

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

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**Although the local environment of a molecule can play an important role in its chemistry, rarely has it been examined experimentally at the level of individual molecules. Here we report the precise control of intramolecular hydrogen-transfer (tautomerization) reactions in single molecules using scanning tunnelling microscopy. By placing, with atomic precision, a copper adatom close to a porphycene molecule, we found that the tautomerization rates could be tuned up and down in a controlled fashion, surprisingly also at rather large separations. Furthermore, we extended our study to molecular assemblies in which even the arrangement of the pyrrolic hydrogen atoms in the neighbouring molecule influences the tautomerization reaction in a given porphycene, with positive and negative cooperativity effects. Our results highlight the importance of controlling the environment of molecules with atomic precision and demonstrate the potential to regulate processes that occur in a single molecule.**

Molecular-level processes are of fundamental importance in chemistry and the atomic-scale surroundings of a molecule are known to be an essential factor as to how it functions in biological and abiological systems<sup>1–3</sup>. Rarely have changes in a molecule's local environment been examined at the single-molecule level, and so far the influence of such changes on the potential energy landscape has been identified only in ensembles of molecules, for instance by comparing the same reaction on different surfaces<sup>4</sup>. By local probing, scanning tunnelling microscopy (STM) has shown that a surface can have a substantial effect on molecular processes via reconstructions<sup>5</sup>, different surface orientations<sup>6</sup> and insulating films<sup>7</sup>. The site at which a molecule adsorbs onto a surface is known to influence its motion<sup>8</sup>, but the effect it has on the function of a single molecule has been reported only once (for changes in isomerization rates), but in that case the precise adsorption site was not known<sup>5</sup>. Moreover, atoms have been attached to molecules on a surface<sup>9–12</sup> and the molecular electronic structure modified by single atoms<sup>13,14</sup>. The influence of the local environment (as defects or other CO molecules) on the hopping of single CO molecules has been observed on a Cu(111) surface<sup>15</sup>, although so far only one study has investigated a chemical process in the vicinity of single atoms<sup>16</sup>. However, the atoms were used only to stabilize molecular switches against rotation. The influence of single atoms on a chemical reaction has not been reported to date. Here we report the control of hydrogen transfer in the inner cavity of single porphycene molecules (that is, tautomerization (Fig. 1a)) by modifying the potential landscape in a controlled way.

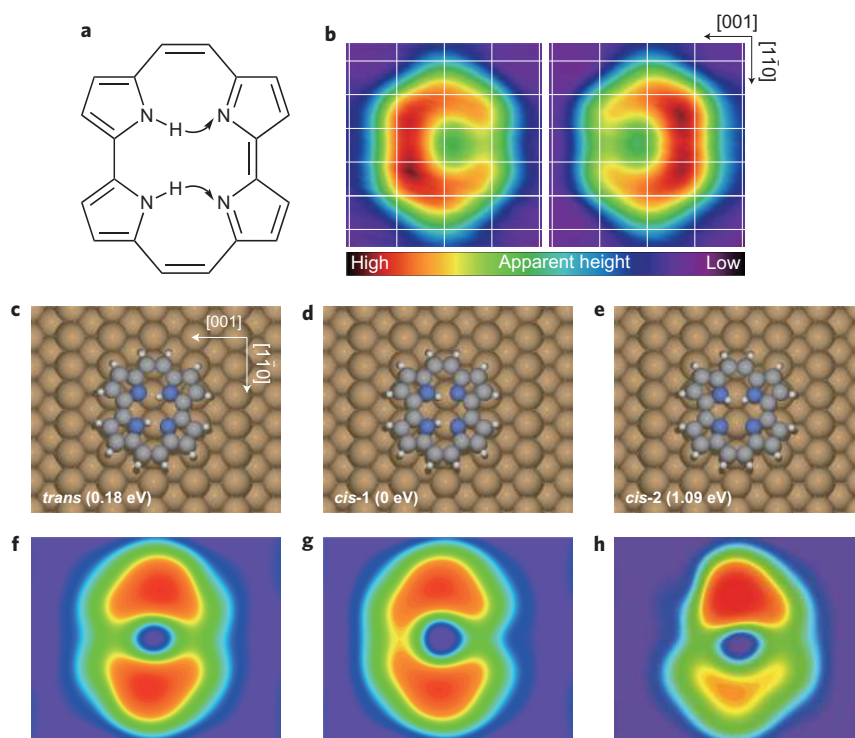
Tautomerization is associated with photochromism<sup>17</sup> and enzymatic reactions<sup>18</sup>. Furthermore, it resembles a switching process, which is a key prerequisite in molecular nanotechnology in which single molecules should act as devices<sup>19–21</sup>. Hydrogen-transfer

reactions are promising in this regard because they have been predicted to allow conductance switching along molecular chains<sup>22</sup>. Porphycene<sup>23</sup>, a planar aromatic molecule (similar to porphyrin and phthalocyanine), is an attractive candidate because the switching process occurs without significant conformational changes and is thus compatible with incorporation into molecular electronics circuits. The understanding and control of the tautomerization process requires direct observation at the single-molecule level. Low-temperature STM has been used only recently to induce such tautomerization reactions for phthalocyanine<sup>24</sup>, naphthalocyanine<sup>7</sup> and porphyrin<sup>25</sup> by electron tunnelling processes of unclear origin<sup>7,25</sup>.

