Electronic Supplementary Material (ESI) for Nanoscale

Supplementary Information

Directional Molecular Sliding at Room Temperature on a Silicon Runway

Xavier Bouju, Frédéric Chérioux, Sébastien Coget, Gwénaël Rapenne, and Frank Palmino

Calculation details

Due to the size of the molecule and the complexity of the substrate, standard density functional theory methods are not applicable with a reasonable computational cost. On the other hand, common potential functions such as those found in molecular mechanics codes are not well adapted for the present molecule/surface interactions. Thus, the best compromise for DETB on SmSi surface appears to be semi-classical methods at the basis of the ASED+ code. Previous calculations on SmSi(111)-8x2 have already proven the reliability of the method [1].

However, it remains a challenging task to determine the full potential energy surface (PES), where the molecule is fully relaxed for each *x,y* position of the center of mass above the surface plane, and then to determine the various trajectories that the molecule follows during surface diffusion.

As a consequence, one just considers straight motions between adsorption sites and only one rotation, meaning that the calculated energy barriers are estimates of the actual path on the PES.

Methods like nudge elastic band method [2], allowing to find saddle points between an initial and a final state on the PES, can not be handled by the used computational code.

One anticipates that the provided numbers are thus slightly overestimated.

Notice that, as the DETB molecule is not chemisorbed on the surface, so that errors should be rather small.

Calculated trajectories of a single molecule

Three movies have been realized by using the xyz coordinates obtained by geometry optimization of DETB molecules adsorbed on a SmSi(111)-7x1 reconstruction. At each position on the surface, the geometry of the DETB molecule is optimized.

Movies 1 and 2 correspond to the sliding of two DETB observed along Sm rows by positioning their main axis, respectively perpendicular and parallel to Sm rows.

Movie 3 corresponds to a DETB molecule passing over a Sm row which have never been experimentally observed.

Sequence of three experimental STM images

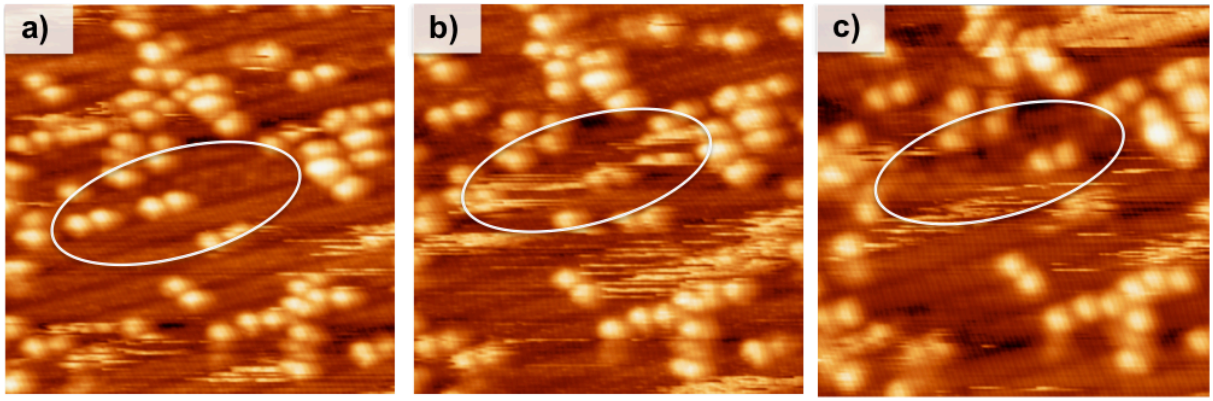

Fig. S1: Three STM images (20x20 nm^2, V_s = 2.5 V, I_t = 0.06 nA) of the same area showing the directional DETB sliding on SmSi(111)-5x1 reconstruction. The white circle indicates the molecule before (a), during (b) and after (c) the diffusion. The defected lines appear clearly in fig S1 b) and are associated to the diffusion during the scan.

References

[1] Y.Makoudi, E.Duverger, M.Arab, F.Chérioux, F.Ample, G. Rapenne, X. Bouju, F. Palmino, *ChemPhysChem* **9**, 1437 (2008).
[2] D. Sheppard, R. Terrell, G. Henkelman, *J. Chem. Phys*. **128**, 134106 (2008).