

Pentacene/TiO₂ Anatase Hybrid Interface Study by Scanning Probe Microscopy and First Principles Calculations

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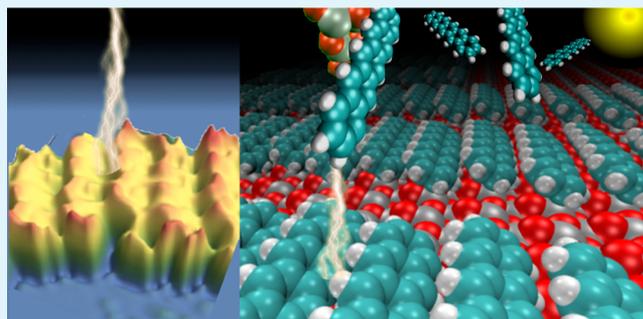
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Supporting Information

ABSTRACT: The understanding and control of the buried interface between functional materials in optoelectronic devices is key to improving device performance. We combined atomic resolution scanning probe microscopy with first-principles calculations to characterize the technologically relevant organic/inorganic interface structure between pentacene molecules and the TiO₂ anatase (101) surface. A multipass atomic force microscopy imaging technique overcomes the technical challenge of imaging simultaneously the corrugated anatase substrate, molecular adsorbates, monolayers, and bilayers at the same level of detail. Submolecular resolution images revealed the orientation of the adsorbates with respect to the substrate and allowed direct insights into interface formation. Pentacene molecules were found to physisorb parallel to the anatase substrate in the first contact layer, passivating the surface and promoting bulk-like growth in further organic layers. While molecular electronic states were not significantly hybridized by the substrate, simulations predicted localized pathways for molecule–surface charge injection. The localized states were associated with the molecular lowest unoccupied molecular orbital inside the oxide conduction band, pointing to efficient transfer of photo-induced electron charge carriers across this interface in prospective photovoltaic devices. In uncovering the atomic arrangement and favorable electronic properties of the pentacene/anatase interface, our findings testify to the maturity and analytic power of our methodology in further studies of organic/inorganic interfaces.

KEYWORDS: hybrid organic/inorganic interfaces, pentacene, anatase, AFM, DFT, thin-film morphology



INTRODUCTION

Organic photovoltaic (OPV) devices, where thin films of organic molecules coated with metal oxide buffers are layered between metallic electrodes, provide an affordable route to manufacturing large-area, lightweight solar cells for universal use. Device operation is enhanced by efficient electron–hole pair (exciton) separation into carrier charges in the organic region and directional intralayer charge mobility. Favorable band alignment at the organic/inorganic interface is particularly important for effective charge injection across the layers, whereas poor contact between the two materials leads to carrier scattering and recombination that degrade device performance. All these factors depend on the electronic

structure of the buried interface; by controlling it, we can enhance the power conversion efficiency of OPV devices.¹

Identifying the atomic arrangement at the organic/inorganic interface is critical to determining the local electronic band alignment. Atomic details of the interface structure are difficult to establish experimentally, so computational techniques are frequently deployed to simulate various molecule–solid contact configurations. Such calculations are made challenging by the large numbers of atoms and degrees of freedom

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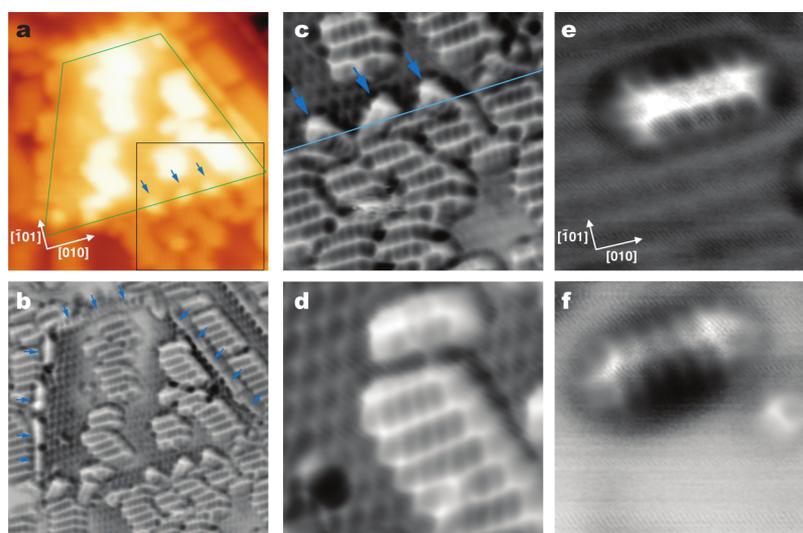


