Supporting Information: Pentacene/TiO_2 anatase hybrid interface study by scanning probe microscopy and first principles calculations

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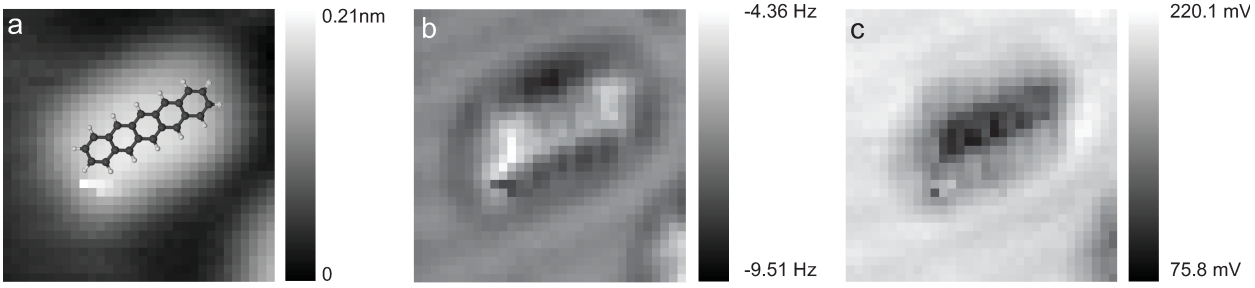

Figure S1: (a) Topographic image measured during the acquisition of a bias-spectroscopy imaging[1] combined with a multi-pass technique.[2] For each pixel of the image, the topographic feedback was set to the probe-surface separation dominated by the van der Waals interaction at which the topographic AFM imaging of both molecule and substrate is normally obtained (Δf= -4.5 Hz in this case). The feedback loop was then opened, the probe was brought closer to the surface the same distance as for obtaining sub-molecular resolution (d= 0.3 nm in this experiment), and a frequency shift vs. bias [Δf(V)] curve was then acquired. The probe was retracted from the surface, and the feedback loop was closed again to the topographic set point (Δf= -4.5 Hz) before moving to the next pixel of the image. Each of these Δf(V) curves was fitted to a quadratic function to obtain the peak voltage and the corresponding frequency shift values that locally minimises the electrostatic interaction. (b) and (c) Maps of the frequency shift and local contact potential difference obtained from the fits to the Δf(V) curves at the probe-surface separation that produces sub-molecular resolution imaging. Acquisition parameters are f_o = 159202 Hz; A= 169.1 Å; K= 26.9 N/m. Image dimensions are (3×3) nm^2. Image reprinted from the Supplementary Information, C. Moreno, et al. Nano Letters 2015, 15, 2257-2262. Copyright 2015 American Chemical Society.

