

**Controlling intramolecular hydrogen transfer in a porphycene molecule
with single atoms or molecules located nearby**

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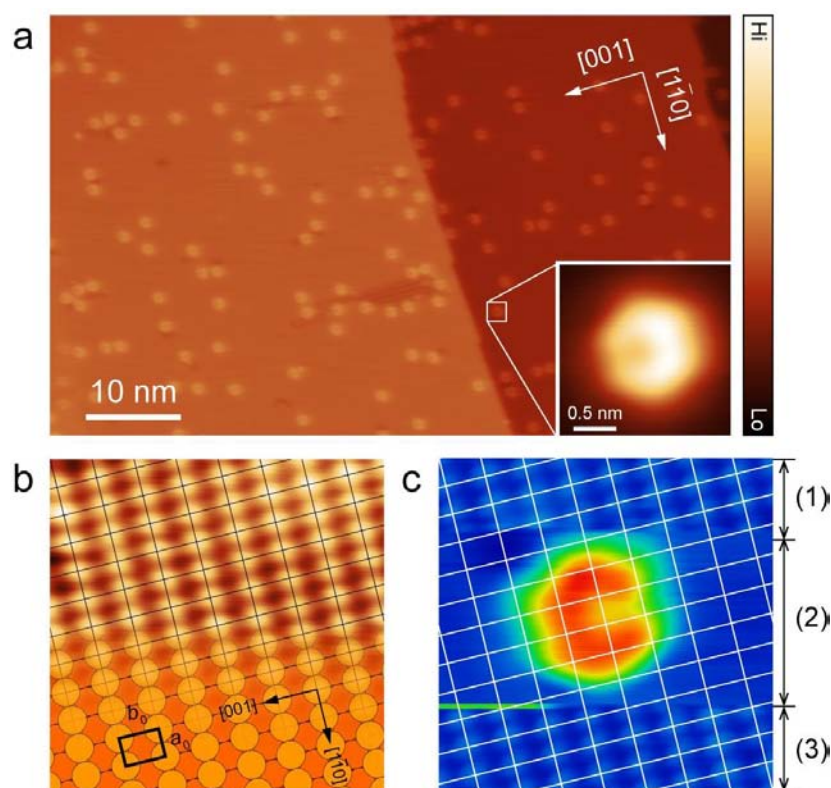
1. Methods

Experimental: Experiments were performed in an ultra-high vacuum chamber (base pressure below 10^{-9} and 10^{-10} mbar in the preparation and STM chamber, respectively), equipped with a low temperature STM (modified Omicron instrument with Nanonis Electronics). The STM images were taken in the constant-current mode at 5 K. Bias voltages refer to the tip voltage with respect to the sample. The Cu(110) surface was cleaned by repeated cycles of argon ion sputtering and annealing. The STM tip was made from a tungsten wire and then optimized *in situ* by indentation into the Cu surface. Porphycene molecules were evaporated from a Knudsen cell (at about 450 K).

Computational: The relative stabilities and geometries of the isolated (gas-phase) and the adsorbed porphycene molecule were determined from periodic, plane-wave density functional theory (DFT) calculations using the Vienna ab-initio simulation program (VASP) [1]. The electron-ion core interactions were treated using the Projector Augmented Wave (PAW) method [2]. The exchange-correlation effects were treated using the optB86B version of the van der Waals density functional [3]. The plane-wave cut-off was 400 eV. The super-cell used in the gas-phase calculations had the dimensions $18.0 \times 15.3 \times 23.8 \text{ \AA}^3$. The Cu(110) surface was represented in a super-cell by a four layer slab with a 7×8 surface unit cell and a 17.63 \AA vacuum region. The atoms in the bottom two layers were constrained at their bulk positions during the relaxations with a calculated lattice constant of 3.60 \AA . The structures were relaxed until all forces were less than 0.01 eV/\AA , with the bottom two Cu layers remaining fixed throughout the geometry optimization. In the structural relaxations only the Γ point was kept in the k -point sampling while in the STM simulations a $2 \times 2 \times 1$ grid was used. These simulations were based on the Tersoff-Hamann approximation [4] and obtained from the calculated local density of states in the vacuum region. The vibrational spectrum of the adsorbed molecule on a rigid substrate lattice was calculated by diagonalising the dynamical matrix that was obtained by finite differences of the calculated forces at symmetric ionic displacements of 0.01 \AA .