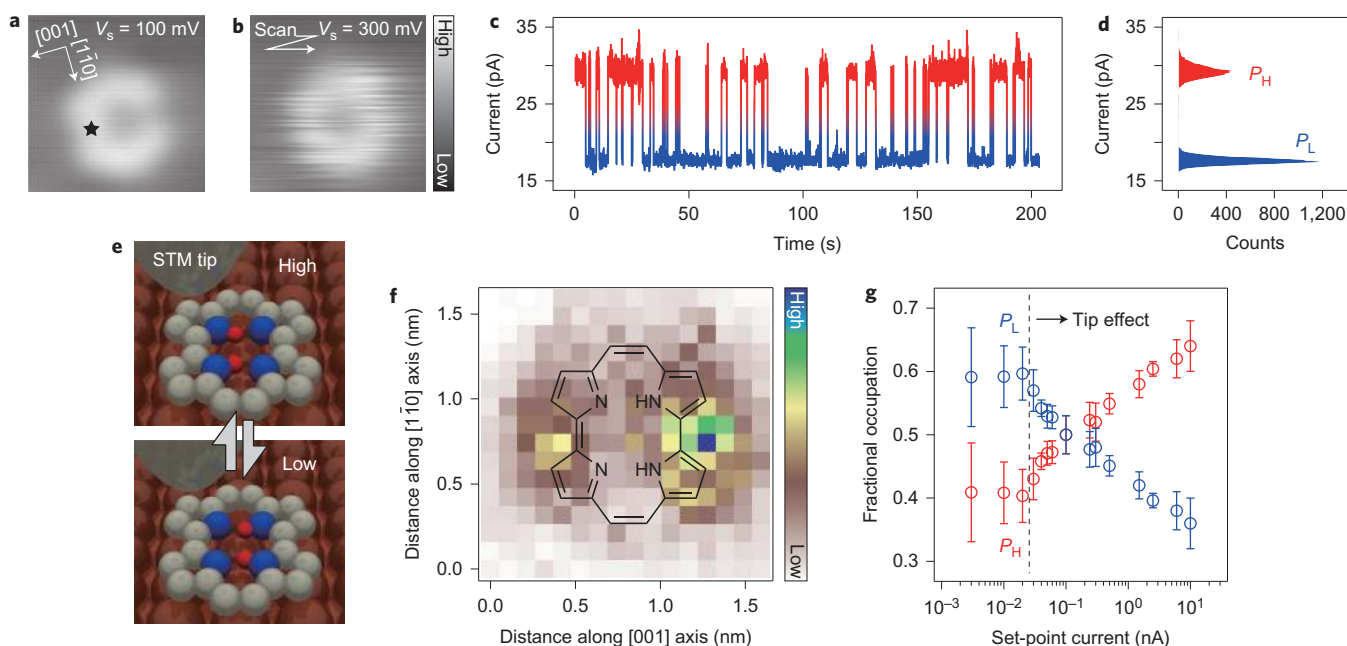
## Results and discussion

Porphycene molecules were deposited onto a Cu(110) surface at room temperature and then studied by STM at 5 K. A single molecule appeared as a crescent-shaped protrusion with the long axis in the  $[1\bar{1}0]$  direction (Fig. 1b), but no other orientation was observed. Figure 1c–e shows the density functional theory (DFT)-calculated structures and their relative energies for three porphycene tautomers, one *trans* and two *cis* configurations (that differ in the hydrogen positions in the cavity). In contrast to the gas phase, in which the *trans* is the most stable tautomer<sup>26,27</sup>, *cis*-1 was found to be the most stable because of the interaction of the non-hydrogenated nitrogen atoms with the copper row underneath (see the calculated energies in Fig. 1c–e and Supplementary Table 1). This new result is also evident in our experiments as the simulated STM image for *cis*-1 (Fig. 1g) is in very good agreement with that of the experiment (Fig. 1b) and no *trans* tautomer was ever found. Porphycene therefore adsorbs as a *cis*-1 tautomer in two mirror orientations on a Cu(110) surface.

