Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information: Real-Space Resolved Surface Reaction: Deprotonation and Metalation of Phthalocyanine

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I. Tautomerization of H_2Pc

H_2Pc adsorbs on Cu(111) tilted by approximately $\approx \pm 7^\circ$ to the high symmetry axes of Cu(111). By injecting charge carriers with $|E| \geq 200\,\text{meV}$ from the STM tip into the molecule we can induce rotations between these orientations. At higher energies a third orientation can be observed, where all molecular arms are aligned with the substrates high symmetry axes. As can be seen in Fig. S1, the electron yield of this orientation exhibits a threshold at 900 meV and a significant increase at 1300 meV. These values are in good agreement with the second and third harmonic of the N-H stretching mode at 816 and 1224 meV, which is known to facilitate tautomerizations of H_2Pc on Ag(111), i.e. a change in the binding position of the central hydrogen atoms.[S1] We therefore assume that the 0° orientation is the preferred adsorption of one tautomer, while the other tautomer adsorbs in the ±7° orientation. Due

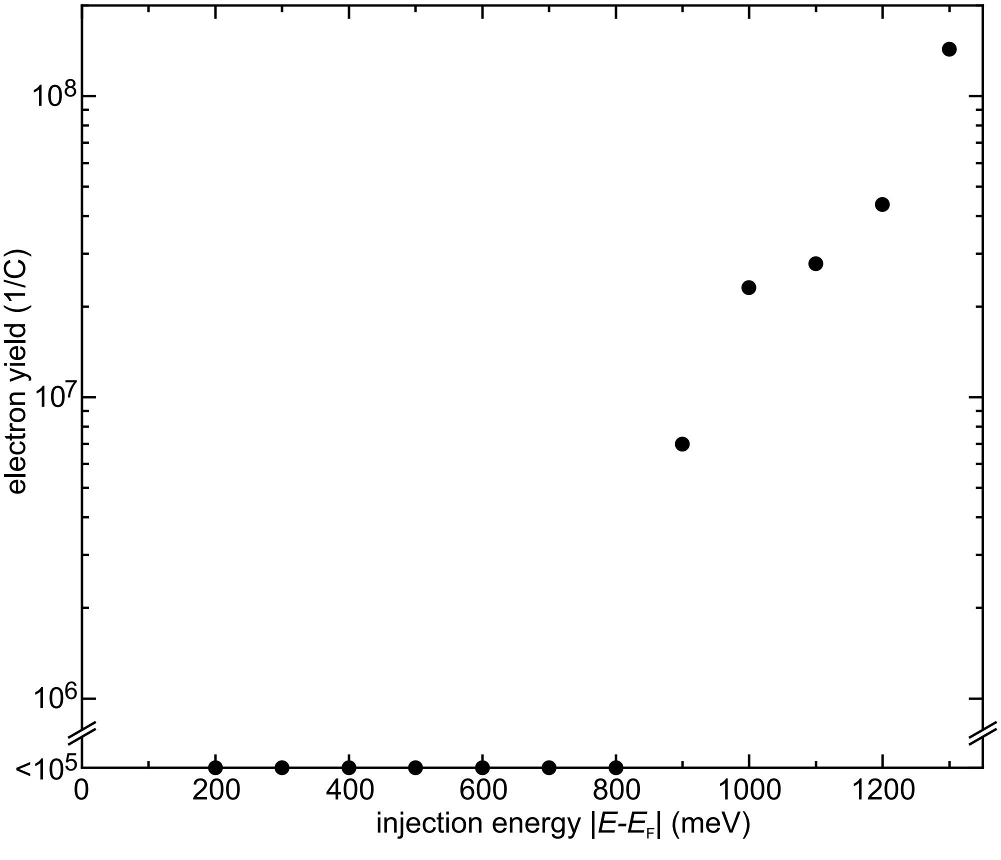

Figure S1: Electron yield of the 0° orientation for different injection energies.

to symmetry mismatch between substrate and molecule the degeneracy of both tautomers is lifted upon adsorption on Cu(111) and after evaporation all molecules can be found in the tautomer, that correspond to the ±7° orientation. A rotation into the 0° orientation then requires a tautomerization and exhibits the known threshold of 816 meV.

II. Molecular nanoprobe

In the **MO**lecular **NA**noprobe (MONA) technique[S2] charge carriers are not injected directly into the molecule, but at a chosen distance d from the molecule (see Fig. S2). The injected charge carriers propagate in the substrate where they eventually hit the molecule, which might induce a change of the molecular state, e.g. rotation or tautomerization, by inelastically scattering or migrating to a molecular orbital. Such a rotation can be detected by comparing STM images before and after the injection. These scans have to be done with non-invasive imaging parameters, i.e. below the excitation threshold of the rotation at $U = 50\,\mathrm{mV}$, $I = 50\,\mathrm{pA}$ for H_2Pc on Cu(111), to exclude the inducing of additional rotations during the scans. Additionally the number of injected charge carriers per pulse has to be

