Quasiparticle electronic structure of two-dimensional heterotriangulene-based covalent organic frameworks adsorbed on Au(111)

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Abstract
The modular nature and unique electronic properties of two-dimensional (2D) covalent organic frameworks (COFs) make them an attractive option for applications in catalysis, optoelectronics, and spintronics. The fabrications of such devices often involve interfaces formed between COFs and substrates. In this work, we employ the first-principles GW approach to accurately determine the quasiparticle electronic structure of three 2D carbonyl bridged heterotriangulene-based COFs featuring honeycomb–kagome lattice, with their properties ranging from a semi-metal to a wide-gap semiconductor. Moreover, we study the adsorption of these COFs on Au(111) surface and characterize the quasiparticle electronic structure at the heterogeneous COF/Au(111) interfaces. To reduce the computational cost, we apply the recently developed dielectric embedding GW approach and show that our results agree with existing experimental measurement on the interfacial energy level alignment. Our calculations illustrate how the many-body dielectric screening at the interface modulates the energies and shapes of the Dirac bands, the effective masses of semiconducting COFs, as well as the Fermi velocity of the semi-metallic COF.

Keywords: covalent organic framework, energy level alignment, substrate screening, dielectric embedding GW, interface

1. Introduction
Covalent organic frameworks (COFs) are micro-porous materials in which non-metallic light atoms form periodic structures via covalent bonds [1, 2]. These crystalline materials could feature different types of bond connectivities, giving rise to a wide range of two-dimensional (2D) [3–6] and three-dimensional (3D) [7–11] topologies. COFs have attracted great attention because of their diverse properties such as high porosity [8, 12, 13], high charge carrier mobilities [14], modularity in synthesis [15–17], etc, in addition to the non-trivial topological properties that are intrinsic to the lattice symmetry [18, 19]. This makes them excellent candidates for applications in gas sensing [20], energy storage [21, 22], spintronics [23, 24], optoelectronics [25], and catalysis [26–28]. While the synthesis of perfectly crystalline COFs remains a challenge [29], most 2D COFs are synthesized by Ullmann coupling [30–32] and self-assembled on metal or insulating substrates [30, 33, 34]. Moreover, their practical applications in field effect transistor-type devices often involve interfaces...
between COFs and metal substrates [35, 36]. Therefore, it is of paramount significance to understand how properties of COFs are modulated by the substrates on which the COFs are synthesized or assembled.

First-principles calculations are an indispensable tool in understanding the properties of COFs and their interactions with metal substrates. For the latter, a key physics is the many-body interaction between the substrate and the COF, namely the dielectric screening of the Coulomb interaction within the COF due to the substrate. This effect renormalizes the fundamental gap of the COF adsorbed on a metal substrate compared to the freestanding COF and is known as the ‘image-charge effect’ [37–40]. Due to the typical large size of the COFs and their interfaces with substrates, most theoretical works have employed density functional theory (DFT) [41, 42] for the determination of the structural, electronic, and magnetic properties [23, 30, 34, 43–49]. However, while most functionals can predict the total energy and density related properties to a good accuracy, the orbital energy levels and energy level alignments of COF–metal interfaces are generally beyond the reach of many functionals. This is because the latter are quasiparticle properties that require a many-body treatment of the correlation effects [39, 40]. Hybrid functionals such as Heyd–Scuseria–Ernzerhof (HSE) [50] improve on band gaps of bulk semiconductors over local and semi-local functionals [51] and have been applied to study COFs and their adsorption on substrates [23, 30, 45, 52–55]. However, they are often still not quantitatively accurate in the determination of the energy level alignment [56] at heterogeneous interfaces. The development of hybrid functionals for this purpose is still at its infancy [57].

Compared to DFT, many-body perturbation theory provides a rigorous theoretical framework in computing quasiparticle properties [58]. Its common approximation is the GW approach [59, 60] where $G$ is the Green’s function and $W$ is the screened Coulomb interaction. However, the relatively high computational cost of first-principles GW has hindered its routine applications to large systems, such as the COF–substrate interfaces. Simplified GW-based schemes exist, such as the DFT + $\Sigma$ [39, 61, 62]. However, DFT + $\Sigma$ cannot capture the dynamical effects of the self-energy and requires an explicit specification of the image-charge plane [62], which may be ambiguous in certain cases. Moreover, it is not trivial to use the original version of DFT + $\Sigma$ to treat a periodic adsorbate such as the COF, because it would be a very drastic approximation to model an orbital of the periodic adsorbate using a single point charge. In fact, reference [63] generalized the original DFT + $\Sigma$ idea in a model to study the properties of COF–substrate interfaces. Although direct GW calculations have been employed in studying freestanding COFs [63–65], to the best of our knowledge, we have not found GW-based calculations of COF–substrate interfaces.