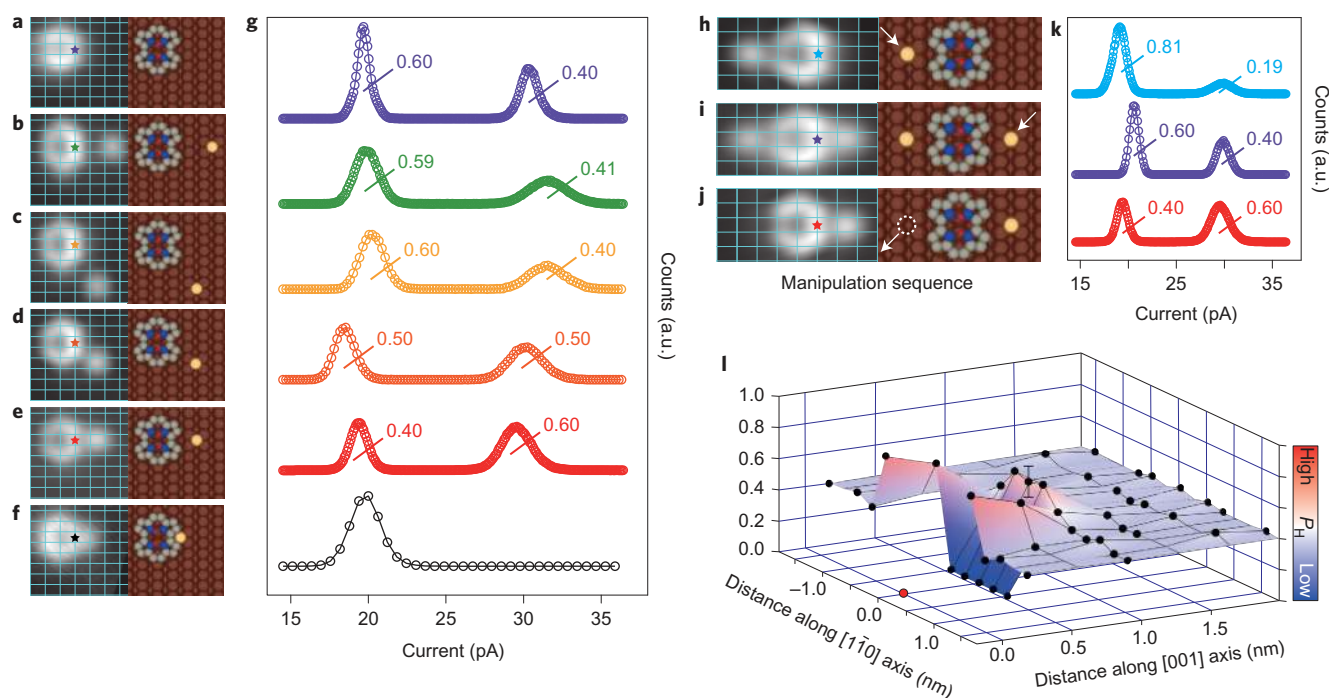
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**Figure 1 | Porphycene molecules on a Cu(110) surface.** **a**, Molecular structure of porphycene (the hydrogen transfer during tautomerization is indicated by arrows). **b**, Typical STM images (an overview is presented in Supplementary Fig. 1) of a single porphycene molecule on Cu(110) ( $1.49 \times 1.42 \text{ nm}^2$  in size;  $I_t = 10 \text{ nA}$  and  $V = 100 \text{ mV}$ ). The underlying substrate is indicated by white lines. **c–h**, Top view of the calculated optimal structures (the relative total energies are indicated) for *trans* (**c**), *cis*-1 (**d**) and *cis*-2 (**e**) configurations on Cu(110) with the corresponding simulated STM images in **f–h** (size,  $2.52 \times 2.04 \text{ nm}^2$ ).



**Figure 2 | STM-induced tautomerization of single porphycene molecules.** **a,b**, STM images of porphycene molecules on Cu(110) at different bias voltages ( $I_t = 2 \text{ nA}$ , image size  $3.24 \times 3.64 \text{ nm}^2$ ). **c,d**, Current trace during a voltage pulse of  $300 \text{ mV}$  (**c**) at a fixed tip position (black star in **a**; set point,  $100 \text{ mV}$  and  $10 \text{ pA}$ ) with the current histogram in **d**. The peak widths in **d** are caused by the experimental noise in the specific current trace. **e**, Schematics of the ‘high’ and ‘low’ states. **f**, Two-dimensional mapping of the tautomerization yield (switching events per electron) measured at  $300 \text{ mV}$  (at constant height with  $30 \text{ pA}$  and  $100 \text{ mV}$  at the position indicated in **a**). The colour scale ranges from 0 to  $8.2 \times 10^{-9}$  per electron and the error is estimated to be about  $\pm 10\%$  (see Supplementary Fig. 3). **g**, Dependence of the fractional occupations (of the ‘high’ and ‘low’ states) on the tip height, given by the set-point current (voltage set point of  $100 \text{ mV}$  and voltage pulses of  $300 \text{ mV}$ ). The tip position during the measurement is at the position indicated in **a**. The error bars correspond to the standard deviation in repeated measurements.



**Figure 3 | Controlling tautomerization by single adatoms.** **a–f**, STM images and schematics of a series of porphycene molecule and Cu adatom configurations on a Cu(110) surface. The grid lines in the STM image represent the Cu(110) surface lattice. **g**, Current histograms over a single molecule for the different adatom positions shown in **a–f**. The STM tip was fixed at the high conductance state (indicated by stars in the STM image) during the current measurement. The tautomerization rate changes with the adatom as, for the transition from the ‘high’ to the ‘low’ state, it is  $0.69 \pm 0.15$  Hz for the isolated molecule and for the large atom–molecule distances (**a–c**) and decreases to  $0.29 \pm 0.08$  Hz for the molecule with a single adatom close to it (**e**). **h–k**, Sequential STM images and schematics of the adatom manipulation (**h–j**) with the corresponding current histograms in **k**. All histograms were acquired with a voltage pulse of 300 mV (set point, 100 mV and 10 pA). **(l)**  $P_H$  map as a function of the lateral adatom–molecule distance (the origin is at the molecular centre). a.u., arbitrary units.