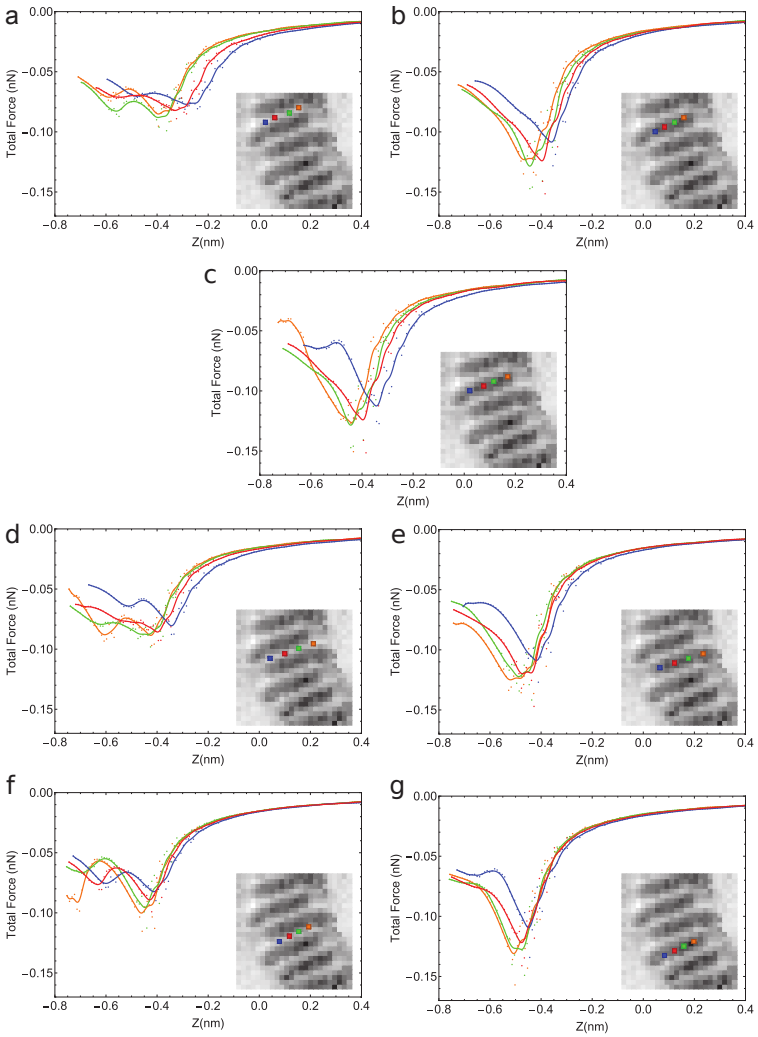

Figure S2: Comparison of the probe-surface total force obtained over different equivalent locations of a pentacene molecular stack deposited on a (101) TiO_2 anatase surface. Panels (a), (d), (f) correspond to force curves located over sites that would correspond to the CH groups at the upper long edge of the molecules. Force curves measured on these locations exhibit weaker maximum attractive forces and the development of a double minima. In contrast, for the same probe-surface separation explored, force curves measured over sites that would correspond to the location of hollow sites —panels (b), (e) and (g)— present a stronger maximum attractive force and the absence of a second minimum. The development of a second minimum on forces measured over locations that would correspond to hollow sites is visible when the probe approaches the sides of the molecule. This behaviour is displayed in panel (c). The set of force curves shown in (c) correspond to the positions explored in (b), but the blue and orange locators were moved one pixel (1.3 Å) towards the edge of the molecule and along the long molecular axis. The magnitude of the maximum interaction force is similar, but when getting closer to edge of the molecule, the development of a second minimum starts to occur.

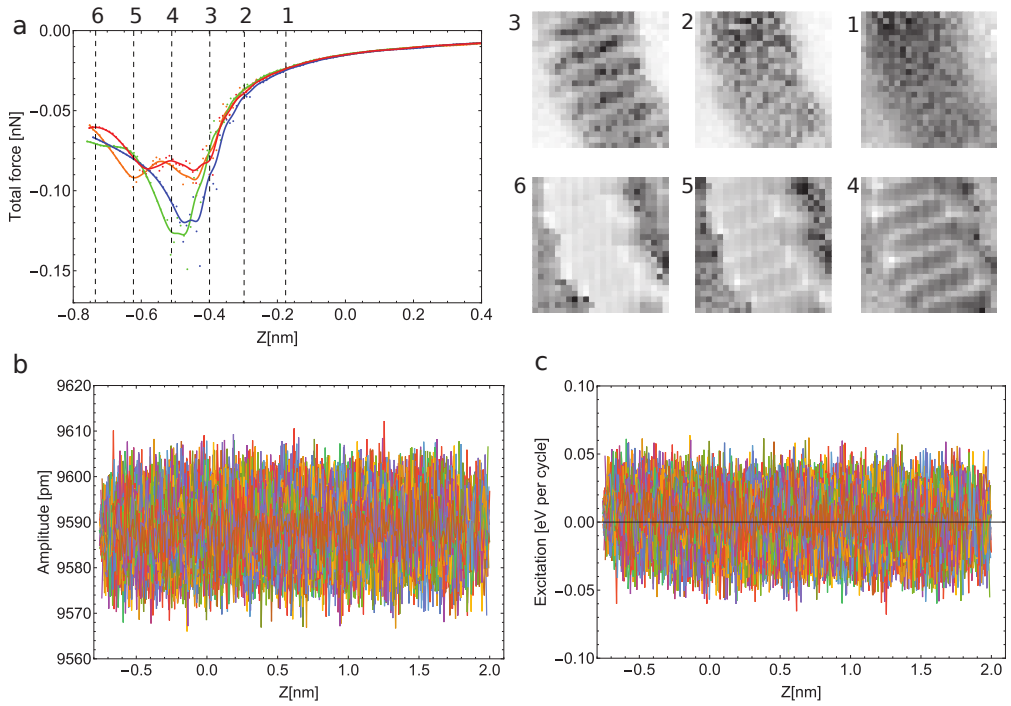

Figure S3: (a) Images of the total force at several probe-surface separations showing the appearance of the force field over the pentacene molecular stack. The force curves shown in the graph are the same as in Fig.4(a). The dotted lines labeled by numbers indicate the probe-surface separation of the corresponding total force image. The origin of the distance axis corresponds to the topographic imaging set point for the acquisition of the force volume. (b) and (c), Variation of the cantilever oscillation amplitude and the energy dissipation per oscillation cycle of the (24×24) curves measured for the force volume.

References

(1) Sadewasser, S.; Jelínek, P.; Fang, C.-K.; Custance, Ó.; Yamada, Y.; Sugimoto, Y.; Abe, M.; Morita, S. New Insights on Atomic-Resolution Frequency-Modulation Kelvin-Probe Force-Microscopy Imaging of Semiconductors. *Phys. Rev. Lett.* **2009**, *103*, 266103.

(2) Moreno, C.; Stetsovych, O.; Shimizu, T. K.; Custance, Ó. Imaging Three-Dimensional Surface Objects with Submolecular Resolution by Atomic Force Microscopy. *Nano Lett.* **2015**, *15*, 2257–2262.