One bottleneck of large-scale GW calculations is the high computational cost of the non-interacting Kohn–Sham (KS) polarizability in the random-phase approximation [66], $\chi^0$, which scales as $O(N^4)$ with $N$ being the system size. An emerging approach for large-scale interfaces leverages the (approximate) additivity of the substrate and adsorbate KS polarizabilities [67–69], greatly reducing the computational cost. This approximation holds when the substrate-adsorbate hybridization approaches zero, valid for most physisorptions. Even with these approaches, one often still needs to compute many empty bands for the combined COF–substrate interface in order to converge the self-energy. For large simulation cells, this is still a formidable task. To tackle this challenge, we proposed an approach in reference [70] where the explicit GW calculations are confined to a simulation cell that only contains the adsorbate, which is embedded in the dielectric environment of the substrate. This is termed ‘dielectric embedding GW’ and was shown to be accurate for a few prototypical physisorbed interfaces.

In this work, we apply the dielectric embedding GW approach developed in reference [70] to a series of 2D heterotriangulene-based COFs adsorbed on Au(111) surface. These COFs feature honeycomb–kagome lattice and we focus on how their electronic properties are modulated by the many-body screening of the Au(111) substrate. The substrate effect is elucidated via a comparison with GW calculations of the freestanding COFs. Note that reference [30] studied the carbonyl-bridged triphenylamine (CTPA/Au(111) interface using both scanning tunneling spectroscopy and HSE calculations. Our result on the CTPA/Au(111) is in quantitative agreement with the experimental measurement [30], validating the method we use. Our results for other COF/Au(111) interfaces provide a theoretical benchmark for future experiments.

This paper is structured as follows: we discuss the structure of the COFs and the COF/Au(111) interfaces in section 2.1, and detail the methodology used for freestanding COFs in section 2.2 and that for the interfaces in section 2.3. We then discuss our results of the various COFs and their respective interfaces with Au(111) in section 3 and conclude in section 4.

2. Systems and methodology

2.1. COF structures and geometry relaxations

2D heterotriangulene-based COFs possess an Archimedean net topology forming the so-called ‘honeycomb–kagome lattice’, which features both corner-sharing triangular moieties and a hexagonal unit cell [18, 72, 73] (figure 1(a)). A well-studied COF with this topology is the CTPA which has a nitrogen atom at the center of each triangulene [X = N and Y = N in figure 1(a)]. By replacing all nitrogen atoms with carbon, one obtains the structure of the triangulene polymer (CTP) [X = C and Y = C in figure 1(a)]. CTPA has been studied both experimentally and theoretically [30, 45, 74], while CTP has only been studied by theory [45]. Here, in addition to CTPA and CTP, we computationally explore another structure by replacing the nitrogen atoms in half of the triangulenes by boron. We call the resulting structure CTP-BN [X = B and Y = N in figure 1(a)]. The relation between CTP and CTP-BN is therefore similar to that between graphene and hexagonal boron nitride (hBN). Variable-cell relaxations of these COFs are performed until all residual forces are less than 0.05 eV Å$^{-1}$, in simulation cells where symmetries are fixed as hexagonal and the lattice constant along the $c$ direction is...
fixed as 30 Å. In such calculations, we use the vdW-DF-cx [75] functional as implemented in the Quantum ESPRESSO [76] package, the optimized norm-conserving Vanderbilt pseudopotentials [77], a 100 Ry kinetic energy cutoff, and the Γ-point sampling. The relaxed in-plane lattice parameters of CTPA, CTP, and CTP-BN are 17.36 Å, 17.41 Å, and 17.46 Å, respectively.

We then model the COF/Au(111) interfaces in simulation cells of hexagonal symmetry with 30 Å as the lattice constant along the c direction, containing three layers of Au(111), as shown in figure 1(b). We fix the in-plane lattice parameters of all COF/Au(111) simulation cells to be 17.36 Å, the optimized value for the freestanding CTPA. We use the same in-plane lattice parameters for all interfaces so that we can use the same χ0 from the Au(111) unit cell to more than one interface (to be specific, CTPA and CTP-BN) in our dielectric embedding GW calculations. This in-plane lattice parameter corresponds to 6 × 6 Au atoms in the (111) plane with an equivalent Au face-centered cubic (FCC) lattice constant of 4.092 Å. This value is very similar to both the experimental lattice constant of 4.065 Å [78, 79] and the optimal vdW-DF-cx lattice constant of 4.108 Å [80]. Therefore, the strain on the Au atoms is very small.

