Electronic Supplementary Material (ESI) for Nanoscale Advances.

On-Surface Chemistry Using Local High Electric Fields

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Electronic Supplementary Information (ESI)

The experiments were conducted on 2d-islands of the second DHTAP layer. These islands are always compact due to the high mobility of the DHTAP molecules for deposition temperatures above 170 K. A typical morphology is shown in Fig. S1.

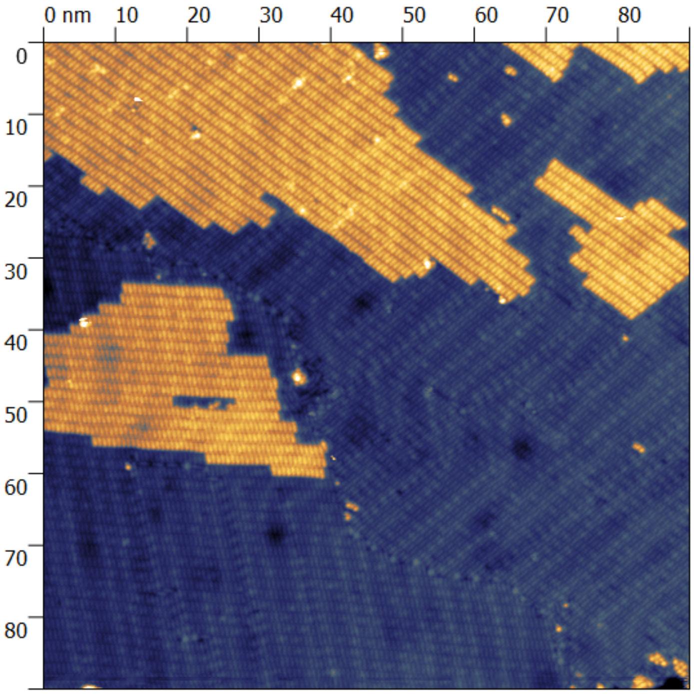


Figure S1. Large scale STM image of 1.4 ML DHTAP on Au(111) deposited at a sample temperature of 250 K. The image was recorded at a tunnelling current of I_t = 10 pA and a sample voltage of U_s = -1 V.

It was possible to trigger dehydrogenation in the first monolayer at small tip sample distances only by applying voltage pulses on top of selected DHTAP molecules. This suggests that in this case the dehydrogenation is triggered by inelastic tunnelling. A typical result of such an experiment is shown in Fig. S2. During these experiments only the symmetric TAP species has been observed, which can be explained by the fact that the MHATP radical is not stable indirect contact with the metallic Au(111) substrate.

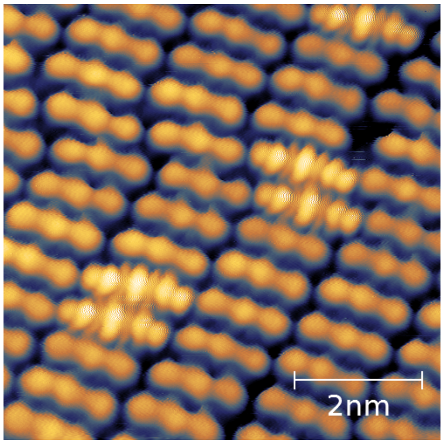


Figure S2. STM image TAP molecules that in the first DHTAP layer that were produced by applying voltage ramp on top of selected DHTAP molecules. Five dehydrogenated molecules can clearly be identified as TAP due to their symmetric shape. The image was recorded at a tunnelling current of I_t = 70 pA and a sample voltage of U_s = 0.9 V.

To estimate the current at higher tip-sample distances for which the tunnelling current is below the noise level of our setup we have recorded a current-distance curve after stabilizing the tip at I_t = 20pA, U_sample = 1.3V over a double layer of DHTAP Au(111) surface (Fig. S3). The redline represents a fit to the initial exponential decrease of the tunnelling current. It can be seen that by retracting the tip by Δz = 900pm the tunneling current should be roughly $I_\mathrm{t} \approx$ 200zA.