2. Overview image and adsorption sites of porphycene molecules

Figure S1a shows an overview STM image after the deposition of porphycene molecule onto a Cu(110) surface. Most of the molecules adsorb as isolated monomers on the clean terrace. The adsorption site of the porphycene molecules was determined by imaging a molecule and the atomic arrangement of the substrate simultaneously. Figure S1b shows an atomically resolved STM image of a Cu(110) surface that has a rectangular lattice.



Supplementary Figure S1: (a) Overview STM image acquired at 5 K ($V = 100$ mV and $I_t = 10$ nA, image size = 44.4×71.8 nm²) after the deposition of porphycene molecule onto a Cu(110) surface at room temperature. The inset shows a magnified image of a single molecule. (b) Atomically resolved STM image of the Cu(110) surface acquired at 5 K ($V = 100$ mV and $I_t = 1$ nA). Black lines represent the Cu(110) surface lattice ($a_0 = 0.255$ nm and $b_0 = 0.361$ nm), the atoms are superimposed on the lower part. (c) STM image of a porphycene molecule on Cu(110) acquired at 77 K. Different tunneling parameters were used to allow atomic resolution on the copper surface and stable imaging of the molecule within one image: $V = 100$ mV and $I_t = 10$ nA in (1) and (3), but $V = 100$ mV and $I_t = 0.1$ nA in part (2) of the image. (b-c) are 2.95×2.95 nm² in size.

A porphycene molecule on the surface is presented in Fig.S1c, where the gap distance is reduced in the bare surface area (1 and 3) to obtain the atomic resolution, while it is increased in area (2) that contains the molecule to minimize the tip–molecule interaction that disturbs the imaging. Areas (1) and (3) are scanned at 100 mV and $I_t = 10$ nA, while area (2) is scanned at 100 mV and $I_t = 0.1$ nA. The Cu(110) surface lattice is then determined from the atom positions of the substrate in the areas (1) and (3) and the corresponding grid is superimposed over the image (Fig.S1c). It becomes clear that the

center of the porphycene molecule is located on a short bridge site of the close-packed copper rows.

3. Calculated structures of porphycene molecule

The calculated relative energies of the various porphycene tautomers – *trans*, *cis-1* and *cis-2* – in the gas phase and adsorbed on Cu(110) in the short-bridge site (shown in Figures 1c, d and e) are provided in Table S1.

Tautomer	Relative Energy (g) (eV)			Relative Energy (ad) (eV)
	<i>Present</i>	<i>Ref. [5]</i>	<i>Ref. [6]</i>	<i>Present</i>
<i>trans</i>	0	0	0	0.19
<i>cis-1</i>	0.077	0.106	0.087	0
<i>cis-2</i>	1.32	1.37	-	1.14