Figure 1. (a) Topographic AFM image of an area of (101) TiO₂ anatase partially covered with pentacene molecules (20 × 20 nm²). Crystallographic orientation is the same in all images. The trapezoid highlights the contour of an anatase island. (b) Intramolecular resolution AFM image simultaneously acquired with the topography displayed in (a) showing details of the adsorption of pentacene molecules at the terraces and steps of the anatase surface (20 × 20 nm²). The arrows point to pentacene molecules adsorbed at the steps in a side-on configuration. (c) Details of the adsorption of pentacene molecules (blue arrows) on the energetically most stable step of this anatase surface, connecting both upper and lower terrace (8.0 × 8.0 nm²). The line indicates the position of the step edge as characterized from the topography. (d) Details of a stack of pentacene molecules simultaneously resolving atomic features of the (101) anatase surface (4.7 × 4.7 nm²). (e,f) Frequency shift images of single pentacene molecules obtained with two different probe terminations (3.0 × 3.0 nm²). Acquisition parameters are free-oscillation first longitudinal resonant frequency (f_0) of the cantilever was 152 471 Hz for (a–d) and 159 202 Hz for (e,f); cantilever oscillation amplitude (A) was 95.9 Å for (a–d), 169.1 Å for (e), and 135.3 Å for (f); cantilever stiffness (K) was 23.7 N/m for (a–d) and 26.9 N/m for (e,f); quality factor of the cantilever (Q) was 44163 for (a–d), 49188 for (e), and 44246 for (f). Topographic set point (Δf) was –3.0 Hz for (a–c), –4.0 Hz for (d), –4.5 Hz for (e), and –14.2 Hz for (f); approach distance toward the surface for submolecular imaging (d) was 300 pm for (b,c,e), 250 pm for (d), and 340 pm for (f). Sample bias was –200 mV for (a–d), 100 mV for (e), and 200 mV for (f).

involved; chemical intuition helps to identify relevant configurations, but without experimental verification there is no guarantee that the computed interface structure resembles the one in the actual device.

In this work, we pursue a combined theoretical and experimental approach to interface structure determination. A metal oxide surface was functionalized by organic molecules at varying degrees of coverage. TiO₂ anatase served as the prototype model oxide buffer material on account of its optical activity and high charge carrier mobility.^{2,3} The (101) facet of an anatase natural crystal was covered with photoactive pentacene molecules; this is an electron acceptor molecule widely employed in organic optoelectronics.^{4,5} These two materials play significant roles in the recent revival of dye-sensitized solar cells,^{6,7} TiO₂ as substrate^{8–10} and pentacene as a candidate for metal-free dyes,^{11,12} which makes their interface a topic of current scientific interest.

Scanning probe microscopy (SPM), atomic force microscopy (AFM)¹³ in particular, can now achieve outstanding submolecular imaging of molecules on flat surfaces.^{14,15} Structural detail is delivered by constant-height close-range scanning techniques with chemically inert CO-functionalized probes.¹⁶ The considerable substrate corrugation of reconstructed metal oxide surfaces or large adsorbates presents a challenge for this imaging method, making it difficult to functionalize the probe with a CO molecule using vertical manipulation techniques or to scan the surface at constant height. To overcome this obstacle, we opt for a “multipass” imaging method. Developed to address high-resolution AFM imaging of large molecules on corrugated substrates, it allows

us to obtain atomic scale resolution detail of both surface and adsorbate simultaneously.¹⁷

Experimental characterization was carried out by combining “multipass” AFM with bias spectroscopy imaging¹⁸ and scanning tunneling microscopy (STM).¹⁹ In multichannel measurements, probe–surface force and tunneling current signals were recorded simultaneously to obtain real-space local information on the chemical and electrical response of the functionalized surface. We employed first-principles density functional theory methods to interpret the contrast formation mechanisms behind AFM and STM imaging and analyze the electronic properties at the surface. Such a comprehensive approach allowed us to study local bonding of the molecules to the crystal substrate, monolayer formation, and thin-film morphology and thus reconstruct the typical interface structure. A similar approach may be employed to characterize the assembly and growth of complex surface nanostructures.

RESULTS AND DISCUSSION

The wide-area AFM scan of pentacene-covered TiO₂ anatase surface shown in Figure 1a features a trapezoidal island typical of the (101) facet morphology.²⁰ Pentacene molecules adsorbed onto the island’s terrace are distinguishable as bright, oblong objects. Submolecular resolution images reveal the pentacene molecules as a series of alternating bright and dim bands, with one long edge of the molecule showing slightly higher contrast in the AFM signal (Figure 1b–d). A closer look to the molecular structures reveals that instead of assembling in a compact cluster, pentacene molecules aggregate into one-dimensional stacks on the terraces. Their long axes are parallel to the [010] crystallographic direction and along the rows of

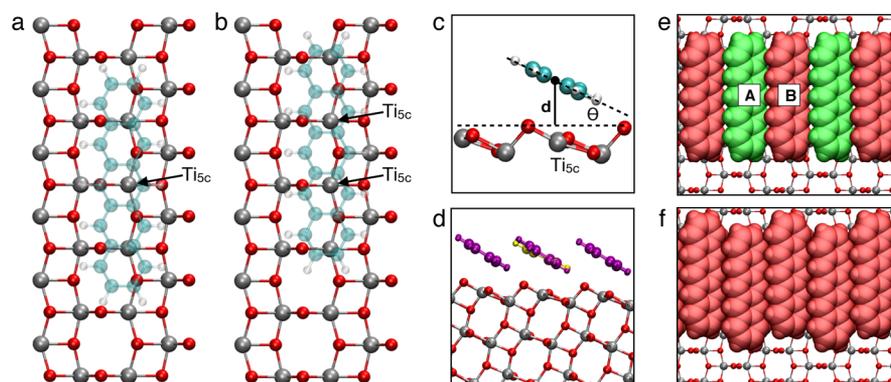


Figure 2. (a) Pentacene adsorption registry A, with the center above a Ti_{5c} atom. (b) Pentacene adsorption registry B, with the center of the molecule above the midpoint between Ti_{5c} atoms. (c) Side view of a physisorbed pentacene molecule, indicating adsorption height d and angle Θ . (d) Side view comparison between the geometries of adsorbed pentacene stack (purple) and isolated molecule (yellow). (e) Pentacene mixed registry A–B stacking (straight stack). (f) Pentacene single registry B–B stacking (offset stack).

