

**SUPPORTING INFORMATION**  
**for Chem. Commun. B700909G**

**Rotation-libration in a hierarchic supra-molecular rotor-stator system:  
Arrhenius activation and retardation by local interaction.**

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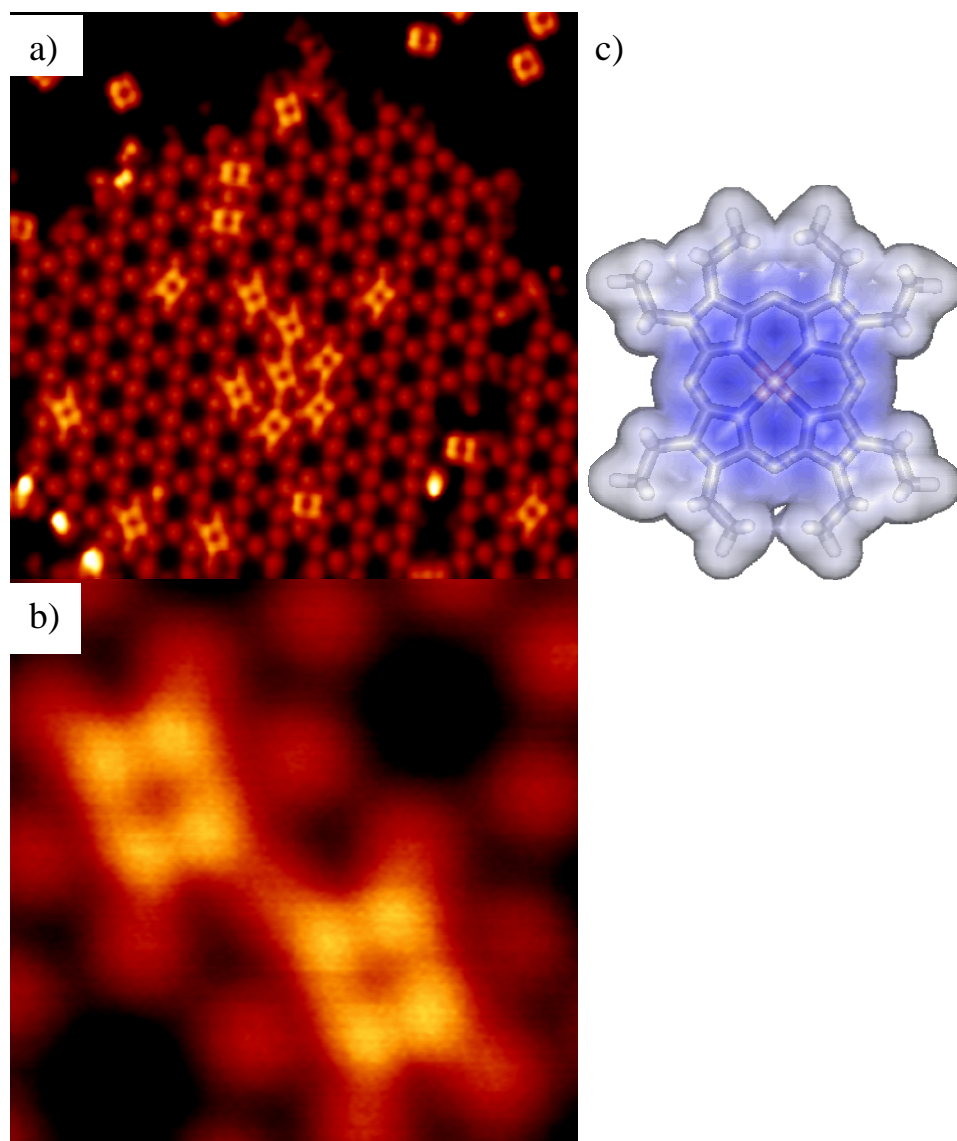
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## **Experimental part: Preparation of the Surface Structures**

