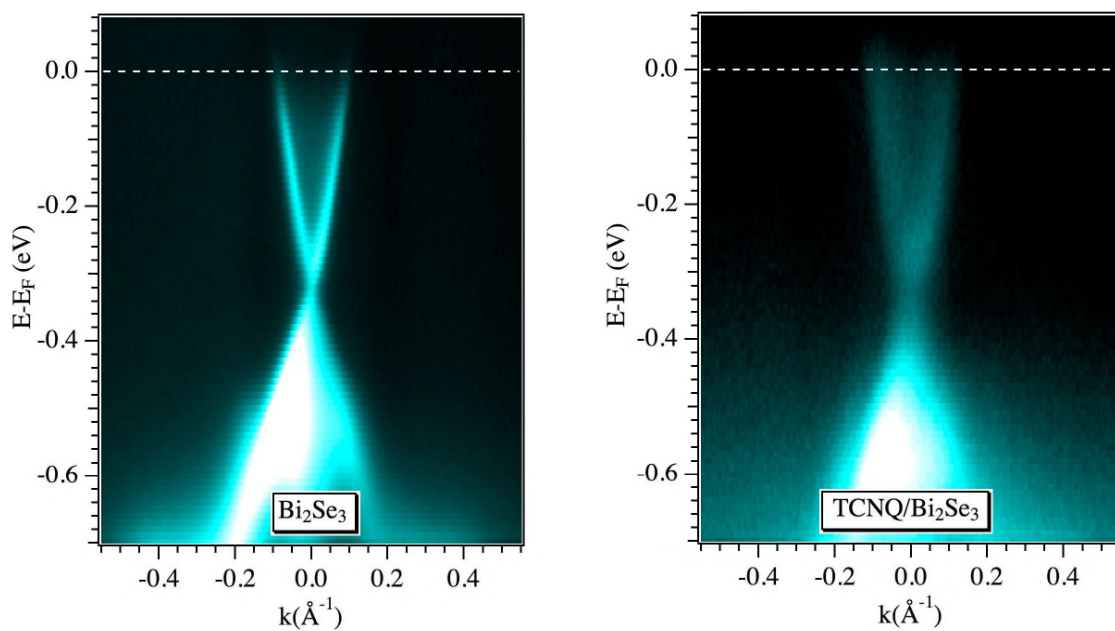

Figure 4: ARPES spectra (a) before and (b) and after deposition of 2.5 ML of TCNQ on the Bi_2Se_3 surface. Spectra have been collected with 50 eV photon energy. The position of the Fermi level is indicated by a white dashed line.

The electronic band structure of Bi_2Se_3 measured by ARPES before and after the deposition of (2.5 ± 0.5) ML of TCNQ is reported in Figures 4a and 4b, respectively. The topological surface state of the pristine sample displays sharp and well-defined Dirac cone close to the Fermi level, with a Dirac point energy of 0.32 eV below E_F, in agreement with previous studies[56, 57] (Figure 4a). No extra electronic states due to "aging effects" can be observed[58, 59], implying a negligible amount of contaminants of the Bi_2Se_3 sample.

The adsorption of TCNQ leads to a considerable broadening of the Dirac surface state (Figure 4b), potentially due to a partial disorder of the molecular overlayer. However, the adsorbed TCNQ does not strongly affect the Bi_2Se_3 electronic structure otherwise. In particular, ARPES data do not show the appearance of any additional electronic states in the valence or conduction bands or significant (>100 meV) upward shifts of the Dirac cone, in contrast to what observed for the adsorption of contaminants and atomic dopants on the same surface[58-61]. We consider these findings a further evidence of the relatively weak TCNQ- Bi_2Se_3 interaction (as also suggested by the XPS measurements reported in the SI).