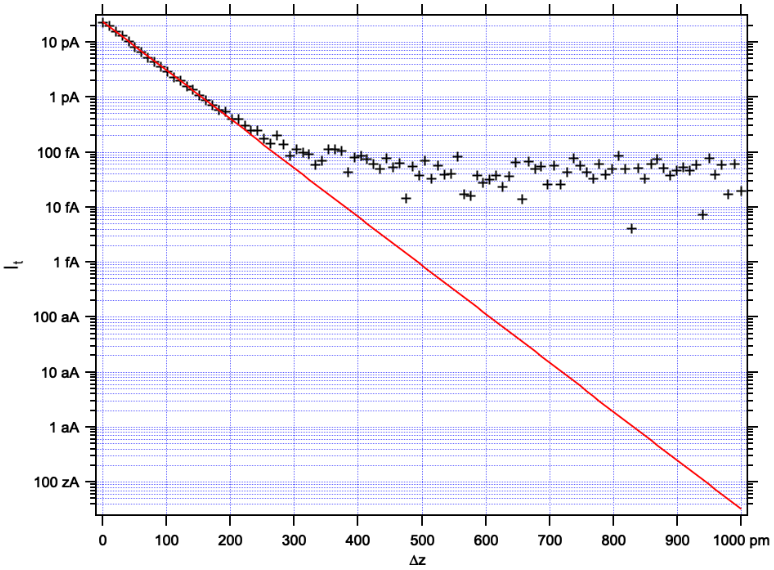


Figure S3. Current-distance spectroscopy recorded at U_sample = 4.1V.

In Fig. S4 the position of the HOMO of the second layer DHTAP molecules can be identified in the dI/dV spectrum. The HOMO is located at $\varepsilon_\mathrm{HOMO}$ = -0.82eV using a Gaussian fit. We have chosen to define the threshold voltage for dehydrogenation U_th at a point where the dI/dV intensity of the orbital is half of the maximum value and to define the error of the threshold voltage as ΔU_th = FWHM/2 using the full width at half maximum of the Gaussian fit. Correspondingly, the value of the threshold voltage for dehydrogenation can be expressed as U_{th} = -(0.7±0.2) V.

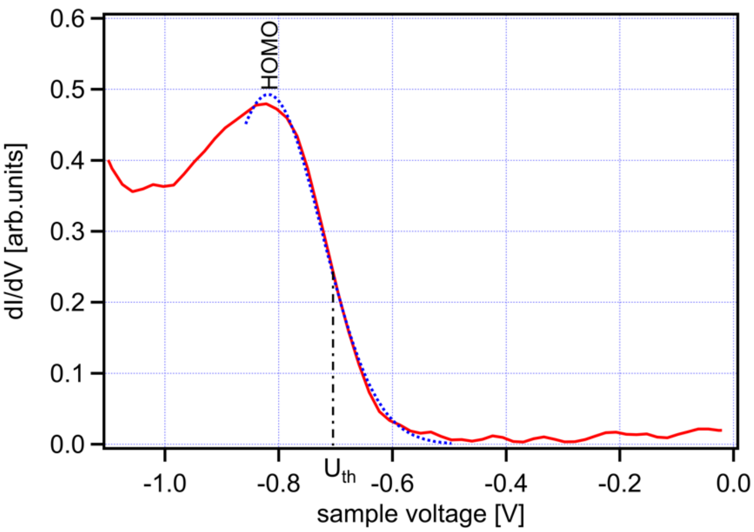
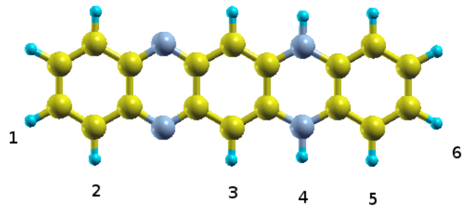


Figure S4. Differential conductivity of the second DHTAP layer for negative sample voltages.

We have calculated the electronic structure and the binding energy of the different hydrogen atoms in the DHTAP molecule Density Functional Theory (DFT) using the QuantumEspresso code [1]. We used the PBE exchange correlation functional [2], norm-conserving pseudo-potentials [3] and a cut-off of 100 Ry on the wave function. In order to simulate an isolated molecule, we used the Martyna-Tuckerman correction to both total energy and SCF potential [4]. In the table we report the binding energy of the different hydrogen atoms of the DHTAP molecule. In the second column, we report the hydrogen binding energy without relaxing the structure of the final molecule, while in the third column we took into account the atomic relaxation after removing the hydrogen. The atom numbers are reported in the figure above. The hydrogen-nitrogen bond (H4) is weaker by roughly 1.6 eV than the hydrogen-carbon bond. We therefore conclude that a deprotonation will occur via breaking the N-H bond.

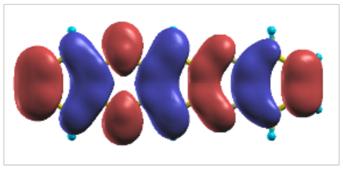
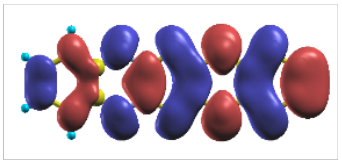
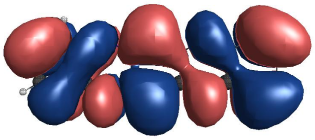
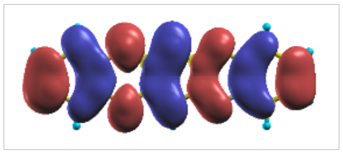
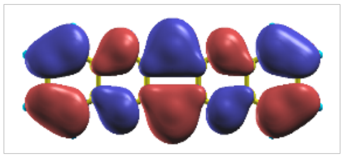
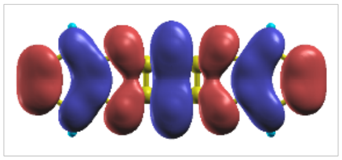


Scheme 1. Structure model of the DHTAP in which the different types of H atoms are indicated.