surface-topping twofold coordinated oxygen (O_{2c}) atoms.²⁰ Details of different stack structures indicate that molecules preferentially join with a small offset perpendicular to the stack direction. The surface features visible in the background of the AFM images help to place the molecular registry between two adjacent rows of O_{2c} above the characteristic sloped groove structure of this anatase surface. The higher AFM contrast at the upper long edge of the molecule suggests a slight tilt in its adsorption geometry.

At ultralow coverages, isolated pentacene molecules randomly populate the terraces of the anatase substrate, exhibiting the same orientation observed for the molecules composing the stacks. Typical examples of submolecular resolution AFM images of isolated pentacene molecules are displayed in Figure 1e,f. Depending on the probe termination, they present a series of features (rings or stripes) along the molecule's long axis. Isolated pentacene molecules are also found decorating the atomic steps of the surface. The island shown in Figure 1a displays the three geometrically inequivalent steps of the anatase (101) facet.²¹ At the upper and side steps of the island, the pentacene molecules adsorb following a side-on configuration with their long axis aligned with the step direction; these molecules are highlighted in Figure 1b by blue arrows. Interestingly, submolecular resolution AFM images of pentacene molecules found at the energetically most stable step²¹ reveal a configuration that is rotated approximately 45° from the orientation of the stacks, with the molecules adsorbing across the step simultaneously connecting upper and lower terraces, as pointed out by arrows in Figure 1a,c.

We employed dispersion-corrected DFT simulations to understand the molecule–oxide interactions and binding strength. Following the adsorption configuration detected for pentacene molecules by the experiments, the molecule was initially placed between the O_{2c} rows and over the sloping groove of the (101) anatase surface, with the short axis slightly tilted to bring the molecular plane parallel to the facet. Figure 2a,b illustrates two possible molecular registries in the [010] crystallographic direction: configuration A, where the center of the pentacene molecule is placed above a fivefold coordinated surface titanium atom (Ti_{5c}) and configuration B, where the center of the molecule is displaced midway between two Ti_{5c} atoms. Structural optimization results, summarized in Table 1, revealed that pentacene physisorbs in both registries with a

Table 1. Comparison of Adsorption Structures and Energies for Single Pentacene in Configurations A and B^a

config.	d [nm]	Θ [deg]	E_{ADS} [eV]	$E_{\text{ADS}}^{\text{VDW}}$ [eV] (%)
A	0.24	23.7	−1.57	−1.54 (98)
B	0.26	22.6	−1.91	−1.67 (87)

^aHere, d and Θ are the molecule adsorption height and tilt angle, as illustrated in Figure 2c. We computed the total adsorption energy E_{ADS} and its dispersion contribution $E_{\text{ADS}}^{\text{VDW}}$ (fractional proportion shown in italic brackets).

similar structure and with adsorption energies $E_{\text{ADS}}^{\text{A}} = -1.57$ eV and $E_{\text{ADS}}^{\text{B}} = -1.91$ eV. Dispersion interactions, known to be important for molecular adsorbates on this surface,²² contribute 98 and 87% to the adsorption energy, respectively. While configuration A is stabilized entirely by van der Waals forces, configuration B is further stabilized by weak chemical bonds with four Ti_{5c} atoms. In the energetically preferred configuration B, the molecule adsorbs in a flat conformation parallel to the sloping groove, with the extremes slightly lowered toward the surface by 10 pm. The molecular axis lies 0.26 nm above the surface-topping plane of O_{2c} atoms and directly above four under-coordinated Ti_{5c} atoms, as illustrated in Figure 2b,c. The tilt angle of 22.6° is similar to the sloped groove and explains the higher contrast in the AFM signal detected over the upper long edge of the molecules. Because the difference between computed adsorption energies is large compared with the temperatures of the sample preparation, we conclude that isolated pentacene molecules at the terraces preferentially attach in registry B.

To gain insights into the formation of pentacene monolayers on the anatase surface, we carried out an investigation of the one-dimensional pentacene stack geometries. A single pentacene molecule was placed onto each of the two sloped surface grooves in the unit cell to simulate full monolayer coverage. Because the atomic arrangement of one groove is shifted in the [010] direction by half-unit cell with respect to the adjacent one, a Ti_{5c} surface site on one groove is aligned with a midpoint between Ti_{5c} atoms on the other. Consequently, molecules adsorbed in a straight line stack correspond to a mixed A–B registry, as illustrated in Figure 2e. A stack of molecules in the same registry can only be obtained if the adjacent pentacenes adsorb with an offset of a half-unit cell, like in Figure 2f. We optimized candidate stack structures of mixed A–B and single B–B registries, formed by assuming a