The molecules were imaged by STM in a stable fashion at low bias voltages (Fig. 2a), and fluctuations appeared at higher voltages (Fig. 2b), which correspond to *cis–cis* tautomerization (sketched in Fig. 2e). Tautomerization was induced purely by STM and not thermally, which occurs at much higher temperatures. We found a threshold voltage of about 150 meV for the hydrogen-transfer process that is induced by vibrational excitation of the molecule via inelastic electron tunnelling<sup>28</sup>. This switching process occurs also at step edges and in molecular assemblies, which rules out rotation of the molecules. The hydrogen transfer was monitored in real time by recording the tunnelling current during a voltage pulse, which resulted in a random telegraph noise between the two *cis-1* states (Fig. 2c). No other state was observed, which suggests that tautomerization proceeds through either a concerted motion of both hydrogen atoms (as in *trans–trans* conversions in the condensed phase<sup>29</sup>) or an intermediate *trans* configuration that is not stable enough to be captured within the STM time-resolution (about 1 ms).

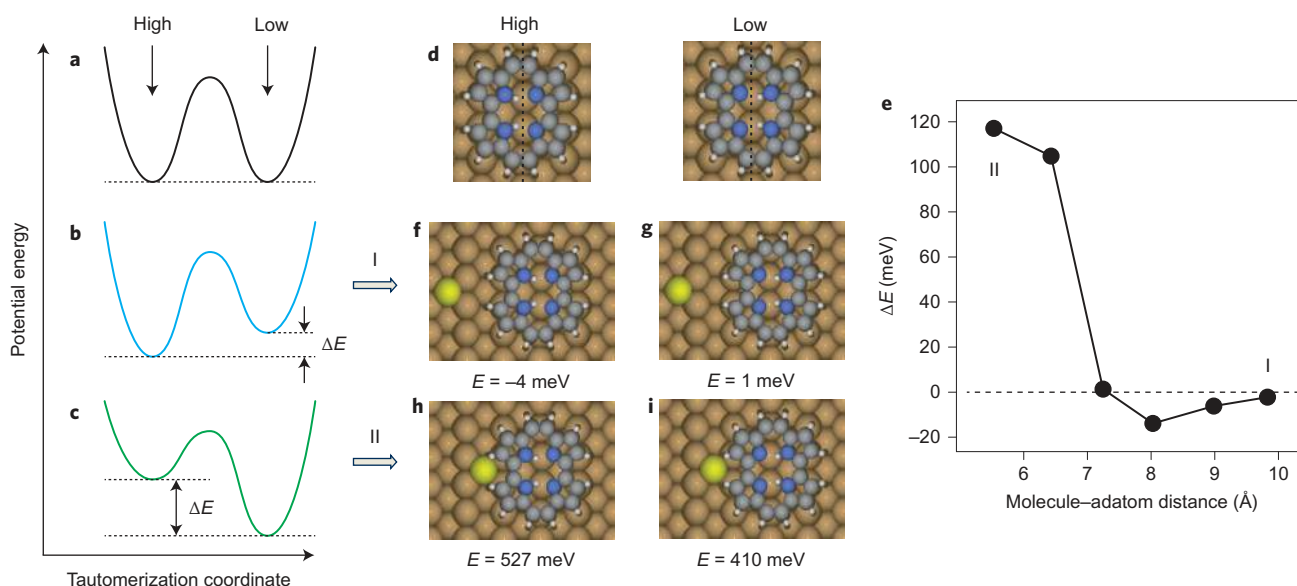
The fractional occupations,  $P_H$  and  $P_L$  (with  $P_H + P_L = 1$ ), of the two *cis-1* states are given by the peak areas in the current-trace histogram (Fig. 2d). These ‘high’ and ‘low’ conductance states correspond to the configurations in which the inner hydrogen atoms are located near to or away from the tip, respectively (Fig. 2e). Two-dimensional mapping of the tautomerization yield (only for hydrogen transfer from right to the left in Fig. 2f) exhibits peaks on both sides of the molecule, that is, at the initial and final positions of the hydrogen atoms during their transfer. Interestingly, the larger yield was measured at the right-hand side, that is the initial side of the hydrogen atoms.

