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COMMUNICATION

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adsorption height varies by about 0.3 \AA with the lateral position x .

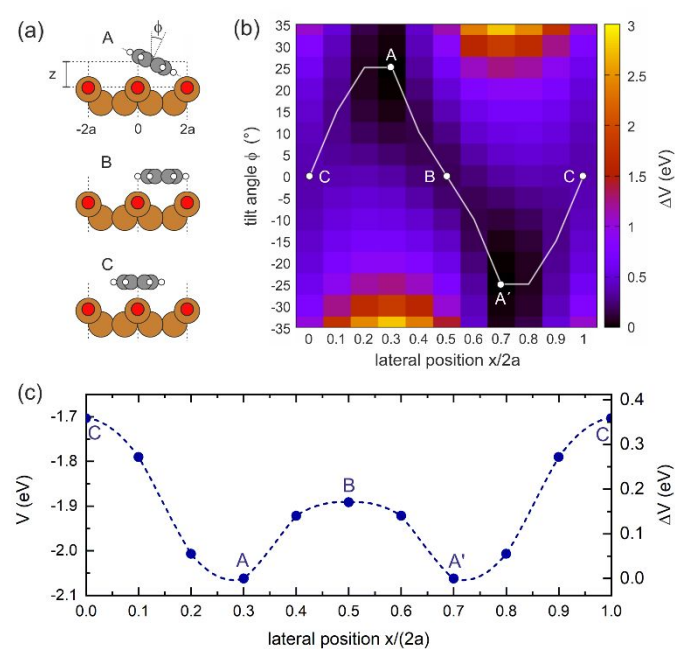


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Yet, according to the DFT results, the molecules are not bent or distorted, such that the azimuthal tilt angle ϕ is the only but central additional parameter that affects the minimum adsorption energy. For a direct comparison of the theoretical findings with the experimental data, STM images were simulated for the most prominent configurations of the DHTAP molecule on the Cu(110)-(2×1)O surface, namely the energetically most favourable site (A), where the molecule is in the tilted position, a molecule centred between two Cu-O rows (B) and the adsorption site right above a Cu-O row (C). Using the Tersoff-Hamann approximation,¹⁷ which assumes tunnelling from/into an atomic s-orbital at the tip, we have evaluated the local density of states in energy windows of $\pm 0.5 \text{ eV}$ with respect to the Fermi level. The results for negative energies (occupied states) are compared in Fig. 3 with the experimental STM images recorded for the same sample bias $V_s = 0.5 \text{ V}$. There is a good agreement of the apparent shapes of the measured (2, 1, 3) and the simulated STM images (B, A, C), respectively, whose nodal structure essentially resembles the shape of the highest occupied molecular orbital of DHTAP.¹² This allows an unequivocal identification of the adsorption sites and tilt of the molecules.⁵ In particular, the croissant-like shape of the species of type (1) in Fig. 1 can now be interpreted to arise from a significant tilt of the DHTAP molecule towards the nearest Cu-O row and the asymmetric bonding configuration of the molecules, rather than to an actual bending or deformation of the molecule. Moreover, the DFT calculations (Fig. 2) reveal that the molecules of type (1) and the mirror symmetric

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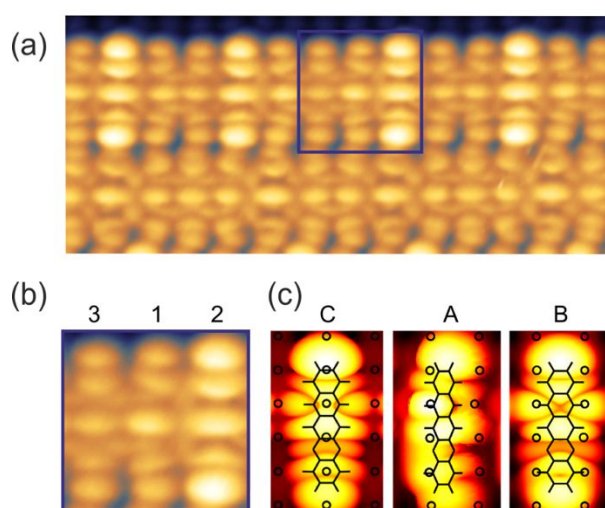


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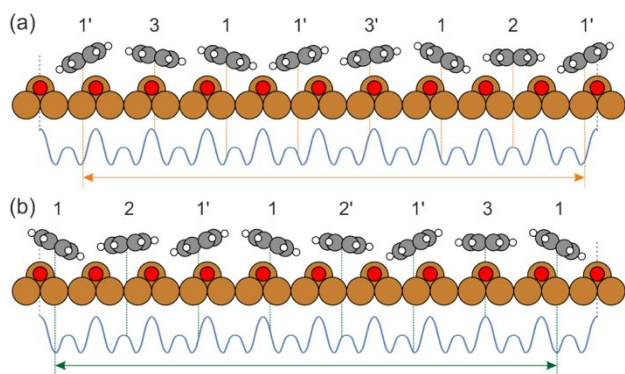


