

# Rotation–libration in a hierarchic supramolecular rotor–stator system: Arrhenius activation and retardation by local interaction†

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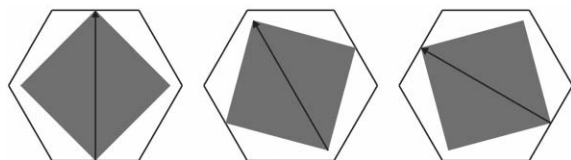
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Fourfold symmetric zinc-octaethylporphyrin (OEP) has been incorporated in the holes of the hexagonal molecular network generated by thermal dehydrogenation of 4,9-diaminoperylene-quinone-3,10-diimine (DPDI) on a Cu(111) surface and displayed hindered rotation; the reorganization between the potential minima, a rotation–libration, which is characterized by an activation energy of  $E_D = 0.17 \pm 0.03$  eV, has been monitored in the STM tunnelling currents as a bi-state “switching”.

The positioning of single molecules on crystal surfaces has opened up the possibility of spatially addressable molecular functional units.<sup>1–3</sup> Their integration within a hierarchically constructed environment exhibiting long range ordering provides the prerequisite for the generation of addressable devices at the nanoscale level.<sup>4,5</sup> In this work we demonstrate how the inclusion of molecules fitting into a pre-fabricated host network with partially matching symmetry leads to a dynamic system which alternates between distinguishable orientational states by way of thermally activated rotation–libration (Fig. 1).

We have recently reported the formation of a highly stable hexagonal molecular network generated by thermal dehydrogenation of 4,9-diaminoperylene-quinone-3,10-diimine (DPDI)<sup>6</sup> on a Cu(111) surface.<sup>7</sup> The highly regular honeycomb structure<sup>8</sup> is commensurate with the Cu substrate [in the form of a  $p(10 \times 10)$  superlattice with a lattice constant of 2.55 nm] and thermally highly stable (up to  $>300$  °C) as a consequence of strong  $\pi$ -bonding between the organic molecules and the surface metal



**Fig. 1** Symmetry considerations: Situation of a square-shaped molecule hosted in a hexagonal confinement adopting three possible equivalent orientations related by  $30^\circ$  rotations of the rotor relative to the stator.

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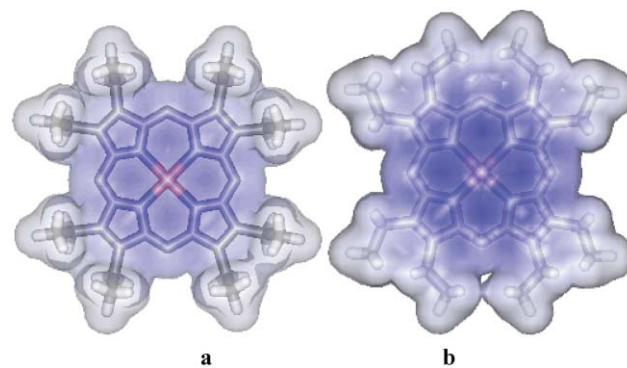
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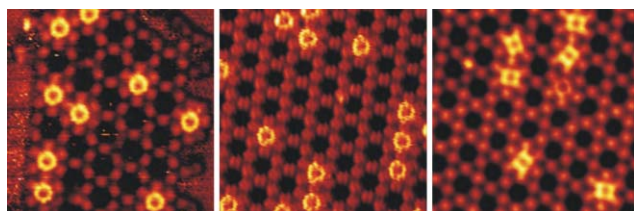
atoms. Due to its structural regularity and stability, this surface structure provides the ideal starting point for the assembly of functional hierarchic aggregates. In particular, the hexagonal “holes” in the network which have a vertex-to-vertex diameter of 16.3 Å provide the opportunity for the local deposition and fixation of other molecules. In Fig. 1 we have schematically depicted the situation of a square-shaped molecule hosted within this hexagonal confinement adopting three possible equivalent orientations related by  $30^\circ$  rotations of the rotor relative to the stator.

Zinc-octaethylporphyrin (OEP) (Fig. 2), which possesses fourfold molecular symmetry and the shape of a truncated square, fits conveniently into the cavities formed by the dehydro-DPDI honeycomb network which thus prohibits translational motion. In Fig. 3 the STM images of Zn-OEP molecules, which are trapped inside the hexagonal pores of the dehydro-DPDI network, are displayed. Notable is the thermal behaviour of the molecules within their cavities. At ambient temperature the approximately square molecules appear as rings due to rapid rotation within the hexagonal cavity compared to the rather slow STM acquisition time in the order of 300 ms/line (Fig. 3, left). Additionally, next to the DPDI network on the bare Cu surface the OEP molecules display a mobile behaviour which is characteristic for a low diffusion barrier.