All  $P_H$  and  $P_L$  values were determined at large STM tip heights where a change in the tip height does not influence the result. In this saturation regime (that is, current set points below 30 pA

(Fig. 2g)), the deviation of  $P_H/P_L$  from one means a higher transition rate from the ‘high’ to ‘low’ state than vice versa because of the inequivalent yields (that is, transition probability per electron) of the two processes (Fig. 2f) for the non-central tip position (indicated in Fig. 2a). In addition, the larger conductance of the ‘high’ state causes a higher current and therefore a higher rate from ‘high’ to ‘low’ than for the opposite direction (resulting in an increase of  $P_L$  at the expense of  $P_H$ ). Both effects were absent if the process was induced at the molecular centre, which resulted in an equal distribution,  $P_L = P_H$  (Supplementary Fig. 2). Interestingly, we found a proximity effect on the tautomerization rates when the tip was approached towards the molecule as the preference for the ‘high’ state continuously increases (Fig. 2g), similar to tip-dependent atomic<sup>30</sup> and molecular<sup>15</sup> dynamics on a metal surface.

To study the proximity effect in detail, we placed single copper atoms by STM manipulation at well-defined adsorption sites close to an individual molecule (Supplementary Fig. 3). The tautomerization was then studied via  $P_H$  and  $P_L$  of the two *cis-1* tautomers. For a molecule without an adatom (Fig. 3a),  $P_H/P_L = 0.67 \pm 0.15$  was found, which did not change when a single atom was added at a relatively large distance in various directions (Fig. 3b,c). However,  $P_H/P_L$  increased up to 1.5 when the adatom was closer to the molecule (Fig. 3d,e). Thus, the presence of a single adatom at a rather large distance of about 0.9 nm from the molecular centre is able to modify the tautomerization, although this distance is substantially larger than the van der Waals radius of a porphycene molecule (0.65 nm). When the adatom was placed at the closest position (Fig. 3f), tautomerization was almost completely quenched and the molecule remained in the ‘low’ state. The high control over the tautomerization was demonstrated in a series in which two





**Figure 4 | Potential well deformation by a single copper atom.** **a–d**, Schematic potential energy curves (**a–c**) of the tautomerization double well in which the two minima correspond to the two *cis-1* configurations ('high' and 'low'), as indicated by the calculated images in **d**. There is a slight molecular displacement of 0.02 nm to the left/right of the copper row underneath (marked by a dashed line). **e**, Calculated energy difference  $\Delta E$  of the two tautomers (that is,  $\Delta E$  is the difference in barrier heights for the 'high' and 'low' states) as a function of the adatom distance from the molecular centre. **f–i**, The adatom configurations I and II, plotted in **f,g** and **h,i**, respectively, correspond to the experimental configurations in Fig. 3e,f. The other adatom configurations are unstable and were obtained in the calculations by constraining the adatom in a plane perpendicular to the [001] direction. The molecule–adatom distance refers to the distance along the [001] direction between the adatom and the copper row beneath the adsorbed molecule. The calculated interaction energies are given below the images in **f–i**.

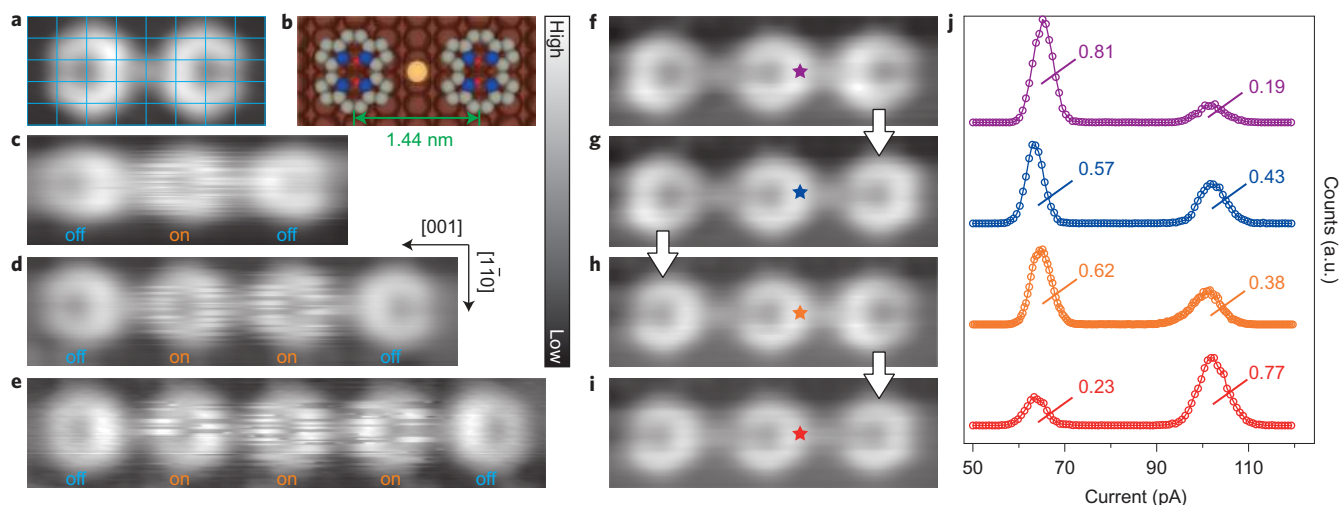
copper atoms were approached and removed from a single porphyrine molecule (Fig. 3h–j). The adatom effect on the populations vanished completely if two adatoms were placed symmetrically on both sides of the molecule (Fig. 3i), which thus compensated for each other and restored the initial  $P_H/P_L$  distribution of a molecule without an adatom.