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We believe that our results are also relevant for other molecular adsorption systems. Indeed, HOC phases have been observed in previous studies.^{8,9,10} For instance, pentacene on Cu(110)-(2 \times 1)O forms a HOC-phase with an epitaxial matrix $\begin{pmatrix} 1 & 4 \\ -3 & 2 \end{pmatrix}$ (see Figs. 1(d) and (e) in Ref. 9) containing three molecules per unit cell. Although the structure is clearly “2D”, a closer inspection reveals that it is actually composed of staggered chains in which the molecules show an alternating image contrast. However, due to the lower quality of the STM image in Fig. 1(d) of Ref. 9, it is unclear to what extent the different adsorption sites and/or the molecular conformation (bending, tilt, ...) are responsible for the stabilization of this superstructure.

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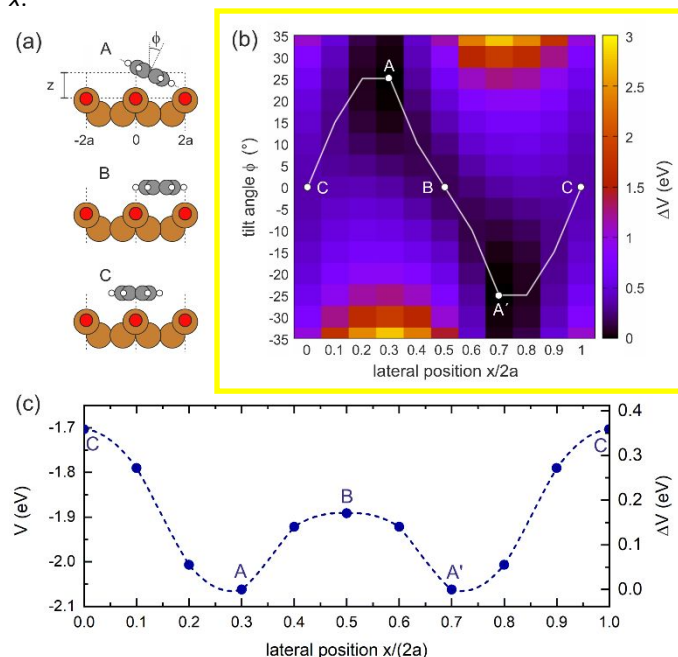


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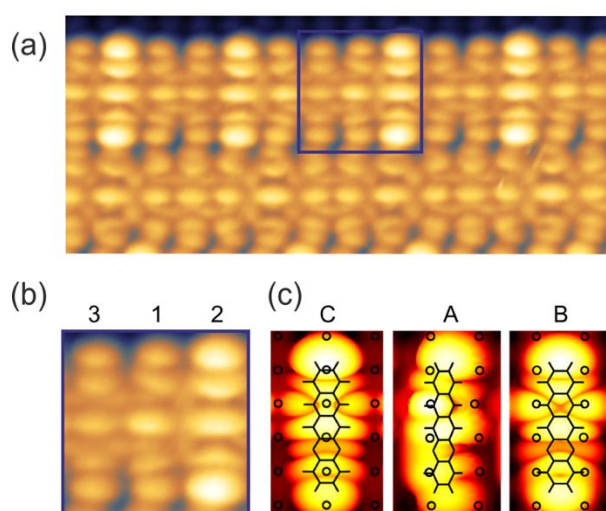


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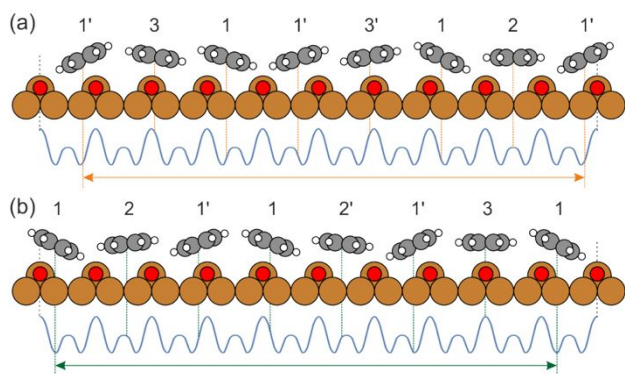


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§ Note that the experimental STM images appear rather symmetric while the calculated ones show a clear difference between the NH and the N positions of the DHTAP molecule. This is because the STM calculations were performed for individual molecules. Indeed, DFT calculations for pairs of DHTAP molecules reveal that two parallel molecules arrange in a head-to-tail fashion, where the NH and N groups of neighbouring molecules form N - H-N bonds at both ends of the molecules, thus yielding a more symmetric electron density distribution.

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