The COF/Au(111) interfaces are relaxed with fixed lattice parameters and all 108 Au atoms in the substrate fixed in their bulk positions. All atoms in the COF are allowed to relax until all forces are below 0.05 eV Å⁻¹. We use a kinetic energy cutoff of 70 Ry and a 3 × 3 × 1 k-mesh, and the vdW-DF-cx [75] functional. The average adsorption heights [d in figure 1(b)] for CTPA, CTP, and CTP-BN on the Au(111) substrate are 3.28 Å, 3.04 Å, and 3.16 Å, respectively. Note that one needs a functional capable of capturing van der Waals dispersion to correctly model such interfaces. We have found from our calculations that the Perdew–Burke–Ernzerhof (PBE) functional [81] yields a higher adsorption height than vdw-DF-cx and does not physically bind the COF and the Au surface. Since the COFs are not perfectly flat, we measure this average adsorption height by averaging out the adsorption heights of all atoms in the COF. Within each COF, the largest deviation from the average values is 0.03 Å for both CTPA and CTP, and 0.15 Å for CTP-BN.

2.2. Quasiparticle electronic structure of freestanding COFs

For the purpose of comparing the electronic structure of the freestanding COFs and those adsorbed on Au substrate, we calculate the quasiparticle properties of all freestanding COFs in simulation cells whose in-plane lattice parameters are consistent with those of the interface, i.e., 17.36 Å, instead of the individually optimized value for each COF. The size of the cells along the c direction is fixed to be 10 Å, a value that we used before [68, 70] and know works well for flat molecules. The COF coordinates are fixed as those in the relaxed COF/Au(111) interfaces. We perform perturbative GW₀ calculations as implemented in the BerkeleyGW package [66], using the PBE functional as the mean-field starting point. The PBE calculations of the freestanding CTPA and CTP-BN are performed using a kinetic energy cutoff of 70 Ry and a 3 × 3 × 1 k-mesh. For CTP, we use a much higher k-mesh of 6 × 6 × 1 to obtain a more accurate description of the bands near the Dirac point.

The GW calculation uses a q-mesh that is the same as the k-mesh in the corresponding PBE calculation. We have checked that a kinetic energy cutoff of 7.2 Ry in the dielectric function—corresponding to 6000 bands in the aforementioned simulation cell—converges the self-energies of individual levels (although the gaps converge at a lower cutoff, 3.3 Ry, corresponding to 2000 bands), as we show in the supplementary material (https://stacks.iop.org/JPCC/33/254004/mmedia). To correctly model the q → 0 limit in the dielectric function, for CTPA and CTP-BN, we include 200 bands in the wavefunctions calculated on a shifted k-grid. For CTP, where bands with linear dispersion touch at the Dirac point (see below), we include 200 bands in the wavefunctions calculated in a much finer k-mesh, 12 × 12 × 1. In all our calculations, we use a slab truncation scheme [82] to eliminate the spurious Coulomb interactions along the c direction. In the self-energy calculations, we model the frequency dependence of the self-energy using the Hybertson–Louie generalized plasmon pole model [60]. The semiconductor screening is applied to CTPA and CTP-BN, and the graphene screening is applied to CTP. The static reminder [83] is applied to all calculations to facilitate the convergence with respect to the number of bands.

2.3. Dielectric embedding GW for COF/Au(111) interfaces

Given the size of the COF/Au(111) interfaces, it is challenging to perform direct GW calculations. In this work, we apply the dielectric embedding GW approach developed in reference [70]. Physically, this method approximates the substrate as a dielectric environment in which the adsorbate is embedded, as schematically shown in figure 2. We refer the interested readers to reference [70] for details of this method, and only list the major steps and computational parameters here. Overall, we approximate the KS polarizability of the interface, χ°_tot, as
a sum of the KS polarizabilities of the Au substrate ($\chi_{\text{Au}}^0$) and that of the COF ($\chi_{\text{COF}}^0$), i.e., $\chi_{\text{tot}}^0 = \chi_{\text{Au}}^0 + \chi_{\text{COF}}^0$. The calculation of $\chi_{\text{COF}}^0$ was detailed in section 2.2. For the $\chi_{\text{Au}}^0$, we first calculate this quantity in the Au(111) unit cell and then uses reciprocal-space folding and real-space truncation techniques to obtain its corresponding quantity within the COF simulation cell, whose dimension is consistent with $\chi_{\text{COF}}^0$. In particular, we truncate the $\chi_{\text{Au}}^0$ into a region of the same size as the freestanding COF simulation cell and centered at the COF adsorbate on Au(111), as illustrated using the red box in figure 2. We also note that the pseudopotential of Au includes semi-core $d$-states that are needed for the accuracy in GW calculations [84].