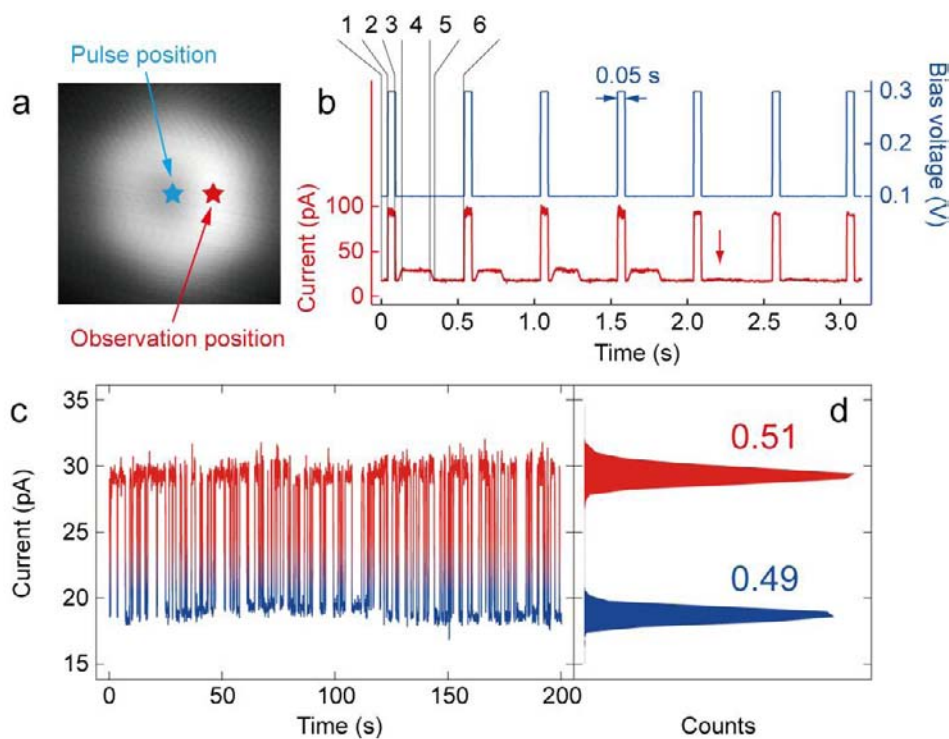
Supplementary Table S1: Calculated relative energies of the various porphycene tautomers in the gas-phase (g) and adsorbed (ad) on Cu(110). The energies are referenced with respect to the most stable tautomer and exclude zero-point energies. A comparison is also made with the corresponding results from other DFT calculations in [5, 6]. The calculated adsorption energy of the *cis-1* tautomer in the present work is 5.46 eV.

4. Lateral tip position dependence of the fractional occupation

The fractional occupations P_H and P_L of the two *cis-1* tautomers show a dependence on the lateral tip position with respect to the molecule during the pulse voltage. Typically (e.g. in Fig.2a and c in the main text), the voltage pulse is applied at a part of a molecule where the inner H atoms are situated (see Fig.2e). In this configuration, one can easily distinguish the two *cis-1* tautomers as the “high” and “low” conductance states in the current trace during the voltage pulse because the molecular appearance changes most there during the switching. However, because of the difference in the intrinsic yield of the “high” and “low” states (Fig.2f) and the current flux we observe unequal values of P_H and P_L (about 0.4 and 0.6) even without the tip proximity effect (as discussed in Fig.2g). Because this asymmetry is caused by tip position, the occupations P_H and P_L are expected to be equal if the pulse voltage was applied at the center of a molecule (instead of the positions of the inner H atoms as for instance in Fig.2a).

To verify this assumption, we applied voltage pulses (to induce tautomerization) at the centre of the molecule, thus eliminating the asymmetry effect. On the other hand, since

it is impossible to identify the tautomer state from the current signal at the center (the switching does not change the current value there), the occupation measurement was conducted in the usual position (over the inner H atoms). Both positions are indicated in Fig.S2a.



Supplementary Figure S2: (a) STM image of a single porphycene molecule where the tip positions during the pulse (blue star) and the observation (red star) are indicated. (b) Measurement scheme of the position dependence of the fractional occupation. (c-d) Current trace and histogram during a voltage pulse of 300 mV over the blue star position in (a), respectively.

The experiment was done in the following manner (summarized in Fig.S2a-b); (1) First the tip is fixed over the center of a molecule (“pulse position”; indicated by the blue star in Fig.S2a) with $I_t = 17$ pA and $V = 100$ mV (the gap conditions are chosen to avoid the tip proximity effect and the voltage is sufficiently below the threshold for tautomerization) and the feedback loop is opened. Then (2) a short voltage pulse of 300 mV is applied for 50 ms (at the “pulse position”) and after the pulse (3) the tip is moved to the “observation position” (indicated by the red star in Fig.S2a) where the molecular configuration can be identified. (4) Identification of the tautomer state from the current value, (5) returning the tip back to the center and (6) wait for the next cycle. Figure S2c shows the concatenated current value in step (4) as a function of time (corresponding to the total pulse duration). If the pulse length is sufficiently shorter than the reciprocal

switching rate, all occurring switching events are detected in this way, which is an important condition for a precise measurement. Figure S2d shows the current histogram obtained by the repeated measurements. In agreement with the expectations above, the fractional occupation of the two states becomes equal because the yield inequality and different current intensities are cancelled at the molecular center.