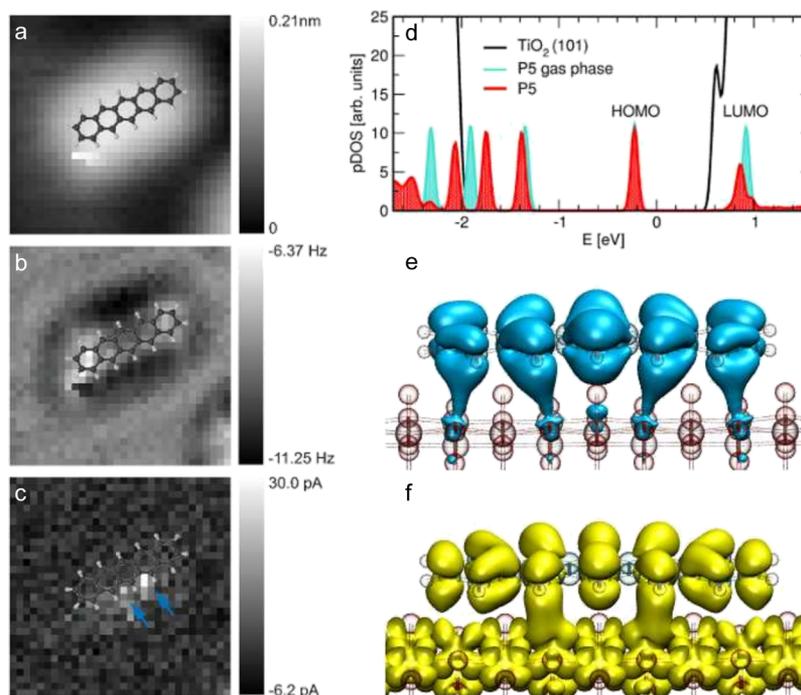


Figure 3. (a) Topography of an isolated pentacene molecule on the surface, over which a bias-spectroscopy imaging measurement based on the acquisition of a $\Delta f(V)$ curve over each pixel of the image was obtained (image size $3 \times 3 \text{ nm}^2$). (b) Δf signal corresponding to a slide of all the measured $\Delta f(V)$ curves at a sample bias of $V = 500 \text{ mV}$. (c) I_t signal associated with the image shown in (b). For additional experimental details, see Figure S1. (d) Partial DOS contributions of the TiO_2 (101) surface and adsorbed pentacene (P5), compared with DOS of pentacene in the gas phase. Gas-phase DOS was aligned with the total system DOS at the Fermi level. (e) System HOMO spatial distribution ($10^{-4} \text{ e}^-/\text{\AA}^3$ isosurface), obtained by integrating total DOS in the energy interval $[0, -600] \text{ meV}$. (f) System LUMO spatial distribution, ($10^{-4} \text{ e}^-/\text{\AA}^3$ isosurface), obtained by integrating total DOS in the energy interval $[650, 1000] \text{ meV}$ (note that image illustrates both molecular LUMO and substrate conduction band states).

maximum overlap of molecules in the stack. Computed adsorption energies per molecule of $E_{\text{ADS}}^{\text{AB}} = -1.96 \text{ eV}$ and $E_{\text{ADS}}^{\text{BB}} = -2.19 \text{ eV}$ confirm that molecular stacking with an offset is energetically favorable on this surface. This finding supports the experimental observation of diagonal stack growth, and the presence of kinks in the stacks, in numerous AFM images (Figure 1).

Stronger binding energies for stacked pentacene molecules compared with isolated ones arise partly from the intermolecular attraction within the stack. To quantify the strength of this interaction, we computed the reference energy for the molecular stack without the substrate and compared it with energy of gas-phase pentacene molecules. This also facilitated the decomposition of the adsorption energy $E_{\text{ADS}}^{\text{BB}} = -2.19 \text{ eV}$ into intrastack and stack–surface contributions. We established that molecule–molecule interactions contribute 16% (-0.36 eV) and the molecule–surface interactions account for 84% (-1.83 eV) of the adsorption energy per molecule in a stack configuration. While the presence of other molecules in the stack appears to reduce the strength of pentacene binding to TiO_2 from -1.91 to -1.83 eV per molecule, the monolayers are overwhelmingly stabilized by molecule–surface interactions in line with recent experimental observations for conjugated adsorbates on (101) anatase.²³ Consequently, each molecule in a stack adopts a local geometry that is almost identical to the isolated molecule, with minimal changes in the tilt angle (see Figure 2d).

The alignment of electronic levels at the molecule–oxide interface is critical to efficient flow of charge between the materials. The decomposed electronic states of the surface and

the molecule adsorbed at a B registry are shown in Figure 3d. The highest occupied electronic states of the molecule, highest occupied molecular orbital (HOMO), HOMO $- 1$, and HOMO $- 2$ appear as narrow peaks in the band gap of the oxide. Frontier molecular states of the physisorbed pentacene remain as discrete and sharp as those of the gas-phase molecule (within the molecular level broadening 0.05 eV), apart from lowest unoccupied molecular orbital (LUMO) which exhibits a double peak. This indicates that the TiO_2 anatase substrate does not significantly hybridize frontier molecular orbital states of pentacene in this adsorption configuration, in contrast to chemisorption on metallic substrates where significant orbital broadening and charge transfer were observed.^{24–26} Bader charge analysis^{27,28} revealed that pentacene transfers only 0.1 e^- to the TiO_2 substrate.