After the $\chi_{\text{Au}}^0$ is summed up from its constituents in the COF simulation cell, the dielectric function is calculated using $\epsilon_{\text{tot}} = [1 - v\chi_{\text{tot}}]^{-1}$ where $v$ is the Coulomb interaction, and the self-energy is calculated via $\langle \phi_i^{\text{COF}}|\Sigma|\phi_j^{\text{COFs}}\rangle$. Similarly, a kinetic energy cutoff of 7.2 Ry is used for $\chi_{\text{Au}}^0$, consistent with that of $\chi_{\text{COF}}^0$.

### 3. Results and discussion

#### 3.1. CTPA and its adsorption on Au(111)

The electronic structure of the CTPA/Au(111) interface has been characterized both experimentally [30, 74] and theoretically [30, 45], which provides a benchmark for our dielectric embedding calculations. Figure 3(a) shows the band structure of the freestanding CTPA calculated in PBE (gray) and GW (blue), respectively. For comparison, we align the VBM of the PBE and GW band structures at $E = 0$. PBE and GW share the same qualitative features of the Frontier bands: for conduction bands, two dispersive Dirac bands cross at the $\Gamma$ point and are sandwiched between two flat bands. The CBM is at $\Gamma$, whose energy is nearly degenerate with other $\mathbf{k}$ points. For valance bands, both PBE and GW predict the VBM at $\Gamma$, giving rise to a direct fundamental gap, calculated to be 1.75 eV in PBE and 4.21 eV in GW. In the GW results, the top valance band appears to be slightly more dispersive than that in PBE (see the effective mass results below). Additionally, the six occupied flat bands (with two pairs of degenerate bands) are lower in energy than the two Dirac bands in GW (i.e., below $-1$ eV), while they are energetically between the two Dirac bands in PBE (i.e., between 0 and $-1$ eV). Note that this difference in the relative positions between the flat and the Dirac bands is also captured by the HSE functional [30], and is due to the different localizations of these bands. To be specific, the two Dirac bands consist of delocalized $\pi$ orbitals, and the flat bands are mainly localized on the oxygen atoms or nearby. Our findings here are consistent with the fact that the magnitude of the GW self-energy generally depends on the localization of an orbital and the mean-field starting point [85].

![Figure 2. A schematic view of the dielectric embedding GW approach applied to the COF/Au(111) interface. Instead of computing the $\chi_{\text{Au}}^0$ and self-energies in the interface (left panel), the GW calculations are confined to a smaller simulation cell of COF only (right panel), with the same dimensions along $a$ and $b$ directions as the interface, but a much smaller lattice constant along $c$. The gray background in the right panel indicates that the COF is embedded in the dielectric environment of the substrate, truncated into the red box as illustrated on the left panel.](image-url)
Figure 3(b) shows the electronic structure of the CTPA/Au(111) interface. We first show the PBE projected density of states (PDOS) of the interface onto the CTPA, with $E = 0$ defined as the Fermi level ($E_F$) of the interface. Then we show the PBE band structure (gray) of the freestanding CTPA [the same one as in figure 3(a)] again, but shift the energies such that the PBE VBM matches $E_{VBM} − E_F$ of the CTPA/Au(111) interface. One can then correlate the band structure with the PDOS. Due to the weak coupling nature of the interface and the neglect of band gap renormalization in PBE, the PBE CBM–VBM gap of the freestanding CTPA matches the CBM–VBM peak distance in the PDOS. Furthermore, we show the dielectric embedding GW band structure (red) of the CTPA (with the substrate screening effect taken into account implicitly, as shown in figure 2). Here, the positions of the bands are chosen such that their energy differences from the corresponding PBE bands match the self-energies in the dielectric embedding GW calculation. Because the PBE VBM (CBM) energy in figure 3(b) matches the $E_{VBM} − E_F$ ($E_{CBM} − E_F$) at the interface, the dielectric embedding GW VBM (CBM) energy therefore reflects our prediction of the corresponding energy level alignment at the interface using a GW-level method. Using this strategy, although the self-energy calculation only explicitly involves the COF in the dielectric embedding GW approach (as shown in the right panel of figure 2), the results reflect the electronic structure of the COF/Au(111) interface.