The dependence of the tautomerization on the presence of a single adatom (Fig. 3l, see also Supplementary Fig. 4) can be rationalized by a modification of the energy barriers and consequently the hydrogen-transfer rates. To understand the adatom-induced change in tautomerization (Fig. 3), we carried out total-energy calculations of the complete surface–molecule–adatom system. In the absence of the adatom, the two states are local minima of a double-well potential and are degenerate in energy (Fig. 4a), which was proved in our experiments by equal occupations  $P_H = P_L$  if the STM tip does not influence the process (Supplementary Fig. 3). As the molecule maximizes the interaction of the nitrogen atoms (without bonded hydrogen atoms) with the copper row underneath, it is located left or right by 0.02 nm of the close-packed copper row in the two tautomers and consequently moves slightly during tautomerization (see calculated images in Fig. 4d).

From the plot of the calculated energy difference  $\Delta E$  between the 'high' and 'low' states (that is,  $\Delta E$  is the difference in barrier heights of the two states) for various adatom–molecule distances (Fig. 4e), we found that the two adsorption configurations in the experiment (I, II for Fig. 3e,f, respectively) reflected the attractive and repulsive branches of the interaction. For configuration I, a negative  $\Delta E$  reflects the smaller total energy (see values in 3e,f) for the left potential minimum (Fig. 4b) and the molecule therefore prefers the adsorption position close to the adatom, that is the 'high' tautomer state (Fig. 4f). The  $\Delta E$  of about 5 meV, although very small compared to the activation energy of about 160 meV that was determined from the Arrhenius plot of thermally induced tautomerization<sup>28</sup>, results in modified transfer rates between the two tautomers and hence a higher population of the energetically

preferred 'high' state, in agreement with the experiment (Fig. 3e). In contrast, at a very small molecule–atom distance (that is, configuration II) the opposite deformation of the double-well potential takes place (that is, the right minimum in Fig. 4c is lower than the left one) and the 'low' state is favoured (Fig. 4i), in agreement with experiments (Fig. 3f). In this case,  $\Delta E = 117$  meV is a large fraction of the activation energy, which results in an efficient quenching of the 'high' state.

Hence, placing a single atom in a specific site with respect to the molecule deforms the potential energy landscape in a characteristic manner and thus changes the internal hydrogen-transfer rate. In general, adsorbate–adsorbate interactions can have contributions from electronic interactions (either substrate related or direct interaction through space) and elastic interactions (caused by surface lattice distortions). Electronic interactions can include chemical bond formation and long-range interactions from Shockley surface states<sup>31</sup>. In our experiments, the latter are excluded as the Cu(110) surface does not exhibit such states. Moreover, a covalent bond formation can be ruled out because of the large distances of 0.45–0.49 nm and 0.23–0.24 nm between the adatom and the outer hydrogen atoms of the molecule for configurations I and II, respectively, compared to the CuH covalent bond distance of 0.15 nm (ref. 32). However, the distances for configuration II are within the range of hydrogen (agostic)-bond interactions of CH...Cu in metallo-organic complexes<sup>33</sup>. To understand the adatom-induced change in tautomerization in Fig. 3, an analysis of the calculated interaction energies (Supplementary Table 2) shows that at rather large adatom–molecule distances (configuration I),  $\Delta E$  is governed mainly by the direct attractive electronic (primarily van der Waals) interaction, but also has contributions from the surface-induced electronic and elastic interactions. The cancellation of the effect for two adatoms on both sides of the molecule (Fig. 3i) can be understood from a general symmetry argument. However, surface-related (repulsive) electronic interaction prevails at short distances (configuration II).



**Figure 5 | Cooperativity in switching single molecules within assemblies.** **a**, STM image of a porphycene dimer. The image was acquired at 100 mV and 20 nA ( $1.79 \times 2.89 \text{ nm}^2$ ). The cyan grid represents the Cu(110) lattice. **b**, Schematic of the dimer. **c–e**, STM images of a trimer ( $1.47 \times 4.33 \text{ nm}^2$ ) (**c**), tetramer ( $1.47 \times 5.70 \text{ nm}^2$ ) (**d**) and pentamer ( $1.47 \times 7.10 \text{ nm}^2$ ) (**e**) near an oxygen row (which does not influence the tautomerization; see Supplementary Fig. 7). Images were acquired at 300 mV and 1 nA to induce continuous switching. **f–j**, STM images (100 mV and 1 nA) (**f–i**) of one and the same trimer in various orientations of the termini molecules, with corresponding current histograms (**j**) acquired at 300 mV (the tip position is indicated by a star in **f–i**; set point, 100 mV and 10 pA). In **f** and **i**  $P_H$  and  $P_L$  are simply inverted because of the mirror-symmetric arrangement of the termini molecules, which proves the experimental method.

