

Controlling intramolecular hydrogen transfer by single atoms and molecules

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Molecular processes and functions are fundamental in nature and play a key role for molecular devices in nanotechnology. Although the atomic-scale environment of each molecule is important in chemical processes, it has only rarely been examined so far in experiments at the level of individual molecules. Here we report the precise control of intramolecular hydrogen transfer reactions in single molecules using scanning tunneling microscopy. By placing a copper adatom with atomic precision nearby a porphycene molecule, we find that the hydrogen transfer rates can be tuned up and down in a controlled fashion, surprisingly also at rather large distances. Furthermore, we extended our study to molecular assemblies where even the hydrogen arrangement in the neighbouring molecule influences the reaction, causing 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 a single-molecule function.

Molecular processes are of basic importance in chemistry and biology and the atomic-scale surroundings are known to be essential for processes in functional molecules in nature^{1,2,3}. Such local changes have hardly been examined at the single-molecule level and their

influence on the potential energy landscape was only identified in ensembles of molecules so far, for instance by comparing the same reaction on different surfaces⁴. Scanning tunneling microscopy (STM) has shown by local probing that a surface can have a substantial effect on the molecular processes via reconstructions⁵, different surface orientations⁶ and insulating films⁷. The adsorption site of a molecule is known to influence molecular motion⁸, while its role for a molecular function was reported only once for changes in isomerization rates but without knowing the precise adsorption site⁵. Moreover, atoms have been attached to molecules on a surface^{9,10,11,12} and the molecular electronic structure has been modified by single atoms^{13,14}. 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) surface¹⁵ while only one study so far has investigated a chemical process in the vicinity of single atoms¹⁶. However, the atoms were only used to stabilize molecular switches against rotation. The influence of single atoms on a molecular function has not been investigated so far. Here we report the control of hydrogen transfer in the inner cavity of single porphycene molecules (i.e. tautomerization; Fig.1a) by modifying the potential landscape in a controlled way.

Tautomerization is associated with photochromism¹⁷ and enzymatic reactions¹⁸.

Furthermore, it resembles a switching process, which is a key prerequisite in molecular nanotechnology where single molecules should act as devices^{19,20,21}. Hydrogen transfer reactions are promising in this regard as they have been predicted to allow conductance switching along molecular chains²². Porphycene²³, a planar aromatic molecule (similar to porphyrin and phthalocyanine), is an attractive candidate because the switching process occurs without strong conformational changes and is thus compatible with the incorporation into molecular electronics circuits. The understanding and control of the tautomerization process require a direct observation at the single-molecule level. Low temperature STM has only recently been used to induce such tautomerization reactions for phthalocyanine²⁴, naphthalocyanine⁷ and porphyrin²⁵ by electron tunneling processes of unclear origin^{7,25}.

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 appears as a crescent-shaped protrusion with the long axis in $[1\bar{1}0]$ direction (Fig.1b) while no other orientation was observed. Figures 1c-e show the DFT calculated structures and their relative energies for three porphycene tautomers: one *trans* and two *cis* configurations (that differ in the H positions in the cavity).

In contrast to the gas phase, where the *trans* is the most stable tautomer^{26,27}, *cis-1* is found to be most stable, due to the interaction of the non-hydrogenated N atoms with the copper row underneath (see calculated energies in Fig.1f-h and Supplementary Table S1). 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 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.

The molecules are imaged by STM in a stable fashion at low bias voltages (Fig.2a) while fluctuations appear at higher voltages (Fig.2b), corresponding to *cis-cis* tautomerization (sketched in Fig.2e). Tautomerization is purely induced by STM and not thermally which occurs at much higher temperatures (T. Kumagai *et al.*, in preparation). We find a threshold voltage of about 150 meV for the hydrogen transfer process that is induced by vibrational excitation of the molecule via inelastic electron tunneling (T. Kumagai *et al.*, in preparation). This switching process occurs also at step edges and in molecular assemblies, ruling out rotation of the molecules. The hydrogen transfer can be monitored in real time by recording the tunneling current during a voltage pulse, resulting in a random telegraph noise between the two *cis-1* states (Fig.2c). Note that no other state is observed, suggesting

that tautomerization proceeds through either a concerted motion of both hydrogen atoms (as in *trans-trans* conversions in the condensed phase²⁸) or an intermediate *trans* configuration which 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 H-atoms are located underneath 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, i.e. at the initial and final position of the hydrogen atoms during their transfer. Interestingly, the larger yield is measured at the right hand side, i.e. the initial side of the H 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 (i.e. current set points below 30 pA; Fig.2g), the deviation of P_H/P_L from 1 means a higher transition rate from the “high” to “low” state than vice versa, due to the inequivalent yields (i.e. 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 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 are absent if the process is induced at the molecular centre, resulting in an equal distribution $P_L = P_H$ (Supplementary Fig.S2). Interestingly, we find a proximity effect on the tautomerization rates when the tip is approached towards the molecule as the preference for the “high” state continuously increases (Fig.2g), similar to tip-dependent atomic²⁹ and molecular¹⁵ dynamics on a metal surface.