Our dielectric embedding GW results agree quantitatively with scanning tunneling spectroscopy measurement [30]. The dielectric embedding GW approach places the CTPA VBM at 1.67 eV below the $E_F$ of the interface while reference [30] reports an energy of 1.63 eV. Moreover, our dielectric embedding GW places the CTPA CBM at 1.14 eV above the $E_F$, which falls in between the CBM onset (0.82 eV) and the CBM peak (1.51 eV) reported in reference [30]. At the GW level of theory, the fundamental band gap of CTPA reduces from 4.21 eV in the freestanding phase to 2.81 eV at the CTPA/Au(111) interface. It is also noteworthy that the occupied flat bands are below the two Dirac bands in the dielectric embedding GW, qualitatively similar to the GW results of the freestanding CTPA.

In addition to the comparison with experiment, we benchmark our dielectric embedding GW results to two other GW-based computational methods, in a similar fashion as we did in reference [70]. To be specific, we compare the following three approaches: (i) dielectric embedding GW, where one calculates $\langle \phi^*_{\text{COF}} | \Sigma | \phi_{\text{COF}} \rangle$ in the COF simulation cell (the right panel of figure 2); (ii) projection GW [86, 87], where one calculates $\langle \phi^*_{\text{COF}} | \Sigma | \phi_{\text{tot}} \rangle$ in the interface simulation cell (the left panel of figure 2); and (iii) substrate screening GW [68], where one calculates $\langle \phi^*_{\text{tot}} | \Sigma | \phi_{\text{tot}} \rangle$ in the interface simulation cell, which is an interface orbital representing CTPA VBM or CBM resonance. In the W of all three methods, we assume additivity of molecular and substrate polarizabilities, i.e., $\chi^0_{\text{tot}} \approx \chi^0_{\text{Au}} + \chi^0_{\text{COF}}$. This approximation has been shown to be valid for most weakly coupled interfaces [68, 69].

To reduce the computational cost, the above comparisons are performed using a lower cutoff for the dielectric function: 3.3 Ry, corresponding to 2000 bands for the embedding GW and 6000 bands for both the projection GW and the substrate screening GW. This parameter has been tested to yield converged band gaps, although the absolute energies of each level (as measured with respect to the vacuum) might not be fully converged, as we show in the supplementary material. Both the dielectric embedding GW and the projection GW yield a CTPA gap of 2.7 eV on Au(111), verifying that the real-space truncation of the substrate polarizability in our dielectric embedding GW approach does not deteriorate the results. The substrate screening GW yields a CTPA gap of 2.3 eV on Au(111), and the difference originates from the fact that $\langle \phi^*_{\text{tot}} | \phi_{\text{COF}} \rangle$ deviates from unity (especially for the CBM), which implies some orbital hybridization upon formation of the interface.

Lastly, to quantitatively characterize the shape of the Dirac bands, we compare the effective masses ($m^*$) at the $\Gamma$ point, from PBE, GW, and dielectric embedding GW. Given the dispersionless nature of the CBM ($m^* \rightarrow \infty$), we only calculate the $m^*$ at VBM, along both $\Gamma \rightarrow K$ and $\Gamma \rightarrow M$ directions. Along $\Gamma \rightarrow K$, the PBE, GW, and dielectric embedding GW results are 0.47, 0.46, and 0.46, respectively, in the unit of $m_0$, the electron mass; along $\Gamma \rightarrow M$, these three values are 0.46, 0.43, and 0.43, respectively. Our PBE results are consistent with reference [45]. We conclude that the bands are slightly more dispersive in GW and embedding GW than PBE, and the substrate does not significantly modulate the dispersion of the bands for this material.

3.2. CTP and its adsorption on Au(111)

If one replaces the nitrogen atoms in the center of the triangular units in CTPA [see figure 1(a)] by carbon, one obtains the structure of CTP. The material is reminiscent of graphene [45], being a semi-metal and featuring Dirac bands crossing at the Fermi level. On the other hand, CTPA can be considered as the analogue of 2D nitrogen in the honeycomb lattice, such that the Fermi level shifts up to the top of the two Dirac bands [45].