The Fermi level of the interface is located at the HOMO 0.7 eV below the TiO_2 conduction band. We analyzed the spatial distribution of this state, illustrated in Figure 3e, to find that it is mostly localized on the molecule and shaped much like the gas-phase pentacene HOMO. While the molecule–surface charge transfer is nearly zero, the HOMO indicates that a small amount of charge is localized in weak molecule–substrate bonds. Four regions of electronic density extend from the molecular backbone toward four Ti_{5c} atomic sites directly below the pentacene. The d_z^2 character of these features points to covalent interactions between the delocalized electrons of the pentacene backbone and the d states of Ti_{5c} atoms. This finding clarifies the small covalent contribution to the binding energy of adsorption configuration B. Considerable dispersion forces dominate pentacene– TiO_2 interactions (87%), stabiliz-

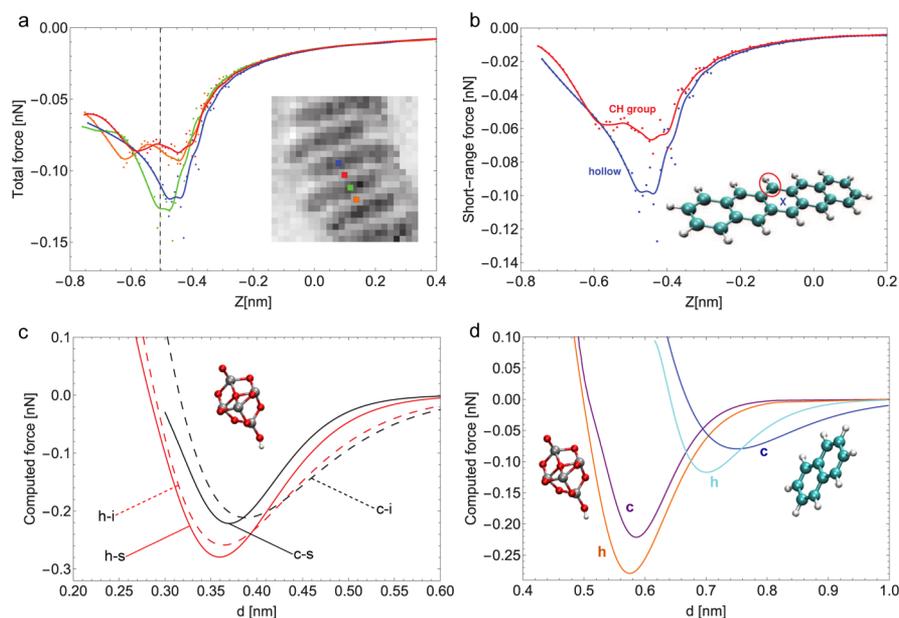


Figure 4. (a) Force curves extracted from a force volume composed by (24×24) $\Delta f(Z)$ curves measured over an area of (3×3) nm² on a stack of pentacene molecules deposited on the TiO₂(101) anatase surface. Acquisition parameters are $f_0 = 152\,471$ Hz, $A = 95.9$ Å, $K = 23.7$ N/m, $Q = 44\,163$. Sample bias was -200 mV. The inset image is a slide of the total force values at the probe–sample separation indicated by the dotted vertical line in (a). (b) Details of the short-range forces of two curves shown in (a) obtained close to a CH group site and a hollow site. The dots denote the force points after conversion from the $\Delta f(Z)$ curves, and the lines correspond to a spline interpolation of the experimental points. (c) Simulated force curves over a carbon atom and a hollow site—see positions in the model depicted in (b)—of an individual molecule (c-i, h-i; dashed lines) and a molecule within a B–B stack configuration (h-s, c-s), respectively. These forces were calculated using the OH group-terminated TiO₂ cluster depicted in (c) as probe model. (d) Comparison of the forces simulated using the TiO₂ cluster and a naphthalene molecule as probe model. A molecular probe produces short-range forces of a magnitude comparable to the experimental counterparts.

ing the molecule in a physisorbed configuration far enough from the surface so that the organic and inorganic layers remain electronically decoupled; nevertheless, such a distance allows the formation of weak covalent bonds (13% of adsorption energy) that supply a direct pathway for electron transfer between the two layers. The LUMO is placed 0.3 eV above the bottom of the conduction band of the oxide, facilitating the transfer of electron charge carriers from the photoactive organic layer into the anatase buffer zone. The LUMO shape (Figure 3f) reveals two principal channels for charge injection below the central part of the molecule. Evidence of localized charge injection can be spotted in the experimental STM image displayed in Figure 3a–c, taken combining multipass imaging¹⁷ with bias spectroscopy imaging,²⁹ see Figure S1 for details. The favorable alignment of molecular levels with respect to the substrate and the corresponding charge injection pathways are strong indicators of efficient charge transfer across the pentacene/TiO₂ interface.

Force spectroscopy data acquired on a volume over the surface provide insights into the AFM imaging contrast mechanisms. The positions that would correspond to the hollow sites at the central part of the molecule exhibit a canonical probe–surface interaction force, with a well-defined single force minimum along the probe–sample separation distance explored (Figures 4a,b, and S2 of the Supporting Information). Upon probing the forces at hollow sites close to the sides of the molecule, the onset of a second force minimum starts to develop (Figure S2). The appearance of a double-force minima is clear when probing the sites that would correspond to the CH groups at the upper long edge of the molecules (Figures 4a and S2). The development of a second

minimum in the probe–surface interaction force over both the hollow and CH site may correspond to a slight bending of the molecule as the probe exerts force on it or to the atomic-scale bending of the probe termination. Multiple minima in the interaction force are usually associated with transitions between different solutions of the probe–surface potential energy upon reducing the probe–sample separation.³⁰ The absence of energy dissipation³¹ (Figure S3) during the acquisition of the force volume points toward an elastic bending due to the interaction with the probe.

