Supplementary Information

Unusual reversibility in molecular break-up of PAHs: the case of pentacene dehydrogenation on Ir(111)

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I. METHODS

A. Experimental

Single adlayers of pentacene on Ir(111) have been experimentally characterized by spot profile analysis low energy electron diffraction (SPA-LEED), scanning tunneling microscopy (STM), high-resolution X-ray photoelectron spectroscopy (HR-XPS), temperature programmed x-ray photoelectron spectroscopy (TP-XPS), X-ray Photoelectron Diffraction (XPD) and temperature programmed desorption (TPD). SPA-LEED, and TPD experiments were carried out in the UHV chamber of the Surface Science Laboratory, while HR- and TP-XPS experiments were carried out at the SuperESCA beamline, both part of the Elettra synchrotron facilities in Trieste, Italy. STM measurements have been performed at the Physics Department of the University of Hamburg, with the LHe-STM of the STM/SPSTM instruments, with the home-built variable-temperature STM.[1]

The Ir(111) single crystal was cleaned by repeated sputtering/annealing cycles using 1.5 keV Ar ions at two alternating incidence angles for the sputtering, and using W filaments placed close to the back side of the sample for electron beam heating up to 1420 K. Temperature was monitored by using two independent k-type thermocouples spot welded on the back of the sample, close to opposite sides. After each sputtering/annealing cycle, the surface was subject to oxidation/reduction cycles to completely remove residual C and O contamination from the surface. At the SuperESCA beamline, it was possible to monitor in situ the C 1*s* and O 1*s* core levels to determine in real time the residual contamination. The sample was cooled to 77 K for all SPA-LEED and HR-XPS measurements in order to reduce the contribution of phonon-induced reduced diffraction intensity (LEED) and phonon broadening (XPS).

Commercially available pentacene powder (Sigma-Aldrich, triple-sublimed grade, purity better than 99.995 %) was used throughout the experiment. The molecules were deposited on the Ir surface by sublimation from a home-built BN crucible heated by a Ta wire and equipped with a thermocouple in direct contact with the pentacene powder for temperature monitoring during the evaporation. The empty crucible was cleaned from volatile impurities in a separate UHV chamber by heating it for 10 h at 670 K. The pentacene was then placed in the crucible and purified in the experimental chamber by repeated flashing at temperatures up to 430 K. All evaporations

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were performed by heating the pentacene in the crucible to 420 K. The pentacene coverage and evaporation rate for all the experiments were calibrated by comparing the C 1s core level spectrum area after pentacene deposition to the C 1s core level spectrum area of a full graphene layer grown by temperature programmed growth (TPG) from ethylene (following the recipe described in Ref. [2], the reference C coverage was assumed to be 2.42 ML). Coverages in this work should always be intended as the number of C atoms for every Ir substrate atom, so that the ML units refer to the C coverage. C 1s spectra were measured with photon energies between 375 and 400 eV, with an overall energy resolution of 50 meV, and were acquired along with a measurement of the Fermi level, which was used for the calibration of the binding energy scale. In order to check for possible x-ray induced molecular break-up we performed several scans along the surface to search for C 1s spectral modifications, without finding appreciable differences. All XPS measurements were performed in normal emission geometry.

TP-XPS experiments have been performed by acquiring in situ XPS spectra at normal emission, with hν=400 eV, while annealing the sample with a linear temperature ramp at 0.25 K/s from 100 K to 1280 K, after pentacene deposition. The average time per spectrum was about 15 s, corresponding to temperature intervals of less than 4 K. In the TP-XPS experiments, in order to determine the amount of pristine pentacene for each spectrum between 100 and 600 K, in a picture where one species transforms into another, a fitting procedure was employed where a sum of two C 1s spectral distributions was fitted to the TP-XPS spectral sequence. The first spectral distribution was obtained by using a sum of 3 Doniach-Šunjič (DS) functions with a Shirley background that empirically describes well the observed high resolution C 1s spectrum at low temperature. A similar procedure was used to empirically determine the lineshape of the C 1s spectrum at 600 K. The fits were performed by only using 3 free parameters, leaving all others fixed. Free parameters were the relative intensities of the two spectral distributions, and an extra Gaussian component, to account for phonon broadening.

TPD curves have been acquired using an SRS 200 residual gas analyzer (RGA) for a mass to charge ratio $m/z = 2$, giving the H_2 desorption rate from the surface: after pentacene deposition, the sample was annealed at a fixed rate of 2.5 K/s while continuously acquiring the intensity of the signal generated by the RGA.