The experiments were conducted in a UHV system consisting of different chambers for sample preparation and characterization (base pressure  $10^{-10}$  mbar). The Cu(111) substrate was prepared by subsequent cycles of sputtering with  $\text{Ar}^+$ -ions and annealing at 870 K. By thermal evaporation from a commercial evaporator (Kentax, 3 cell evaporator) at a rate of about 0.5 ML/min thin DPDI films were prepared on the Cu(111) surface while the substrate was kept at RT. To obtain the dehydro-DPDI honeycomb network the coverage must be less than 0.7 monolayers and the sample has to be annealed at 300°C. This was done by radiative heating. Onto such a sample a small amount of ZnOEP molecules (less than 10% of a monolayer) is deposited from another crucible which is located in the same evaporator. The investigation of the samples was carried out with a commercial LT-STM (Omicron) at room temperature, at 77 K and at 5 K. Furthermore, the possibility exists to counterheat the sample in the STM by radiative heating and thus, to vary by this means the sample temperature between 5 K and 150 K.

**Figure S1**

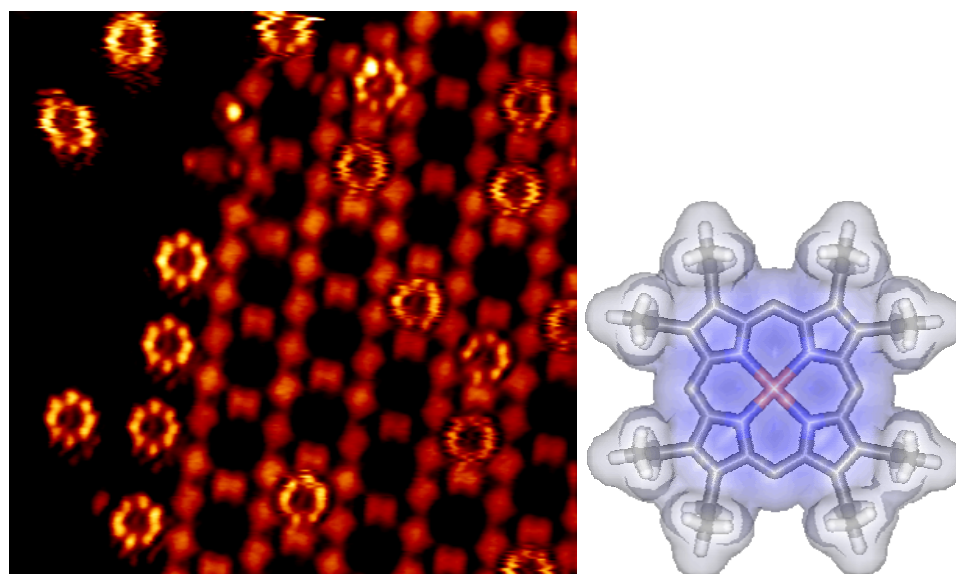
The two STM ((a) 30nm x 30nm; (b) 5nm x 5nm) images measured at 5 K display the internal structure of OEP molecules which are either trapped inside the pores of the hexagonal DPDI network or adsorbed on the bare Cu surface. For both situations the molecules consist of four lobes and show a rectangular appearance which can be explained by the arrangement of the ethyl legs displayed in the chemical structure in c).



**Figure S2**

STM image (16 nm x 16 nm, 77 K) visualizing the different appearances of OEP which was deposited onto the (111)-oriented Cu surface covered with the dehydro-DPDI honeycomb network. The OEP molecules within the pores show mainly a blurred appearance while some on the bare metal surface exhibit eight dots for each molecule. The structure model on the right displays the most probable configuration to explain the occurrence of the eight dots for each molecule.

It should be noted that the appearance of the molecules is square-like compared to the rectangular appearance at 5 K.



**Figure S3**

Arrhenius plot for the determination of the energy barrier for the hindered rotation libration of the OEP molecules trapped inside the pores of the dehydro-DPDI network. The data points were determined at 5 different sample temperatures: 77 K, 78 K, 79 K, 80 K and 84 K.