Force spectroscopy experiments were simulated by approaching a probe model to key pentacene sites—an uppermost C atom site and the central ring of the molecule, Figure 4c—to clarify in detail probe–molecule interactions and associated atomic rearrangements in the presence of the substrate. We deployed first a TiO₂ cluster probe model with a chemically passive OH group termination; such a probe was shown to produce the dominant AFM contrast in atomic resolution imaging of the bare (101) anatase surface.²⁰ Computed AFM force spectroscopy curves presented in Figure 4c testify to a stronger attractive interaction above pentacene rings as opposed to the carbon backbone, in agreement with the experimental force curves, as displayed in Figure 4a. The maximum attraction over the ring site is reached by lowering the probe by a further 50 pm, reflecting the topographic 50 pm height difference between the carbon and the ring site in the atomistic model. Upon inspection of the calculated forces, the pentacene AFM contrast seems to be in line with the standard AFM imaging modes of pentacene and carbon nanostructures composed of aromatic rings^{16,32,33} recorded with different probe terminations, where additional repulsive force contributions above C atom sites locally reduce interaction strength.

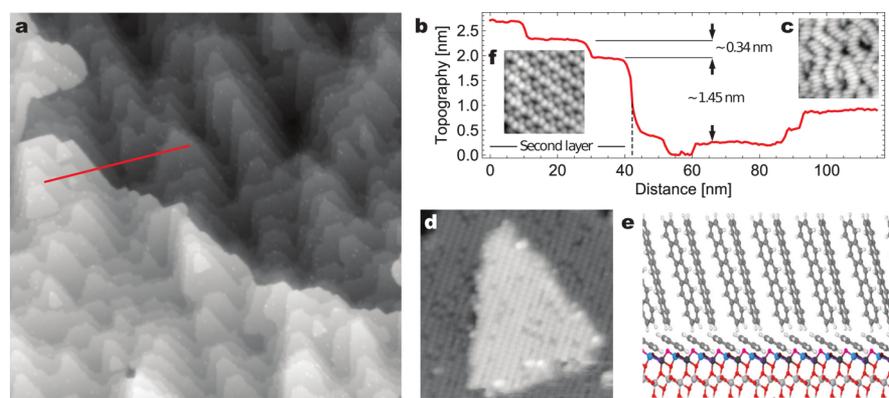


Figure 5. (a) Topographic AFM image showing a boundary between the first and second layers of pentacene molecules adsorbed on the (101) TiO_2 anatase surface. Image size is (300 nm \times 300 nm). (b) Line profile marked in (a). (c) Topographic AFM image revealing the structure of the first layer of pentacene molecules, that corresponds to the lower topographic contrast in (a). Image size is (10 nm \times 10 nm). (d) Topographic (static) STM image showing the typical surface morphology of the second layer of pentacene molecules. Image size is (25 nm \times 25 nm). (e) Artistic representation denoting a possible vertical, slightly tilted configuration of the second layer of pentacene molecules grown over an almost fully pentacene passivated (101) TiO_2 anatase surface. (f) Image of the variation of the frequency shift over a (4 nm \times 4 nm) area of the second layer of pentacene molecules upon applying a multipass method, bringing the probe 230 pm closer to the surface during the second pass with respect to the topographic set point. The contrast of this image was inverted to mimic the appearance of a topographic image. Acquisition parameters are $f_0 = 152\,828$ Hz, $K = 23.8$ N/m, $Q = 34833$. Δf set point was -6.5 (a), -2.0 (c), -8.0 Hz (f). Oscillation amplitude was 112.5 (a), 168.8 (c), and 67.6 Å (f). Sample bias was -0.3 (a,c), -0.2 (f), and 2.5 V (d). Current set point was 20 pA for (d).

AFM simulations were repeated over the same sites in a pentacene B–B stack to explore how probe–surface interactions change with monolayer formation. Theoretical force spectroscopy curves for isolated and stacked pentacene are compared in Figure 4c. In the stack, the onset of attraction is shifted to lower probe heights, but the repulsive interactions are slightly reduced, indicating that the intermolecular bonding within the stack weakens the pentacene–probe interactions.