5. Estimation of the error in the tautomerization yield

The yield of the tautomerization in Fig.2f was determined by a statistical analysis of the dwell time of the two states that are denoted “high” and “low” in the current trace, for instance in Fig.2c. Specifically, a more sophisticated method was used to obtain the map, which is explained in the previous section.

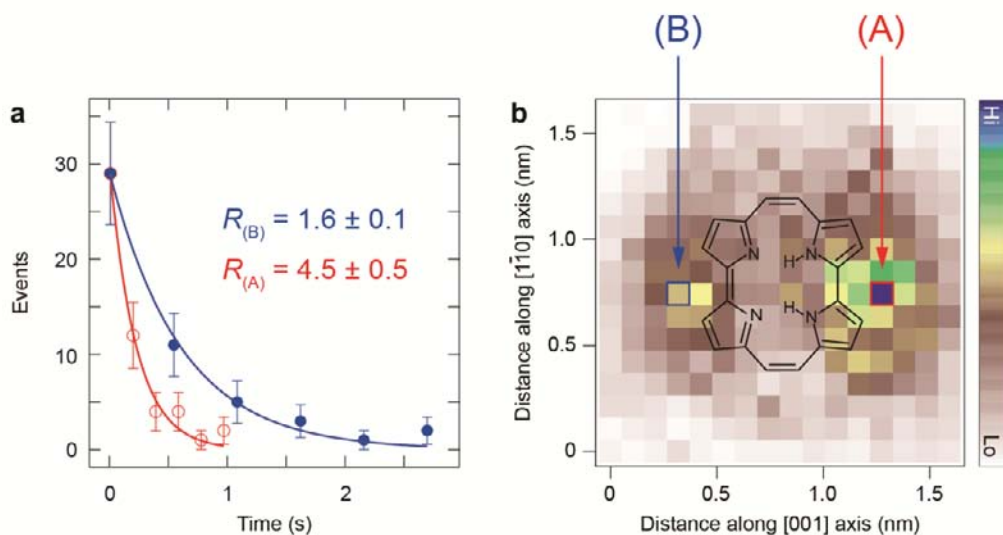


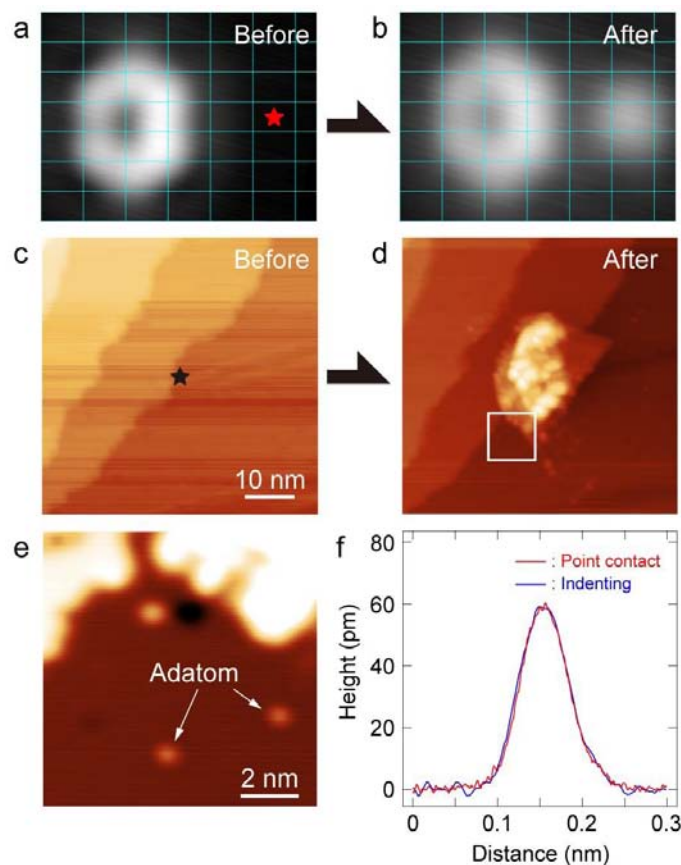
Figure S3: (a) The distribution of the dwell time at the positions (A) and (B) in (b). (b) is identical with Fig.2f.