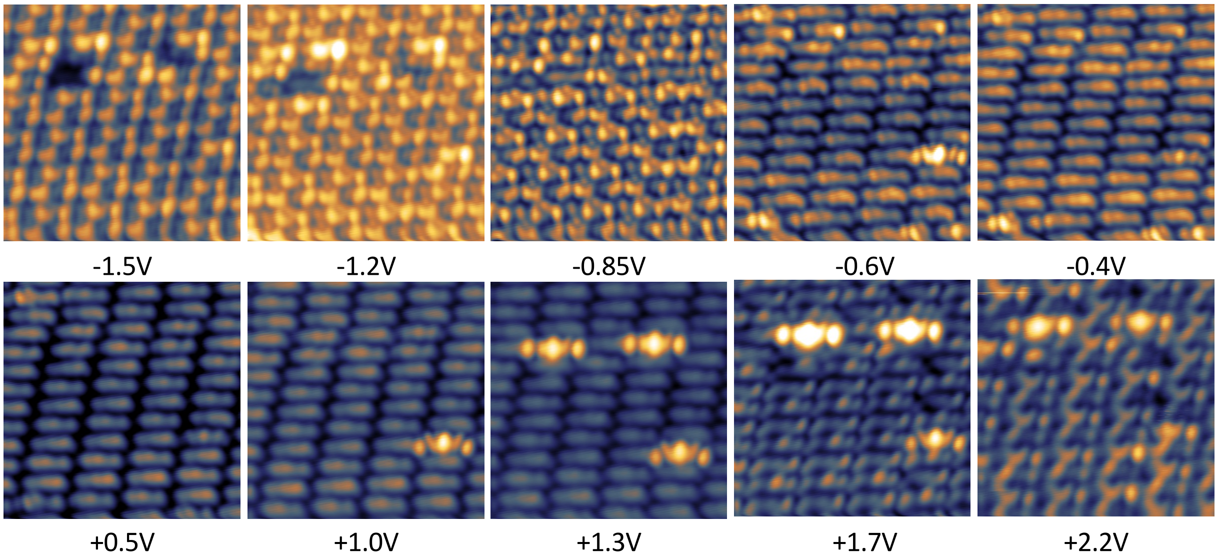
Hydrogen	Vertical Transition Binding Energy [eV]	Relaxed Structure Binding Energy [eV]

H1	3.826	3.5989
H2	3.891	3.6428
H3	3.940	3.6757
H4	2.349	2.0763
H5	3.897	3.6481
H6	3.881	3.6588

Even for the MHTAP (not shown here) the N-H is considerably weaker than the C-H bond, which again favours deprotonation by N-H bond scission.
The following table summarizes the calculated frontier orbitals of the different molecular species.

	HOMO	LUMO
DHTAP		
MHTAP		 SOMO
TAP		

From this it is obvious that imaging of the second layer molecules will largely depend on the sample bias voltage. To illustrate this, we display in Fig. S5 a series of STM images taken at different sample bias voltages. We can observe that in the region of the gap (-0.4 V to +0,5 V) all three species are rather identic. The frontier orbitals become, however, visible if the corresponding voltage is used for tunnelling. It should, however, be noted at this does not apply to the DHTAP LUMO because at 2.2 V it becomes even difficult to distinguish individual molecules. The calculated orbitals of DHTAP, MHTAP, and TAP are shown for reference.



-1.5V -1.2V -0.85V -0.6V -0.4V

+0.5V +1.0V +1.3V +1.7V +2.2V

Figure S5. STM images of the second DHTAP layer a different sample bias voltage. The area corresponds to the one of Fig. 1 of the main manuscript.

References:

[1] Giannozzi, P., Baroni, S., Bonini, N., Calandra, M., Car, R., Cavazzoni, C., ... & Dal Corso, A. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *Journal of physics: Condensed matter*, *21*(39), 395502. (2009)

[2] Perdew, J. P., Burke, K., & Ernzerhof, M. Generalized gradient approximation made simple. *Physical review letters*, *77*(18), 3865. (1996)

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[4] Martyna, G. J., & Tuckerman, M. E. . A reciprocal space-based method for treating long-range interactions in ab initio and force-field-based calculations in clusters. *The Journal of chemical physics*, *110*(6), 2810-2821. (1999)