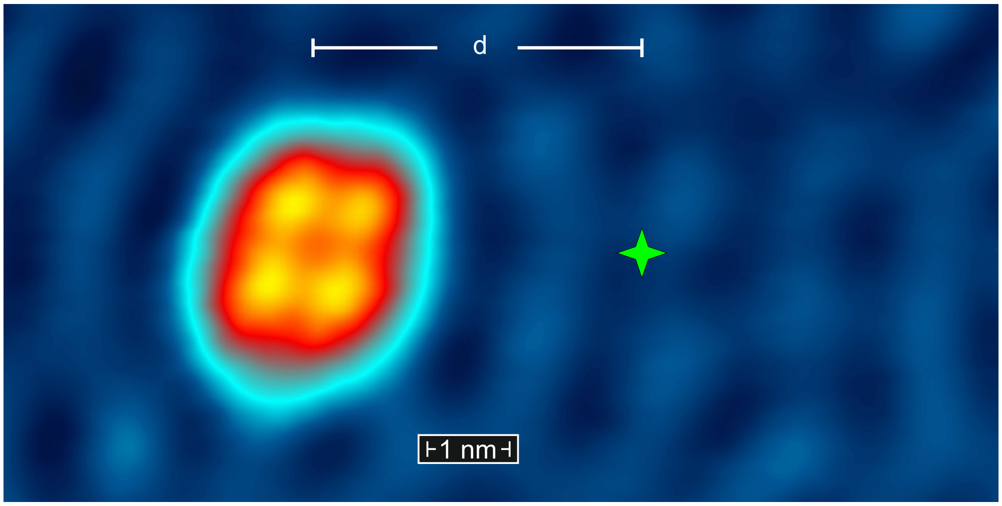

Figure S2: STM topography image ($U = 50\,\mathrm{mV}$, $I = 50\,\mathrm{pA}$) of a H_2Pc molecule on Cu(111). The injection point is marked as a green star in a distance $d = 4\,\mathrm{nm}$ from the molecular center.

adjusted to reduce the probability of multiple rotation events during a single pulse to an insignificant level. Because of the statistical nature of this process, between 1000 and 5000 injection pulses with subsequent scan have to be analyzed for each data point. The rotation rate is calculated in electron yield dividing the number of observed switches by the total amount of injected charge.

Based on the transport path, the measured electron yield provides information about the charge carrier transport in the substrate, the coupling between molecule and substrate as well as the rotational behavior. By varying for example the injection energy, information about these three processes can be extracted. An additional comparison to on-top measurements allows to disentangle the individual contributions: the transport path is important only for MONA measurements, whereas the rotational behavior as well as the coupling should be comparable for both techniques.

III. Temperature dependent molecule distribution

The distribution of H_2Pc, H_0Pc and CuPc for different postannealing temperatures from room temperature to 300°C were determined by classifying each molecule in large overview scans. For all temperatures over 1000 molecules have been analyzed. Fig. S3 shows exemplary $(20 \times 20)\mathrm{nm}^2$ overview scans for each temperature.

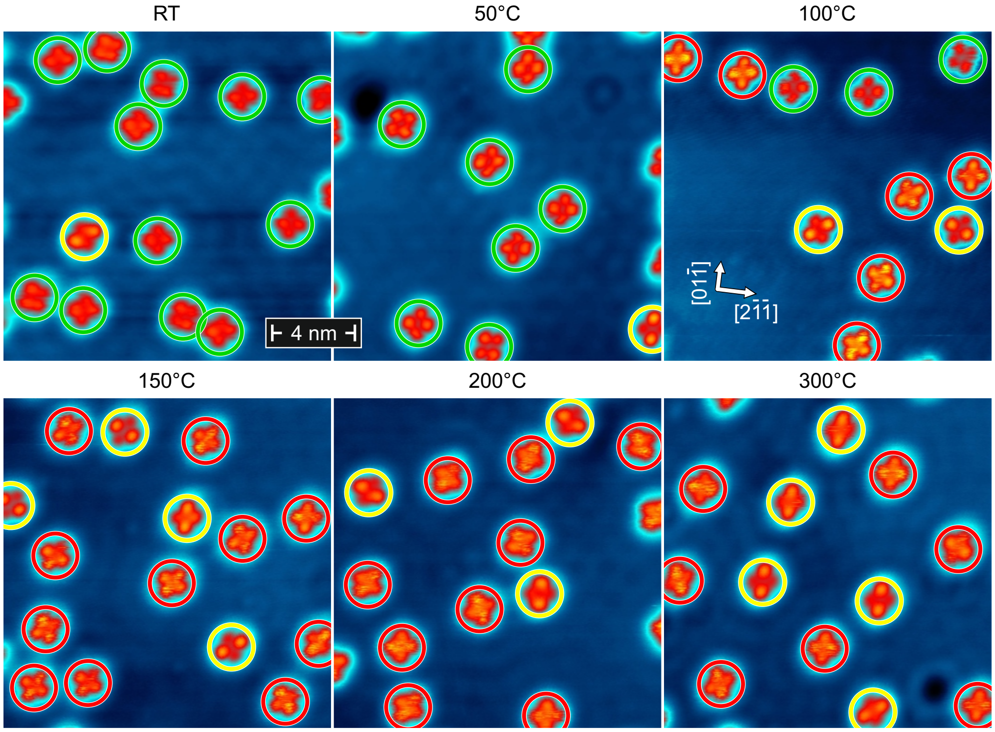

Figure S3: Overview scans of Cu(111) after the evaporation of H_2Pc molecules for different postannealing temperatures. H_2Pc molecules are marked with green, H_0Pc with yellow and CuPc with red circles. Scan parameters: $U = -400\,\mathrm{meV}$, $I = 50\,\mathrm{pA}$.

References

(S1) Kügel, J.; Klein, L.; Leisegang, M.; Bode, M. Analyzing and Tuning the Energetic Landscape of H_2Pc Tautomerization. *J. Phys. Chem. C* **2017**, *121*, 28204–28210.

(S2) Leisegang, M.; Kügel, J.; Klein, L.; Bode, M. Analyzing the Wave Nature of Hot Electrons with a Molecular Nanoprobe. *Nano Letters* **2018**, *18*, 2165–2171.