To determine the rate, we plot the histogram (distribution) of the dwell times. Such a case is illustrated in Fig.S3a for two opposite positions over the molecule (thus reflecting the “high”→”low” and “low”→”high” transitions). The corresponding pixels are indicated in Fig.S3b. A substantial difference can be seen in the two distributions. The rate R is determined by fitting the curve to an exponential function [$A \exp(-Rt)$], that is validated in the Markov process with A and t as prefactor and time. As indicated in the figure, we estimate an error bar of around $\pm 10\%$ in the rate from the least-square approach. Additionally, there is an error (noise) in the current as seen in Fig.2c, resulting in a systematic error when calculating the yield (i.e. rate/current). However, we can ignore this as it equally affects both processes. Accordingly, the total error does not

change if we include it in our calculations.

6. Creation of single Cu adatoms

Cu adatoms were created with the STM tip by two different methods that are the soft point contact [7] and the more destructive tip indentation method [8].



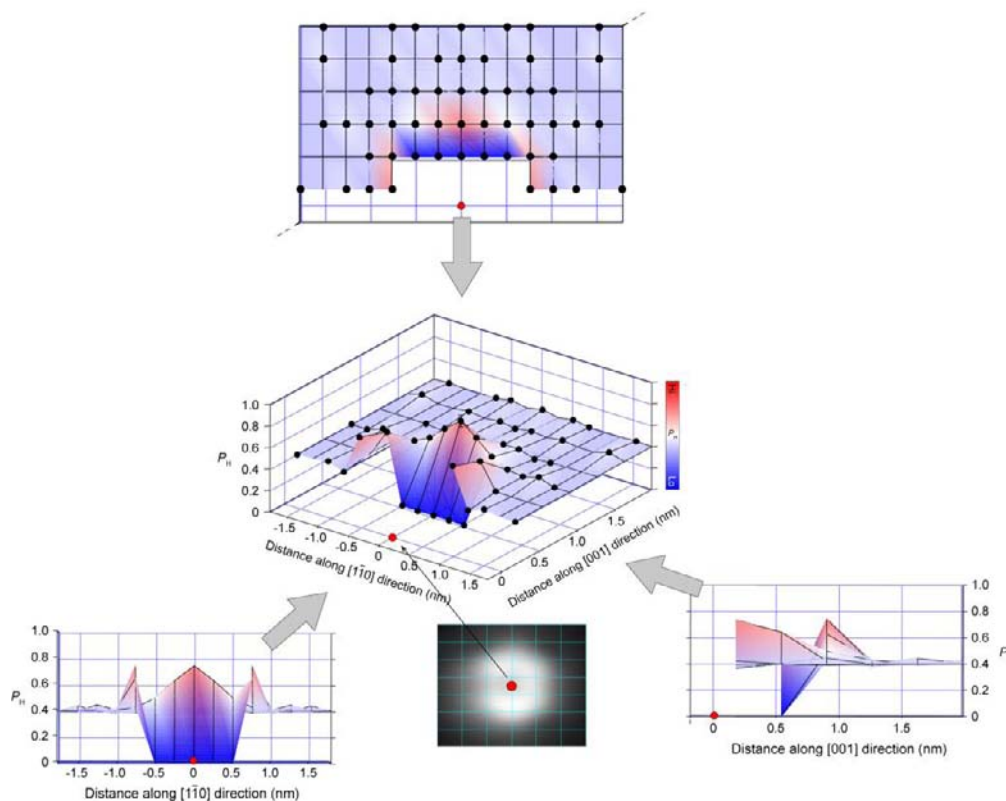
Supplementary Figure S4: (a-b) Cu adatom formation on a Cu(110) surface by the point contact method (grid lines represent the Cu(110) lattice). (c-e) Cu adatom formation by STM tip indentation into the surface (at the position of the black star). (e) STM image of a small area (white rectangle in (d)), with three individual Cu adatoms created by the process. (f) Comparison of adatom height profiles from the point contact (red) and the indentation method (blue).