The remarkable control of the tautomerization raises the question of cooperativity<sup>1</sup>, that is the influence of neighbouring molecules. In addition to single molecules, small porphycene clusters were found after deposition close to oxygen rows that did not alter the tautomerization properties (Supplementary Fig. 5). Figure 5a shows a dimer in which each molecule exhibits the same appearance as an isolated monomer (*cis-1* state). A small protrusion is resolved between the molecules, which we tentatively assign to a copper adatom<sup>34</sup>. The adsorption site of copper atoms between two adsorbed molecules (Fig. 5a) is different from that of isolated adatoms and is caused by the additional atom–molecule interaction, similar to the adatom-mediated self-assembly of alkanethiolate molecules<sup>35</sup>.

In a dimer, the tautomerization is almost quenched, which reveals negative cooperativity. This quenching effect remains for the outer molecules in longer rows, whereas the inner molecules show continuous switching (Fig. 5c–e). To understand the cooperative influence in more detail, we studied the hydrogen transfer in the central molecule of a trimer for all (four) possible tautomer states of the two termini molecules (Fig. 5f–i). The influence of the copper adatoms is cancelled in the inner molecule, because the adatom effects compensate each other (as in Fig. 3i). Although the STM tip was always placed in the same position over the central molecule (indicated in the STM images), a clear variation of  $P_H/P_L$  is observed. This is a cooperative effect, in which the tautomerization properties are not only modified by the presence of other molecules, but even by the tautomer state of neighbouring molecules of the same species. Probably, this modification is caused by a change of the intermolecular distances and interactions from the slightly different adsorption positions of the two tautomers. Also, in longer molecular chains (Supplementary Fig. 6) the tautomerization of each individual molecule is determined predominantly by its two adjacent molecules (in the same way as in Fig. 5f–i), and the second neighbour molecules have a negligible effect.

These experiments demonstrate the high sensitivity of an elementary reaction to the exact position of individual atoms and molecules in the vicinity, which most probably is a general phenomenon and not restricted to tautomerization in porphycene. We

expect that this control over chemical reaction rates by subtle changes in the atomic-scale environment can be extended to other systems and will thus improve the understanding of fundamental molecular processes. Further tuning of molecular functions might be achieved by atomic nanostructures or intermolecular coupling that should be attractive in the quest to design molecular devices for information processing at a single-molecule level. In particular cooperative switching, in which each process is affected by the state of an adjacent molecule, seems very promising in this regard.

## Methods

Experiments were performed under ultrahigh vacuum conditions (base pressure in the  $10^{-10}$  mbar range) with a low-temperature STM (modified Omicron instrument with Nanonis Electronics). 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 copper surface. Porphycene molecules were evaporated from a Knudsen cell (at a temperature of about 450 K).

In the calculations, the relative stabilities and geometries of an isolated (gas phase) and an adsorbed porphycene molecule were determined from periodic plane-wave DFT calculations and a van der Waals density functional. The STM simulations were obtained from the calculated local density of states in the vacuum region.

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## References

- Hunter, C. A. & Anderson, H. L. What is cooperativity? *Angew. Chem. Int. Ed.* **48**, 7488–7499 (2009).
- Dunitz, J. D. Chemical reaction paths. *Phil. Trans. R. Soc. Lond. B.* **272**, 99–108 (1975).
- Harikumar, K. R. *et al.* Cooperative molecular dynamics in surface reactions. *Nature Chem.* **1**, 716–721 (2009).
- Robota, H. J., Vielhaber, W., Lin, M. C., Segner, J. & Ertl, G. Dynamics of interaction of  $\text{H}_2$  and  $\text{D}_2$  with Ni(110) and Ni(111) surfaces. *Surf. Sci.* **155**, 101–120 (1985).
- Dri, C., Peters, M. V., Schwarz, J., Hecht, S. & Grill, L. Spatial periodicity in molecular switching. *Nature Nanotech.* **3**, 649–653 (2008).
- Aleman, M. *et al.* Adsorption and switching properties of azobenzene derivatives on different noble metal surfaces; Au(111), Cu(111) and Au(100). *J. Phys. Chem. C* **112**, 10509–10514 (2008).