Simulated AFM spectroscopy curves over the pentacene stack can be directly compared with the short-range interaction data extracted from a force volume and depicted in Figure 4b. Although the general behavior of the curves is fairly reproduced, we found the computed maximum attractive interactions of 0.20–0.25 nN considerably larger than the 0.06–0.10 nN short-range force values recorded in the experiments. Such a result points to a different chemical termination of the AFM probe than the initial model considered for these computations. This presents a conundrum because AFM probes were in situ conditioned to be coated by TiO_2 from the substrate, and no other apex termination has been identified to produce weaker probe–surface interactions than the OH group.²⁰ In the absence of other contaminant material that might alter the chemical composition at the probe apex, we hypothesized that the probe may have picked up a molecule during the scan.³⁴ To verify the possibility of AFM imaging by a probe terminated with pentacene, force spectroscopy simulations over an isolated molecule were repeated with a naphthalene molecule as a model probe. Such a probe allowed us to include contrast-defining interactions between the low-lying aromatic rings of the pentacene molecule, while presenting the weakly interacting C–H bond toward the substrate in an analogy to the OH group-terminated probes that produce atomic resolution AFM images in the anatase surface.²⁰ Computed spectroscopy curves with a naphthalene probe are compared with those resulting from the OH-terminated TiO_2 cluster model in Figure 4d. The ordering and relative position of the curve minima between the two key sites remains the same, pointing to the same AFM contrast mode in the imaging of pentacene for both probe

models. Notwithstanding, the naphthalene-terminated probe exhibits maximum attractive interactions of 0.07–0.11 nN that are 2–3 times smaller than for the TiO_2 cluster case; values that show a reasonable agreement with the experimental results. Small discrepancies, as well as the lack of elastic effects associated with double minimum force spectroscopy signatures, can be explained by the randomly chosen orientation of the molecular probe model and the approximation of a pentacene probe with a naphthalene molecule.

In order to investigate pentacene thin-film formation on the anatase (101) surface, we conducted an experimental AFM characterization of the pentacene growth beyond the first molecular layer, and found that the second pentacene layer presents a completely different morphology. Figure 5a displays a surface region where these two layers coexist. A distinct boundary—an abrupt step approximately 1.45 nm high (Figure 5b) crossing the image from the upper-left to the lower-right side—separates these two well-differentiated regions. AFM images reveal that the domain with lower topographic contrast corresponds to a phase of pentacene adsorbed into planar molecular stacks that covers the anatase surface almost in full, as depicted in Figure 5c. Similar AFM images taken on the region with higher topographic contrast present well-ordered periodic features with a rectangular-like pattern, with a repeating unit much smaller than the pentacene molecule length, as illustrated in Figure 5d. The 1.45 nm height difference between the domains does not relate to the morphology of the anatase surface (with an atomic step height of approximately 0.34 nm), but rather points toward the second layer of pentacene molecules growing in a slightly tilted, vertically oriented configuration over a pentacene-passivated anatase surface, for example, as illustrated in Figure 5e. Although the reactive anatase (101) surface promotes horizontal monolayer growth, it is sufficiently passivated by the first molecular layer so that further layers grow vertically. High-resolution molecular AFM images acquired with the multipass method¹⁷ over the region with higher topographic contrast reveal an internal and complex structure within the rectangular unit cell (Figure 5f), denoting a high-density packing of the

vertically oriented pentacene molecules. Although the packing, orientation, and tilting of the molecules in the second layer is difficult to discern from our AFM images, our results suggest that subsequent pentacene monolayers may resemble the bulk configuration of pentacene organic solids.

With prospective applications of pentacene as thin-film component in organic transistors³⁵ and light-emitting diodes³⁶ among other organic devices, we extend our discussion to AFM studies addressing pentacene thin-film growth on different buffer materials.³⁷ Unlike metals, metal oxides present relatively inert substrates for pentacene attachment. Studies on SiO₂,³⁸ ITO,³⁹ LaSrMnO₃,⁴⁰ Al₂O₃,⁴¹ and HfO₂⁴² surfaces all found that molecules adsorb in standing or tilted configurations, at odds with our findings. Dendritic aggregation and monolayer growth has been well characterized on SiO₂⁴³ and Al₂O₃, in contrast to the planar stacking growth mechanism observed for the first layer of pentacene on TiO₂(101) anatase. On this substrate, not only do we observe horizontal monolayer growth, but the molecules aggregate parallel to each other in the departure from the herringbone arrangement in bulk⁴⁴ and vertical monolayers. These features can be attributed to the strong molecule–substrate dispersion interactions and the topological constraint of the sloping grooves of the surface. A recent study supports our finding that pentacene adsorbs horizontally on the sloping terrace of anatase¹¹ (albeit with a greater adsorption energy of -2.48 eV, the structural details were not disclosed). Similar adsorption behavior was reported for pentacene on the (110) surface of the rutile polymorph.⁴⁵ We conclude that TiO₂ presents a more reactive substrate for dispersion-dominated pentacene thin films than other metal oxides, which is consistent with the benzene adsorption trend on metal oxide substrates.¹¹ The stronger bonds and orbital overlap with TiO₂ should enhance charge injection across the hybrid organic/inorganic interface.

CONCLUSION

The atomistic details of the hybrid organic/inorganic boundary inside heterostructure devices critically define the electronic properties of this interface, and through it, those of the entire device. We have employed several AFM and STM experimental techniques in combination with first-principles simulations to characterize the interface between pentacene thin films and TiO₂ anatase; two materials with superior electrical properties frequently used in optoelectronic devices. A multipass AFM imaging technique allowed us to overcome the technical challenge of simultaneously imaging the substrate, steps, molecular adsorbates, and layers with atomic scale resolution. An inert AFM probe termination, here an adsorbed pentacene molecule, met the other necessary condition for submolecular imaging. Consequently, we were able to detect the relative orientation of molecular adsorbates with respect to each other and the substrate, which greatly facilitated the computational study of adsorption.