Upon cooling to 77 K the rings become noisy, indicating a lower rotational symmetry of the predominant orientation of the mobile units (Fig. 3, middle) and a slower hopping between local potential minima. Finally, at 5 K the dynamic behaviour is frozen and a rectangular shape of the OEP units is clearly revealed (Fig. 3, right). This observation indicates two different conformationally related shapes of the OEP units. On the one hand at elevated



**Fig. 2** (a) Chemical structure of octaethylporphyrin (OEP) with all eight ethyl groups pointing upwards; (b) rectangular structure observed at 5 K with flat arrangement of the ethyl substituents.



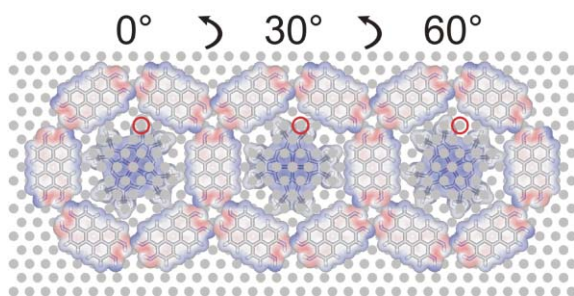
**Fig. 3** STM images (16 nm × 16 nm) showing the different thermal behaviour of the OEP molecules which are trapped inside the hexagonal pores of the dehydro-DPDI honeycomb network. The left image was recorded at room temperature, the middle one at 77 K and the right one at 5 K. One can see that the thermally activated rotation of the trapped OEP molecules is slowed down to occur within the time frame of the imaging of the STM tip (300 ms/line) at liquid nitrogen temperature while at liquid helium temperature the rotation is frozen.

temperature the ethyl groups point upwards, leading to an eight-lobed structure with fourfold symmetry (Fig. 2a). On the other hand the ethyl groups arrange themselves flat on the substrate in pairwise opposite directions at very low temperatures, distorting the molecular square to a rectangle observed at 5 K (Fig. 2b and supporting information).<sup>9</sup>

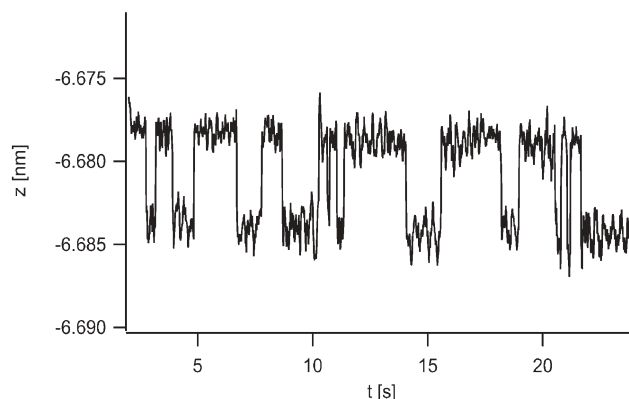
A model of the OEP–Zn complex on the hexagonal Cu(111) surface and within a hexagonal cavity formed by the commensurate dehydro-DPDI network is shown in Fig. 4. The preferred orientations of the guest molecule are both determined by the structure of the substrate lattice<sup>10,11</sup> and by the size and (commensurate) symmetry of the organic network and its interaction with it.

If the tip of the STM is laterally placed above a trapped OEP molecule in the temperature range around 77 K, at which the activated motion is slowed down to give orientational lifetimes of several seconds, the reorganization between the potential minima may be monitored as a “switching” between different tunnel currents at the given spot. Not unexpectedly, these switching events can be best observed if the tip is placed off-centre with respect to the trapped OEP complex, since the peripheral area of the tetragonal molecule within its hexagonal cavity will experience the greatest structural variation upon the 30° rotational events discussed above.

The STM height signal, recorded with the feedback loop turned on, is shown in Fig. 5 with a time resolution of 20 ms for each data



**Fig. 4** Model for the arrangement of the OEP molecule inside the honeycomb dehydro-DPDI network on Cu(111). Two subsequent 30° rotations of the confined OEP molecule with respect to the hexagonal network are illustrated. A possible peripheral position of the STM tip is indicated by the red circle and clearly demonstrates the alternation of the molecular environment.