In the point contact method, the tip touches the surface only slightly after a vertical approach, while the tip is crashed into the surface in the indenting method. Before both procedures, the W tip is brought in contact with the surface to improve the tip quality by covering its apex with Cu atoms. Subsequently either the point contact or the indenting method is started. Figure S4a-b show subsequent STM images during a Cu adatom creation by the point contact method. The tip was fixed over the 4-fold hollow position

of a Cu(110) surface (indicated by red star in Fig.S4a), and then the tip was approached toward the surface. After the formation of a point contact with the surface, a single Cu adatom was found there in the subsequent image (Fig.S4b).

For further confirmation, single Cu adatoms are created using the well-known tip indentation method. Typical conditions are a vertical approach of $\Delta z = 3-4$ nm from a scanning set point with an increased bias voltage of 3-4 V during the indentation. Figures S4c-e show an example where the tip is crashed into the surface (Fig.S4c) with an STM image of the same area afterwards (Fig.S4d). The modification of the surface, which can be clearly seen in Fig.S4d, is typically accompanied by single adatoms in the vicinity of the tip crash (Fig.S4e of the area indicated in Fig.S4d) as has been reported for the Ag(111) surface [8]. They exhibit a typical apparent height of about 60 pm with the height profile shape in Fig.S4f that is in perfect agreement with those created by the point contact method.

7. Occupation map as a function of the lateral adatom-molecule distance



Supplementary Figure S5: P_H map as a function of the lateral adatom-molecule distance. The black dots represent the data points that are actually measured. The red circle indicates the short-bridge site of a Cu(110) surface.

8. Calculations on the interaction between porphycene molecule and adatoms

In order to understand the behavior of the energy difference ΔE between the two mirror-symmetric orientations of the *cis-I* tautomer (corresponding to the “high” and “low” states in the presence of the adatom), we have investigated various electronic and elastic contributions to the interaction energy E_{int} between the adatom and the molecule.

		E_{int}	$E_{\text{int}}^{(\text{d})}$	$E_{\text{int}}^{(\text{rigid})}$	$E_{\text{int}} - E_{\text{int}}^{(\text{rigid})}$	$E_{\text{int}}^{(\text{rigid})} - E_{\text{int}}^{(\text{d})}$
		Total interaction energy	Interaction energy without surface (vdW)	Electronic contribution (vdW)	Elastic contribution	Substrate-related electronic contribution
I	“high”	-4	-26 (-25)	9 (-83)	-13	35
	“low”	1	-15 (-16)	16 (-72)	-15	31
II	“high”	527	-145	553	-26	698
	“low”	410	-122	414	-4	536
		ΔE	$\Delta E^{(\text{d})}$ (vdW)	$\Delta E^{(\text{rigid})}$	$\Delta E - \Delta E^{(\text{rigid})}$	$\Delta E^{(\text{rigid})} - \Delta E^{(\text{d})}$
I	“high”-“low”	-5	-11 (-9)	-7 (-11)	2	4
II	“high”-“low”	117	-23	139	-22	162

Supplementary Table S2: Calculated different contributions to the interaction energy of the Cu adatom in the configuration I and II (Fig. 4 in the main text) and for the two orientations of the cis-I tautomer corresponding to the “high” and “low” states (all energies are given in meV). The values in the parentheses are the contributions from the van der Waals (vdW) interactions as obtained here from the non-local part of the correlation energy in the optB86B functional.