STM images were acquired for the pentacene covered surface with a coverage of 0.3 ML and a deposition temperature of T=300 K. The measurements were performed at 25 K using an electrochemically etched W probe tip cleaned by standard in situ procedures. All presented STM images were obtained in constant current mode with tunneling voltage V=-500 mV and tunneling current I=100 pA, and processed using Gwyddion software.[3]

B. Theoretical simulations

Density functional theory calculations have been carried out using the VASP code. The Projector Augmented Wave (PAW) method was used to account for the core electrons, with the 6s and 5d electrons of Ir and the 2s and 2p electrons of C explicitly included in the valence. Single particle orbitals were expanded in plane-waves using a kinetic energy cut-off of 400 eV. Surfaces were modeled with the usual slab geometry, using a 12×6 supercell with 4 layers, of which the bottom two were kept frozen at the bulk interatomic distances. The large cell was chosen so that a densely packed layer with 4 molecules could be simulated. The vacuum was 17.8 Å for the clean surface and 15 Å for the system with the pentacene molecules adsorbed on the surface. Only the Gamma point was used to sample the Brillouin zone. C 1*s* core-level BEs have been estimated in the final-state approximation, therefore including also final state effects due to core-hole screening.

The energy-dependent XPD curves were simulated by using the EDAC software package.[4] The overall C 1s photoemission intensity at normal electron emission was calculated as an incoherent sum of the intensities arising from each C atom of the pentacene molecule. A slab of Ir atoms arranged according to the (111) surface termination was added as a substrate in the calculations. The geometrical parameters of the simulations were set to match the features of the photoemission experiment, i.e. linear polarization, sample at 300 K, angle between the x-ray beam and the analyzer $\beta = 70°$.

II. NEB CALCULATIONS

Nudged Elastic Band (NEB) calculations were performed to find the minimum energy pathway between the initial and final states of pentacene dissociation. The climbing image NEB method is employed to ensure the saddle point corresponding to the correct energy barrier is properly located [5].

At the top of Figure S1, we report the values for the energy barrier calculated for the H removal. These values were calculated for each non-equivalent H atom in pentacene. Depending on the C-H bond we found a barrier ranging from 1.12 eV for H in configuration 2, which corresponds to a C-H