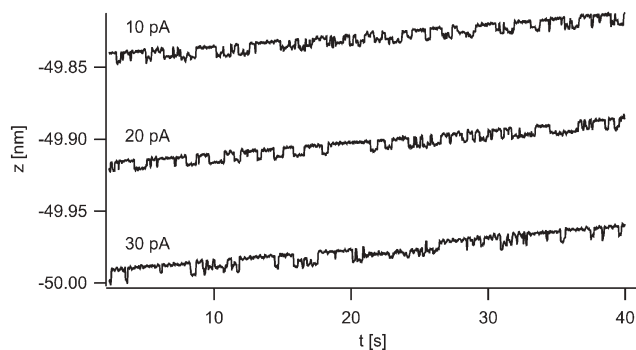


**Fig. 5** Tip height *versus* time measurements recorded at constant current conditions while keeping the sample temperature at 78 K. The tip was placed above the periphery of an OEP molecule with a current set point of 20 pA. The magnitude of the tip height fluctuations is in the order of 0.1 Å compared to the 1.5 Å maximum *z* excursion while scanning OEP adsorbates on Cu(111). The ‘high’ state occurs for about twice the duration of the ‘low’ state which is in good agreement with the model presented in Fig. 4. The degeneracy of the different rotor states implies that the geometric cross section of the ethyl residues (approximately 8/12) determines the relative frequency of electron tunnelling. This happens through either the ethyl groups or through the vacuum gap and consequently determines the relative occurrence of measured ‘high’ or ‘low’ *z* excursions.

point. A bi-state signal with the rising and falling edges of switches between two approximately fixed heights, which is clearly distinct from the inherent noise level of the STM, is observed. Depending on the exact position of the tip and the tunnelling conditions, the height difference between the two plateaus is about 0.05–0.10 Å which corresponds to a difference in tunnelling current of 2–4 pA.

In order to obtain information about the magnitude of the activation barrier between the local rotational (potential) minima, measurements of the switching between the two states were performed at variable temperatures (77–84 K). The average switching frequency was counted manually from the measured signals and plotted logarithmically *vs.*  $1/kT$ . The energy barrier  $E_A$  is derived from an Arrhenius plot and amounts to  $E_A = 0.17 \pm 0.03$  eV, whilst the determination of the pre-exponential frequency factor  $k_0$  gave a value of about  $10^{11.5 \pm 2} \text{ s}^{-1}$ .<sup>12</sup> Both the energy barrier and the frequency factor are to be seen as lower boundaries because at elevated temperatures (lower  $1/kT$  values) switching events are missed due to the finite time resolution of the STM feedback loop. Activation barriers for surface-located rotors range from 100 meV to 300 meV, and their magnitudes depend in an as yet incompletely understood way on the surface structure and the molecular environment.<sup>13,14</sup>

In a further experiment we demonstrated how the rotational motion of the trapped molecules may be locally manipulated. At a temperature of 80 K the lateral tip position and the bias voltage were kept constant whilst the current setpoint of the feedback loop was changed from 10 pA to 20 pA and finally to 30 pA. Fig. 6 shows the *z*-signal of the tip above an OEP molecule which was trapped inside the dehydro-DPDI honeycomb network.<sup>15</sup> Notably, the signal at higher setpoints (smaller tip–sample distance) shows fewer falling and rising edges, which indicates a slow-down of the OEP motion under the increasing proximity with



**Fig. 6** Tip height *versus* time measurements recorded at constant current conditions while keeping the sample temperature at 80 K for three different current setpoints. The tip was placed above the periphery of an OEP molecule which was trapped inside the dehydro-DPDI honeycomb network. Counting the “switches” for the given period of time gives 112 (10 pA), 96 (20 pA) and 77 (30 pA), corresponding to the lifetimes of a given orientation of 0.36, 0.42 and 0.52 s, respectively.

the STM tip. We associate these observations with the degeneracy of the host–guest system which is lifted by the local interaction in the proximity of the STM tip asperity or the inhomogeneity of the electric field.<sup>16</sup>

We have thus shown that the tunnelling current through the OEP molecule is modified by the hopping processes between different rotational states originating from rotational diffusion between equivalent potential minima. Exceptionally low frequencies of 0.2 Hz at 77 K are observed within the confinement of the surface network structure. An array of identical devices is achievable due to the specific guest–host interaction of the hierarchically assembled supramolecular entities, which goes well beyond earlier observations of rotational diffusion of molecular entities on well-defined substrates.<sup>13</sup> Moreover, the possibility to locally probe and influence molecular motion by specific modification of the host–guest architectures and to study the physico-chemistry of confined molecules at surfaces provides an alternative to and goes beyond other confined systems like zeolites or confined molecular liquids. In principle, this not only applies to molecular motion but also to specific host–guest interactions as well as to chemical transformations within the confinements.

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