Figure 4(a) shows our calculations of the band structure of the freestanding CTP at both PBE (gray) and GW (blue) levels. Here, all the bands are shifted with respect to the Dirac point that is set as $E = 0$. Same as CTPA, the GW and PBE band structures share the same qualitative feature: a flat CBM and the Dirac cone structure around the Fermi level. GW shows a widening of the Dirac bands than PBE, as can be seen at the $M$ and $\Gamma$ points. Also same as CTPA, we see that the occupied flat bands are shifted further away from the two Dirac bands in GW. Notably, close to the Dirac point at $K$, we notice a ‘kink’ making the GW band structure deviate from the linear dispersion. This phenomenon is reminiscent of that in graphene, which was carefully discussed in reference [88] and was also observed in experiment [89]. Such a ‘kink’ affects the way we compute the Fermi velocity, as we discuss below.

Figure 4(b) shows the electronic structure of the CTP/Au(111) interface, which is a semi-metal/metal interface. We present the results using similar strategies as we did for...
CTPA in figure 3, such that the energies reflect our prediction of the quasiparticle electronic structure at the CTP/Au(111) interface using the dielectric embedding \(GW\). We note that the ‘kink’ close to the Dirac point that we observed in the \(GW\) band structure of the freestanding CTP is less pronounced in the embedding \(GW\) results. A similar observation has been reported in graphene, where an increase in the electrostatic doping diminishes the ‘kink’ [90].

Lastly, we compare the Fermi velocities calculated using PBE, \(GW\), and dielectric embedding \(GW\). Figure 5(a) shows the zoomed-in view of the PBE (gray dots) and \(GW\) (both filled and unfilled blue circles) band structures near the Dirac point (K), and one can clearly see the ‘kink’ in the \(GW\) band structure. To compute the PBE Fermi velocity, we perform a linear fit (gray dashed lines) using all gray dots shown in figure 5(a), resulting in \(0.32 \times 10^6\) m s\(^{-1}\). To compute the \(GW\) Fermi velocity, due to the ‘kink’, we perform a linear fit (blue dashed lines) using only the filled blue circles, which is consistent with the practice in reference [88]. This procedure yields Fermi velocities of \(0.42 \times 10^6\) m s\(^{-1}\) and \(0.51 \times 10^6\) m s\(^{-1}\) for the conduction and valence band, respectively. Figure 5(b) shows the zoomed-in view of the dielectric embedding \(GW\) band structure near the Dirac point (both filled and unfilled red circles). One can see that the ‘kink’ is not as pronounced as in the \(GW\) calculation. To compute the embedding \(GW\) Fermi velocity, we again perform a linear fit (red dashed lines) using only the filled red circles, resulting in \(0.41 \times 10^6\) m s\(^{-1}\) and \(0.49 \times 10^6\) m s\(^{-1}\) for the conduction and valence band, respectively.

3.3. CTP-BN and its adsorption on Au(111)

If one replaces half of the nitrogen atoms in the centers of the triangulenes in CTP by boron, one obtains the structure of CTP-BN. Equivalently, it can be obtained by replacing the carbon atoms in the centers of the triangulenes in CTP with boron and nitrogen—in a similar fashion as one obtains hBN from graphene. To the best of our knowledge, CTP-BN has neither been synthesized nor computationally discussed. Here, we use PBE, \(GW\), and dielectric embedding \(GW\) approaches to explore its electronic structure in the freestanding phase and upon adsorption on Au(111). As we show below, similar to hBN, the nitrogen and boron ‘doping’ in CTP-BN opens the gap at the K point compared to CTP, resulting in a wide-gap semiconductor.

Figure 6(a) shows the band structure of the freestanding CTP-BN, used PBE (gray) and \(GW\) (blue), respectively. For comparison, we align the VBM of the PBE and \(GW\) band structures at \(E = 0\). Similar to the above two COFs, PBE and \(GW\) are qualitatively similar in the features of the Dirac bands, with both the VBM and CBM located at the K point. Compared to PBE results, the occupied flat bands are shifted away from the dispersive Dirac bands in \(GW\). Notably, at the \(\Gamma\) point, PBE predicts one of the flat bands as the top valence band, while \(GW\) predicts the dispersive Dirac band as the top

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**Figure 4.** (a) PBE (gray) and \(GW\) (blue) band structures of the freestanding CTP; (b) PBE (gray) and dielectric embedding \(GW\) (red) band structures of the CTP, with band energies shifted such that the energy of PBE Dirac point, \(E_D\), matches the corresponding energy level alignment at the CTP/Au(111) interface, i.e., \(E_D - E_F\). The PBE PDOS of the CTP/Au(111) interface onto the CTP is shown for comparison. The positions of the embedding \(GW\) bands are chosen such that their energy differences from the corresponding PBE bands match the self-energies in the dielectric embedding \(GW\) calculation. In this way, the Dirac point in the dielectric embedding \(GW\) reflects the prediction of \(E_D - E_F\) at the CTP/Au(111) interface using this approach.