The adatom is considered to be either in configuration I or II (see Fig.4 in the main text). ΔE is equal to the difference of the interaction energies between the “high” and “low” state. The electronic and elastic, respectively, contributions are obtained by calculating:

- The direct interaction energy $E_{\text{int}}^{(\text{d})} = E[\text{P}(\text{g})+\text{Cu}(\text{g})] - E[\text{P}(\text{g})] - E[\text{Cu}(\text{g})]$, where $E[\text{P}(\text{g})+\text{Cu}(\text{g})]$ is the total energy in the absence of the substrate but with the geometry of the adsorbed porphycene molecule, $E[\text{P}(\text{g})]$ is the energy of the isolated porphycene molecule in the absence of the substrate but in the equilibrium geometry of the adsorbed, isolated molecule and $E[\text{Cu}(\text{g})]$ is the energy of the Cu atom.

- The interaction energy $E_{\text{int}}^{(\text{rigid})}$, similar to $E_{\text{int}}^{(\text{d})}$ but this time with the Cu substrate atoms fixed at their original positions of the bare substrate. Structural relaxations of the Cu adatom and the porphycene molecule are allowed.

All calculated values for the various contributions to E_{int} and ΔE are shown in Table S2. The contribution $E_{\text{int}}^{(\text{rigid})}$ corresponds to the electronic interaction whereas the difference $E_{\text{int}} - E_{\text{int}}^{(\text{rigid})}$ correspond to the elastic interaction due to lattice distortion. The substrate-related electronic interaction is given by the contribution $E_{\text{int}}^{(\text{rigid})} - E_{\text{int}}^{(\text{d})}$.

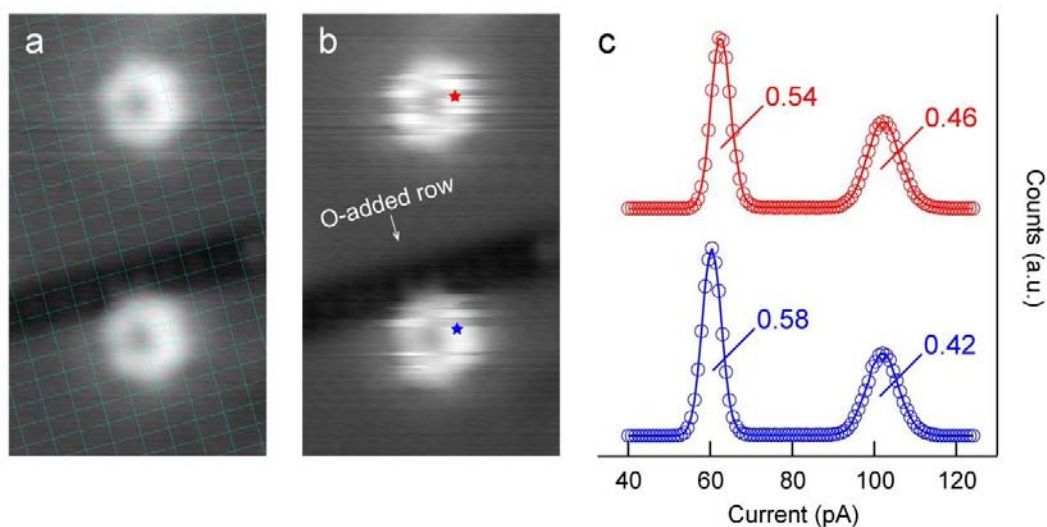
The main conclusions obtained for our analysis based on the calculated values in Table S2 are:

- The small negative value (-5meV) for ΔE of adatom configuration I shows that the “high” state is slightly favored, whereas the large positive value (117 meV) for adatom configuration II shows that the “low” state is strongly favored (as visualized in Fig.4b-c).
- ΔE of configuration I is mainly determined by the *direct* attractive electronic (mainly van der Waals) interaction but has also contributions from the *substrate-related* (attractive elastic and repulsive electronic) contributions.
- In configuration II, the interactions are dominated by the *substrate-related* electronic contributions.
- The direct interaction $E_{\text{int}}^{(\text{d})}$ (without surface) is attractive for both configurations (I and II) and is dominated by the van der Waals interaction at the large adatom-molecule distance corresponding to configuration I, which also determines the sign of ΔE . On the surface, the substrate-related electronic interaction $E_{\text{int}}^{(\text{rigid})} - E_{\text{int}}^{(\text{d})}$ makes the total electronic interaction $E_{\text{int}}^{(\text{rigid})}$ repulsive.
- The elastic interaction ($E_{\text{int}} - E_{\text{int}}^{(\text{rigid})}$) due to the copper lattice distortion is weakly attractive and gives a substantial contribution to the total energy at the large adatom-molecule distance (configuration I), while it is negligible as compared to the electronic interaction for configuration II.