All the experimental evidence clearly points to a neutral state for TCNQ adsorbed on Bi_2Se_3: STM measurements performed in the sub-monolayer regime evidence an unoccupied LUMO peak and a H-bond assembly, energetically favorable for neutral species[49], whereas ARPES and XPS data in the multi-layer coverage range display an almost unperturbed Bi_2Se_3 electronic structure. Hence, despite the common charging behavior observed for TCNQ on a number of more reactive surfaces[62-68], on Bi_2Se_3 TCNQ adsorbs as a *neutral* species forming characteristic hydrogen bonded networks, similarly to what observed on other inert surfaces[49, 62]. This is different to what reported for $CoPc/Bi_2Se_3$[44] or $MnPc/Bi_2Te_3$[39, 40], where a notable charge transfer to the substrate

was measured: the adsorption of TCNQ on $Bi_2Se_3(0001)$ does not significantly modify the TI surface electronic structure.

To get further information about the strength of interaction between TCNQ and the Bi_2Se_3 substrate we have performed additional *ab initio* calculations. Since the H-bonded molecular TCNQ layer studied here is not commensurate with the substrate, the calculations have been
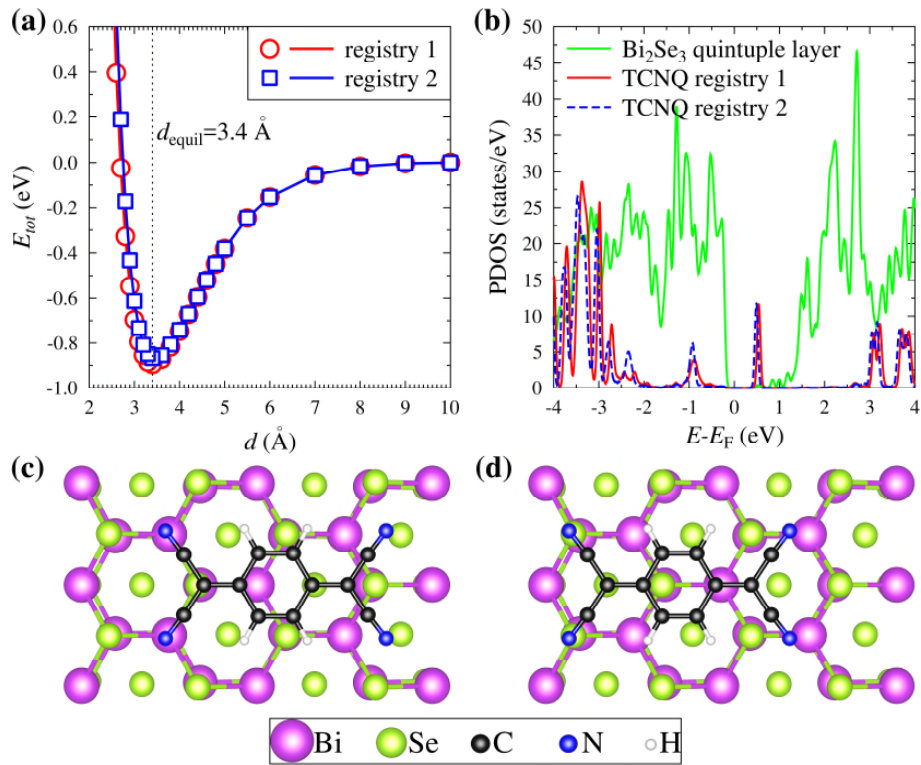
Figure 5: (a) Total energy as a function of the TCNQ monomer vertical distance to $Bi_2Se_3(0001)$ for the two different registries shown in panels (c) and (d). (b) Projected densities of states onto TCNQ and Bi_2Se_3 orbitals at the equilibrium adsorption distance (3.4 Å). The Bi_2Se_3 DOS corresponds to the one calculated for the adsorption configuration shown in (c), registry 1. The Bi_2Se_3 DOS for the adsorption configuration in (d), registry 2, is not shown since the differences between the two are marginal.

performed for a single TCNQ molecule adsorbed on the Bi_2Se_3 surface. Figure 5a shows the dependence of the total energy on the adsorption distance calculated for two different adsorption registries of the TCNQ molecule with respect to the $Bi_2Se_3(0001)$ substrate (shown in Figures 5c and 5d). Despite representing two extreme cases in terms of local binding strength (see discussion in the SI), the two registries yield very similar adsorption energies (around 0.9 eV) and essentially identical equilibrium distances of 3.4 Å, that correspond to the physisorption of TCNQ on $Bi_2Se_3(0001)$.