**Figure 5.** Zoomed-in view of (a) PBE (gray circles), \(GW\) (both filled and unfilled blue circles), and (b) dielectric embedding \(GW\) (both filled and unfilled red circles) band structures near the Dirac point of CTP. In both (a) and (b), to compute the Fermi velocity, a linear fitting (dashed lines) is performed only for the states represented by the filled circles. We use the same convention of \(E = 0\) as in figure 4, \(a_0\) is the Bohr radius.

**Figure 6.** (a) PBE (gray) and \(GW\) (blue) band structures of the freestanding CTP-BN; (b) PBE (gray) and dielectric embedding \(GW\) (red) band structures of the CTP-BN, with band energies shifted such that the value of the PBE VBM matches its energy level alignment at the CTP-BN/Au(111) interface, i.e., \(E_{VBM} - E_F\). The PBE PDOS of the CTP-BN/Au(111) interface onto the CTP-BN is shown for comparison. The positions of the embedding \(GW\) bands are chosen such that their energy differences from the corresponding PBE bands match the self-energies in the dielectric embedding \(GW\) calculation. In this way, the embedding \(GW\) VBM (CBM) reflects the prediction of \(E_{VBM} - E_F\) at the interface using this approach.
Dirac band within the valence bands of CTPA (cf figures 3, 5, and 6). However, in the Γ point, being a maximum along one direction (Γ → M), this band reaches a maximum at this point, resulting in the so-called ‘Mexican hat’ shape [91]. Notably, this shape is also observed in the dielectric embedding GW band structure of CTPA/Au(111), for one of the deeper valence bands around −3 eV in figure 3(b), while absent in the freestanding CTPA.

These results suggest that this ‘Mexican hat’ shape stems from the substrate effect, in line with reference [91].

To quantify the shape of the bands from different levels of theory, we calculate effective masses based on quadratic fittings of the bands. For PBE, we fit the filled gray circles using a quadratic form (gray dashed line). For both GW and dielectric embedding GW, we perform the fitting in two regions: one in close proximity to Γ (filled blue/red diamonds and the green dashed lines), and one outside this region (filled blue/red circles and the orange dashed lines). The goal behind this strategy is to both characterize the actual curvatures at Γ (green dashed lines) and show how GW and dielectric embedding GW modulate the overall shape of PBE bands (orange dashed lines).

The results are summarized in table 1. Positive values indicate convex bands that are usually observed at the CBM of a typical semiconductor. Negative values indicate concave bands that are usually observed at the VBM of a typical semiconductor. As we discussed above, the curvatures of the GW and dielectric embedding GW bands are qualitatively different from that of the PBE, for the top valance band in close proximity to the Γ point. We therefore list the effective masses calculated in both regions: the values within parentheses are calculated in the region in close proximity to Γ (filled blue/red diamonds in figure 7), and the values outside the parentheses are calculated outside this region (filled blue/red circles in figure 7). It would be of interest to see if future experiments could unveil the precise curvature and shape of this band to verify our computational results.

3.4. Discussion on the structure–property relationship

We provide a brief comparative discussion on the three COFs we studied: CTPA, CTP, and CTP-BN. In this section, we focus on the structure–property relationship and the physical effect of the substrate. As we showed above, CTP is reminiscent of graphene, being a semi-metal with Dirac bands crossing at the K point at the Fermi level (figure 4), which results from the honeycomb lattice. CTPA can be obtained by replacing all carbon atoms at the center of the triangulene moieties with nitrogen. This is equivalent to a chemical electron doping such that the Fermi level is shifted up. As a result, both Dirac bands become fully occupied and the conduction bands are similar to those of CTP, with crossing Dirac bands sandwiched between two flat bands. A similar discussion between CTPA and CTP can be found in reference [45]. Starting from CTP, the CTP-BN can be obtained by replacing the central carbon atoms by nitrogen and boron, respectively, in a similar manner as how one obtains hBN from graphene. This opens up the gap at the K point, resulting in a wide-gap semiconductor with direct band gap at the K point. Comparing CTP-BN (figure 6) and CTPA (figure 3), one can see that the CBM of CTPA is flat (a feature of the honeycomb lattice), while the CBM of CTP-BN is dispersive (which can be considered physically evolving from a Dirac band in CTP).