9. Influence of the oxygen added-row reconstruction

Molecular clusters longer than a trimer can be found close to oxygen rows on a Cu(110) surface [9]. A molecule nearby the row is in the same adsorption site and geometry as the one on a clean terrace (Fig.S6a). It is important to note that the row does not have an influence on the tautomerization (Fig.S6b) and there is no difference in the fractional occupation of the two cis-1 states within the experimental error (Fig.S6c). This appears surprising in view of the results with single copper atoms (Fig.3), but might be

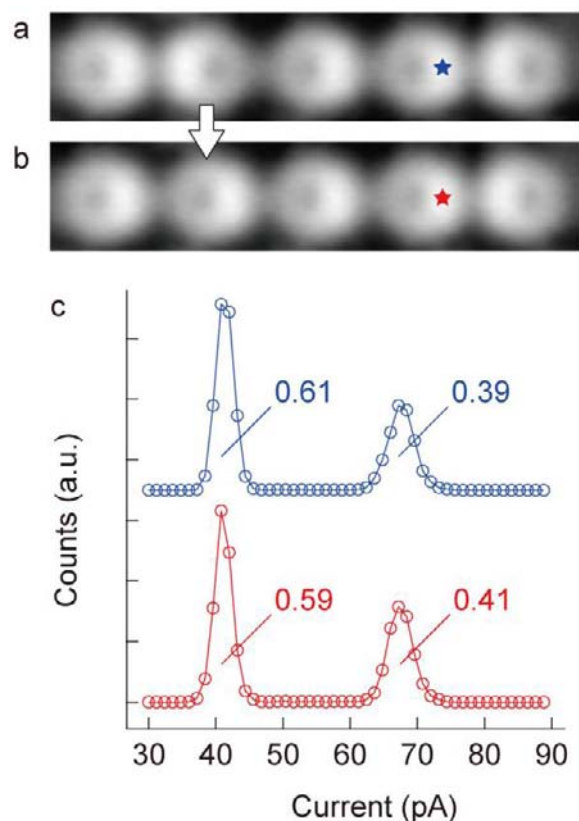
explained by a symmetry argument: The influence of the O-added row could be cancelled because the molecule is located at the middle of the row, maintaining the symmetry along the [001] direction and resulting in degeneracy of the two states (high and low). Although the symmetry along the [1-10] direction is still broken, this case might be similar to the symmetric placement of single atoms that keep the symmetry along the [001] direction (Fig.3i) – and consequently the degeneracy of the two states – and therefore leave the tautomerization rates unchanged.



Supplementary Figure S6: (a-b) Typical STM images of porphycene molecules on a Cu(110) clean terrace and located nearby oxygen added row structure (acquired at 100 mV (a) and 250 mV (b) with $I_t = 2$ nA; image size is 6.0×3.3 nm²). (c) Current histogram measured over a molecule on the clean terrace (red) and nearby the added row (blue).

10. Second neighboring molecule in molecular assemblies

After investigating the cooperative effect between adjacent molecules (Fig.5 in the main text) we also studied the cooperative effect from a second neighboring molecule in porphycene clusters. As shown in Fig.S7, a pentamer of five molecules was used for this experiment. The current histogram was measured at the second molecule from the end (indicated by star in Fig.S7a and b) while the orientation only of the second neighboring (from the left terminus) was changed (as indicated by an arrow). In the current histogram (Fig.S7c), there is no difference between the two cases, which reveals that – while the tautomer state of the direct neighbor molecules is important – the influence from the second neighboring molecules is negligible.



Supplementary Figure S7: (a-b) STM images of a pentamer (i.e. row of five molecules) where one of the molecules is switched from one *cis-1* tautomer to the other. (c) Current histogram measured over the second molecule from the end (indicated by star in (a) and (b)).

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