Submolecular resolution AFM images reveal that the first layer of pentacene molecules physisorb horizontally on the anatase surface, with the conjugated backbone of the molecule parallel to the typical sloping terraces of anatase. Individual pentacene molecules are also found decorating the step-edges of the anatase (101) surface, with an adsorption geometry that varies with the particular step structure. At the surface terraces, pentacene molecules self-organize into planar molecular stacks for coverages below one monolayer. The anatase surface is passivated by these molecular stacks that compose the first

pentacene layer, so that the second pentacene layer adopts a high-density packing of vertically oriented molecules, promoting a thin-film growth that is compatible with the bulk structure of the pentacene organic crystal.

Among the metal oxides typically used as buffer layers in electronic heterostructure devices, TiO₂ stands out as the only substrate known to date that binds pentacene in a horizontal geometry at the organic/inorganic interface. Substantial molecule–surface dispersion interactions stabilize the physisorbed adsorption configuration further above the surface, where electronic structure coupling between the pentacene and anatase is limited. Adsorbed pentacene introduced sharp molecular states into the band gap of the substrate, but it is the molecular LUMO that supplied the direct orbital overlap with the substrate necessary for charge transfer. The position of the pentacene LUMO in the conduction band of anatase implies barrier-free injection of electron charge carriers from the organic molecules into the substrate. Higher levels of theory are needed to accurately compute the alignment of electronic levels between the pentacene thin films and the TiO₂ substrate. Nevertheless, the localized charge injection pathways and the favorable level alignment at this interface are indicators that these materials would contribute efficient thin-film devices for photovoltaic applications.

METHODS

A UNISOKU Ltd. ultrahigh vacuum (UHV) cryogenic dynamic AFM equipped with a homebuilt optical interferometer for the detection of the cantilever dynamics was used for the experiments. Measurements were accomplished at a 77 K probe–sample temperature using the frequency modulation detection scheme.⁴⁶ Platinum iridium-coated silicon cantilevers (PPP-NCLPt-20, Nanosensors, Switzerland) were excited to their instantaneous first mechanical resonant frequency keeping the oscillation amplitude (A) constant. The tunneling current flowing between probe and surface averaged over multiple cantilever oscillation cycles⁴⁷ ($\langle I_t \rangle$) was simultaneously detected during topographic AFM imaging using a commercial SPM controller (Nanonis SPM Control System, SPECS, Germany). The shift of the first mechanical resonant frequency (Δf) from the free-oscillation value upon forces acting on the cantilever probe was used to regulate the probe–surface separation. Submolecular resolution AFM imaging was performed using a multipass method.¹⁷ Force spectroscopy^{48,49} was performed by recording Δf as a function of the probe–sample relative vertical displacement (Z) over a rectangular matrix of pixels superimposed to a previously imaged area of the surface, closing the feedback loop upon displacement of the probe between adjacent pixels.¹⁷ The total probe–surface interaction force was obtained by applying an inversion procedure⁵⁰ to the recorded $\Delta f(Z)$ curves. Topographic effects due to the acquisition procedure were properly compensated.^{17,51} Further details about protocols for in situ probe conditioning and anatase sample preparation can be found elsewhere.²⁰ Molecular deposition was carried out by exposing a clean anatase surface to pentacene molecules sublimated from a homebuilt evaporation cell upon reaching 160 °C in UHV. The substrate was kept at room temperature during the pentacene deposition, and coverage was regulated by adjusting the exposure time.

All DFT simulations were carried out with the VASP code,⁵² the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional,⁵³ and semiempirical DFT-D2 dispersion corrections.⁵⁴ We employed PBE projector augmented wave potentials and a planewave cutoff of 500 eV. An onsite $U = 4$ eV was applied to the substrate Ti atoms to adjust the position of gap states with respect to the conduction band minimum of TiO₂, following other studies of anatase surfaces.^{55,56}

We employed the TiO₂ anatase (101) surface model previously used for adsorption studies on this surface.²⁰ The 10.57 Å × 23.12 Å × 40 Å model surface area accommodates two sloped surface grooves for pentacene attachment. Single pentacene images were laterally

separated by $dx = 6 \text{ \AA}$ and $dy = 9 \text{ \AA}$ between different simulation cells, whereas adjacent pentacene stack images were separated by $dy = 7.4 \text{ \AA}$. The tall unit cell allowed 24 \AA between surface slabs in adsorption simulations and 13.8 \AA between them in AFM simulations. The same unit cell was used for isolated pentacene and surface reference calculations. Geometry optimizations were performed with a Γ -point k -point grid until atomic forces were reduced below 0.01 eV/\AA . Such k -space sampling was selected by downscaling the converged ($6 \times 6 \times 2$) k -point setting for bulk unit cell calculations of TiO_2 anatase when upscaling the unit cell toward the large (1×6) unit area surface geometry. Adsorption energies and electronic properties were obtained using a $4 \times 2 \times 1$ k -point mesh.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acsami.8b09203](https://doi.org/10.1021/acsami.8b09203).

AFM images obtained from the combination of a multipass technique with bias-spectroscopy imaging; comparison of force curves over different equivalent surface locations obtained from a force volume spectroscopy measurement; and force curves, force images, amplitude, and dissipation signal associated with the force volume (PDF)

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Notes

The authors declare no competing financial interest.

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