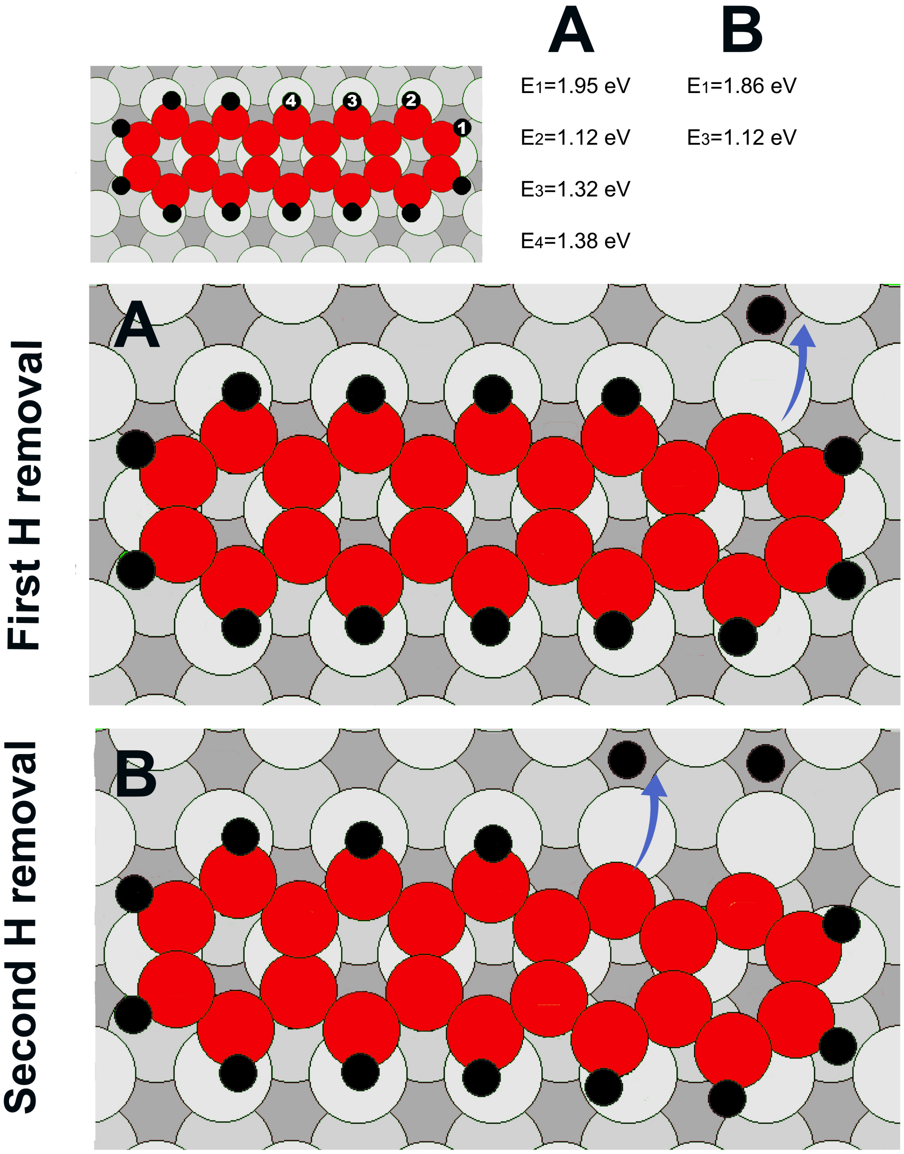

FIG. S1. Computed energy pathways for the first and second removal of H atoms from a pentacene molecule adsorbed on Ir(111). On the top left the labelling of the various H atoms configurations is reported.

bond close to the molecular edge (Fig. S1-central panel) to 1.95 eV for H in configuration 1, which corresponds to the C-H bond exactly at the edge of the molecule. For the removal of the second H atoms we calculated the barrier for removing H atoms in configuration 1 and 3 (Fig. S1-bottom panel), i.e. those atoms which are close to the first one. For H in configuration 3, which shows the lowest barrier (E_3 = 1.12 eV), we have also found that the presence of the firstly removed H atoms in the three-fold site decreases the barrier by about 0.1 eV.

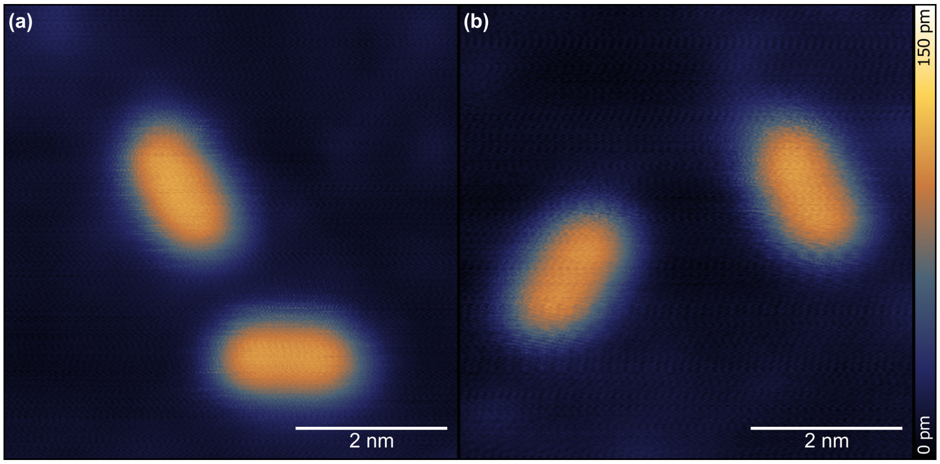

FIG. S2. STM images of two isolated molecules obtained (a) at room temperature and (b) after annealing to 530 K. Tunnelling parameters: U = -100 mV, I = 100pA .

III. ADDITIONAL STM MEASUREMENTS

In Figure S2, STM micrographs of two pentacene molecules is reported acquired before (panel a) and after (panel b) annealing the sample at 530 K. It is possible to notice that no substantial differences are observed, indicating that the dehydrogenated molecules are indistinguishable in these STM data from the intact pentacene molecules. This suggests that the identification of partially dehydrogenated or hydrogenated molecules is a very difficult task for pentacene on Ir(111), given the reactivity of this metal surface. Therefore, it was not possible to resolve changes in the molecule upon dehydrogenation by using STM, as it is possible to obtain on the Au(111) surface [6], on which pentacene interacts in a weak way.

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