When the three COFs are adsorbed on Au(111), the dielectric screening of the metal substrate has different impacts on the three COFs. For wide-gap semiconductors, i.e., CTPA and CTP-BN, the gap of the adsorbate is renormalized and hence becomes fully occupied and the conduction bands are similar to those of CTP, with crossing Dirac bands sandwiched between two flat bands. A similar discussion between CTPA and CTP can be found in reference [45]. Starting from CTP, the CTP-BN can be obtained by replacing the central carbon atoms by nitrogen and boron, respectively, in a similar manner as how one obtains hBN from graphene. This opens up the gap at the K point, resulting in a wide-gap semiconductor with direct band gap at the K point. Comparing CTP-BN (figure 6) and CTPA (figure 3), one can see that the CBM of CTPA is flat (a feature of the honeycomb lattice), while the CBM of CTP-BN is dispersive (which can be considered physically evolving from a Dirac band in CTP).

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Table 1. Effective masses (m*) of CTP-BN, calculated using PBE, GW, and the dielectric embedding GW, at both Γ and K points, for both CB and VB. All values are in unit of m0. Positive values indicate convex bands that are usually observed at the CBM of a typical semiconductor. Negative values indicate concave bands that are usually observed at the VBM of a typical semiconductor. Due to the complexity of GW and embedding GW valence bands near the Γ point, the m* values are calculated in two different regions: values outside (inside) the parentheses are obtained from fitting of the filled circles (diamonds) in figure 7.

|       | Γ → K | Γ → M | K → Γ | K → M |
|-------|-------|-------|-------|-------|
| CB    | CB    | CB    | CB    | CB    |
| VB    | VB    | VB    | VB    | VB    |
| PBE   | −0.81 | 0.12  | −0.83 | 0.12  |
| GW    | −0.92 | 0.27 (1.06) | −0.91 | 0.25 (−0.46) |
| Embedding GW | −0.94 | 0.27 (−0.31) | −0.92 | 0.26 (−0.26) |

smaller than that of the freestanding COF by about 1.5 eV for both cases. The dispersion of the Frontier bands is only slightly different for most cases, as evidenced from the comparison of the effective mass results between GW and dielectric embedding GW for the two COFs. The only exception is the Γ → K direction in CTP-BN, where our results suggest that the substrate changes the sign of the band curvature, resulting in the so-called 'Mexican hat' shape, a point to be verified by future experiments. For the semi-metal COF, i.e., CTP, the adsorbate remains a semi-metal, with the Fermi velocity marginally smaller than that of the freestanding CTP. The Fermi velocity we determined using dielectric embedding GW for this COF is close to that of a similarly structured COF adsorbed on Au(111) [74], but is lower than that of graphene on the Au(111) surface (0.8 × 10^6 m s⁻¹ [92]).

Finally, we comment that because of the nature of the dielectric embedding approach, we only captured the many-body effect (dielectric screening) in the modulation of the shapes and effective masses of the COF bands by the substrate, and left out the one-body effect (orbital hybridization and charge transfer). Nevertheless, we expect that our approach provides quantitative descriptions of the band gap renormalization and interfacial energy level alignments, as we showed in the explicit comparison against experimental results for the CTPA/Au(111) interface.

4. Conclusions

In this work, we investigated the quasiparticle electronic structure of heterogeneous interfaces formed between 2D heterotriangulene-based COFs and Au(111), with the aim of understanding the interactions between these 2D COFs and metal substrates. The calculations of such large-scale interfaces were made possible thanks to the newly developed first-principles dielectric embedding GW approach. In particular, we focused on the band gap renormalization, energy level alignment at the interface, and the modulation of the shapes of the COF bands by the substrate. We considered three COFs: CTPA, CTP, and CTP-BN, and showed how the band gaps and the shapes of their Dirac bands—as measured by the effective masses and Fermi velocities—vary between the freestanding COFs and those adsorbed on Au(111). Our results on the CTPA/Au(111) interface quantitatively agree with experiments, and our results on the CTP/Au(111) and CTP-BN/Au(111) interfaces provide benchmark results for future experiments and calculations.

Supplementary data

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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