- Liljeroth, P., Repp, J. & Meyer, G. Current-induced hydrogen tautomerization and conductance switching of naphthalocyanine molecules. *Science* **317**, 1203–1206 (2007).
- Kim, H. W. *et al.* Control of molecular rotors by selection of anchoring sites. *Phys. Rev. Lett.* **106**, 146101 (2011).
- Yamachika, R., Grobis, M., Wachowiak, A. & Crommie, M. F. Controlled atom doping of a single C<sub>60</sub> molecule. *Science* **304**, 281–284 (2004).
- Gross, L. *et al.* Trapping and moving metal atoms with a six-leg molecule. *Nature Mater.* **4**, 892–895 (2005).
- Repp, J., Meyer, G., Paavilainen, S., Olsson, F. E. & Persson, M. Imaging bond formation between a gold atom and pentacene on an insulating surface. *Science* **312**, 1196–1199 (2006).
- Ecija, D. *et al.* Assembly and manipulation of rotatable cerium porphyrinato sandwich complexes on a surface. *Angew. Chem. Int. Ed.* **50**, 3872–3877 (2011).
- Soe, W.-H. *et al.* Manipulating molecular quantum states with classical metal atom inputs: demonstration of a single molecule NOR logic gate. *ACS Nano* **5**, 1436–1440 (2011).
- Uhlmann, C., Swart, I. & Repp, J. Controlling the orbital sequence in individual Cu-phthalocyanine molecules. *Nano Lett.* **13**, 777–780 (2013).
- Heinrich, A. J., Lutz, C. P., Gupta, J. A. & Eigler, D. M. Molecule cascades. *Science* **298**, 1381–1387 (2002).
- Nacci, C., Erwin, S. C., Kanisawa, K. & Fölsch, S. Controlled switching within an organic molecule deliberately pinned to a semiconductor surface. *ACS Nano* **6**, 4190–4195 (2012).
- Tokumaru, K., Arai, T. & Moriyama, M. Photochromism by the way of intramolecular hydrogen transfer in –N–H–N– bond. *Mol. Cryst. Liq. Cryst.* **246**, 147–149 (1994).
- Tapia, O., Andres, J. & Safont, V. S. Theoretical study of transition structures for intramolecular hydrogen transfer in molecular models representing D-ribulose 1,5-bisphosphate. A possible molecular mechanism for the enolization step in rubisco. *J. Phys. Chem.* **98**, 4821–4830 (1994).
- Joachim, C., Gimzewski, J. K. & Aviram, A. Electronics using hybrid-molecular and mono-molecular devices. *Nature* **408**, 541–548 (2000).
- Aviram, A. & Ratner, M. Molecular rectifiers. *Chem. Phys. Lett.* **29**, 277–283 (1974).
- Heath, J. R. & Ratner, M. A. Molecular electronics. *Phys. Today* **56**, May, 43–49 (2003).
- Benesch, C. *et al.* Switching the conductance of a single molecule by photoinduced hydrogen transfer. *J. Phys. Chem. C* **113**, 10315–10318 (2009).
- Vogel, E., Köcher, M., Schmickler, H. & Lex, J. Porphycene – a novel porphyrin isomer. *Angew. Chem. Int. Ed. Engl.* **25**, 257–259 (1986).
- Sperl, A., Kröger, J. & Berndt, R. Controlled metalation of a single adsorbed phthalocyanine. *Angew. Chem. Int. Ed.* **50**, 5294–5297 (2011).
- Auwärter, W. *et al.* A surface-anchored molecular four-level conductance switch based on single proton transfer. *Nature Nanotech.* **7**, 41–46 (2012).
- Kozłowski, P. M., Zgierski, M. Z. & Baker, J. The inner-hydrogen migration and ground-state structure of porphycene. *J. Chem. Phys.* **109**, 5905–5913 (1998).
- Wu, Y.-D. *et al.* Porphyrin isomers: geometry, tautomerism, geometrical isomerism, and stability. *J. Org. Chem.* **62**, 9240–9250 (1997).
- Kumagai, T. *et al.* Thermally and vibrationally induced tautomerization of single porphycene molecules on a Cu(110) surface. *Phys. Rev. Lett.* (in the press).
- Gil, M. *et al.* Unusual, solvent viscosity-controlled tautomerism and photophysics: meso-alkylated porphycenes. *J. Am. Chem. Soc.* **132**, 13472–13485 (2010).
- Stroschio, J. A. & Celotta, R. J. Controlling the dynamics of a single atom in lateral atom manipulation. *Science* **306**, 242–247 (2004).
- Bogicevic, A. *et al.* Nature, strength, and consequences of indirect adsorbate interactions on metals. *Phys. Rev. Lett.* **85**, 1910–1913 (2000).
- Ram, R. S., Bernath, P. F. & Brault, J. W. Fourier transform emission spectroscopy: the vibration–rotation spectrum of CuH. *J. Mol. Spectrosc.* **113**, 269–274 (1985).
- Castro, M., Cruz, J., López-Sandoval, H. & Barba-Behrens, N. On the CH...Cu agostic interaction: chiral copper(II) compounds with ephedrine and pseudoephedrine derivatives. *Chem. Commun.* 3779–3781 (2005).
- Haq, S. *et al.* Clean coupling of unfunctionalized porphyrins at surfaces to give highly oriented organometallic oligomers. *J. Am. Chem. Soc.* **133**, 12031–12039 (2011).
- Maksymovych, P., Sorescu, D. C. & Yates, J. T. Gold-atom-mediated bonding in self-assembled short-chain alkane-thiolate species on the Au(111) surface. *Phys. Rev. Lett.* **97**, 146103 (2006).

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### Author contributions

T.K. and L.G. conceived the experiments and discussed the results. T.K. performed the STM measurements and analysed the data. F.H., J.S., K.K. and M.P. carried out the DFT calculations. S.G. and J.W. provided the molecules. T.K., M.P. and L.G. wrote the paper.

### Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at [www.nature.com/reprints](http://www.nature.com/reprints). Correspondence and requests for materials should be addressed to L.G.

### Competing financial interests

The authors declare no competing financial interests.