The densities of states projected onto different atomic orbitals of TCNQ and Bi_2Se_3 are shown in Figure 5b for the two registries at the equilibrium adsorption distance. It is clear from Figure 5b that the interaction between an individual TCNQ molecule and the Bi_2Se_3 surface is independent of the registry and is very weak, because there is neither charge transfer nor any significant hybridization between the HOMO/LUMO of TCNQ and the Bi_2Se_3 substrate.

Since the TCNQ monomer is expected to be equally or possibly even more reactive than the H-bonded TCNQ network, these results further point towards a weak interaction of the H-bonded network with $Bi_2Se_3(0001)$, in agreement with the STM and photoemission results.

Conclusion

By performing detailed STM investigations we provide evidence that a TCNQ molecules arrange themselves in an ordered H-bonded organic network on the Bi_2Se_3 surface. The presented results strongly suggest a physisorbed TCNQ on Bi_2Se_3 surface, with negligible charge transfer, in agreement with DFT calculations. Additionally, ARPES and XPS measurements performed on multilayer TCNQ/Bi_2Se_3 confirm a *nearly* unperturbed topological surface state and no significant

modifications of the topological electronic structure. This type of organic network represents the first step towards the realization of an ordered array of local magnetic moments on a TI surface and, possibly, drive the system to novel and relevant phenomena as predicted by theory[26].

Methods Section

The Bi_2Se_3 samples used are (0001) oriented single crystals grown by the modified Bridgman method. These samples have been previously characterized by X-ray diffraction, low-energy electron diffraction and Auger electron spectroscopy[56, 69, 70]. Samples were cleaved in-situ in ultra-high vacuum (UHV) conditions at a base pressure of low 10^{-9} mbar. TCNQ molecules (purchased from Sigma Aldrich, no further treatment) were evaporated onto the Bi_2Se_3 sample held at room temperature (RT). STM measurements were performed at 77K and 100K in two different UHV chambers (base pressures of low 10^{-10} mbar), with typical tunneling current of few tens of pA up to hundred pA. XPS and ARPES investigations were carried out at RT at the APE and VUV end-stations (base pressures of low 10^{-10} mbar) at the ELETTRA synchrotron by depositing increasing amounts of TCNQ molecules on a freshly cleaved Bi_2Se_3 surface.

First principle DFT calculations have been performed using the Vienna Ab initio Simulation Package (VASP) that is a plane wave based code[71-73]. We have used the GGA-PBE approximation to treat exchange and correlation[74], as well as van der Waals corrections within the vdW-DFT[75, 76] approach to give an adequate description of an individual TCNQ molecule on the Bi_2Se_3 surface. For a description of the TCNQ-Bi_2Se_3 interaction we used a quintuple layer thick slab, whose crystal structure was obtained from the experimental data[69]. Concerning the lateral extension of the surface supercell, it is enough to use a rectangular $2\sqrt{3} \times 2$ supercell that contains eight atoms

in each layer. The sufficiency of the lateral separation between the molecules located in the neighboring cells (4.04 Å in this case) was confirmed on the basis of a test calculation that revealed essentially no changes in the unsupported molecule density of states with the increase of separation. The k-point sampling of the two-dimensional Brillouin zone was chosen to be 5×9×1 and the energy cut-off for the plane wave expansion was set to 400 eV.

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