To study the proximity effect in detail, we placed single Cu atoms by STM manipulation at well-defined adsorption sites close to an individual molecule (Supplementary Fig.S3). The tautomerization is then studied via P_H and P_L of the two *cis*-1 tautomers. For a molecule without adatom (Fig.3a), $P_H/P_L = 0.67 \pm 0.15$ is found, which does not change when adding a single atom at a relatively large distance in various directions (Fig.3b-c). However, P_H/P_L increases up to 1.5 if the adatom is 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 is placed at the closest position (Fig.3f), tautomerization is almost completely quenched and the molecule remains

in the “low” state. The high control over the tautomerization is demonstrated in a series where two copper atoms are approached and removed from a single porphycene molecule (Fig.3h-j). Note that the adatom effect on the populations vanishes completely if two adatoms are placed symmetrically on both sides of the molecule (Fig.3i), thus compensating each other and restoring the initial P_H/P_L distribution of a molecule without adatom.

The dependence of the tautomerization on the presence of a single adatom (Fig.3l, see also Supplementary Fig.S4) 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 have done 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 is proven in our experiments by equal occupations $P_H = P_L$ if the STM tip does not influence the process (Figs.S3). 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 slightly moves during tautomerization (see calculated images in the upper left of Fig.4a).

From the plot of the calculated energy difference ΔE between the “high” and “low” state (i.e. ΔE is the difference in barrier heights of the two states) for various adatom-molecule distances (Fig.4d), we find that the two adsorption configurations in the experiment (I and II for Fig.3e and f, respectively) reflect the attractive and repulsive branches of the interaction. For configuration I, a negative ΔE reflects the smaller total energy (see values in (e-f)) for the left potential minimum (Fig.4b) and the molecule therefore prefers the adsorption position close to the adatom, i.e. the “high” tautomer state (Fig.4e). The energy difference ΔE of about 5 meV, although very small compared to the activation energy of about 160 meV determined above, 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 (i.e. configuration II) the opposite deformation of the double well potential takes place (i.e. the right minimum in Fig.4c is lower than the left one) and the “low” state is favored (Fig.4h), 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 (either substrate-related or direct interaction through space) and elastic interactions (due to surface lattice distortions). Electronic interactions can include chemical bond formation and long-range interactions from Shockley surface states³⁰. 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 due to the large distances of 0.45-0.49 nm and 0.23-0.24 nm between the adatom and the outer H atoms of the molecule for configurations I and II, respectively, compared to the CuH covalent bond distance of 0.15 nm³¹. However, the distances for configuration II are within the range of H (agostic) bond interactions of CH...Cu in metallo-organic complexes³². To understand the adatom-induced change in tautomerization in Fig.3, an analysis of the calculated interaction energies (Table S2) shows that at rather large adatom-molecule distances (configuration I), ΔE is mainly governed by the *direct* attractive electronic (primarily van der Waals) interaction but has also 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. On the other hand,

surface-related (repulsive) electronic interaction prevails at short distances (configuration II).

The remarkable control of the tautomerization raises the question about cooperativity¹, i.e. the influence of neighboring molecules. In addition to single molecules, small porphycene clusters are found after deposition close to oxygen rows that do not alter the tautomerization properties (Supplementary Fig.S5). Figure 4a shows a dimer where 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 Cu adatom³³. Note that 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 molecules³⁴.

In a dimer, the tautomerization is almost quenched, revealing 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). Note that the influence of the Cu adatoms is cancelled in the inner molecule, because the adatom effects

compensate each other (as in Fig.3i). Although the STM tip is 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, where the tautomerization properties are not only modified by the presence of other molecules, but even by the tautomer state of neighboring molecules of the same species. This modification is probably caused by a change of the intermolecular distances and interactions from the slightly different adsorption positions of the two tautomers. Note that also in longer molecular chains (Supplementary Fig.S6) the tautomerization of each individual molecule is predominantly determined by its two adjacent molecules (in the same way as in Fig.5e-h) while the second neighbor 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 is most likely 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 of designing

molecular devices for information processing at a single-molecule level. In particular cooperative switching, where each process is affected by the state of an adjacent molecule, seems very promising in this regard.

Methods Summary

Experiments were performed under ultra-high 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 Cu 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 the isolated (gas-phase) and the adsorbed porphycene molecule were determined from periodic, plane-wave density functional theory (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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Supplementary Information Methods, Figures S1-S7, Tables S1-S2

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Figure captions

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.S1) 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-e) Top view of the calculated lowest energy 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) Current trace during a voltage pulse of 300 mV at a fixed tip position (black star in (a); set point: 100 mV and 10 pA) with the current histogram in (d). The peak widths in (d) are due to 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 mV (at constant height with 30 pA and 100 mV at the position indicated in (a)). The color scale ranges from 0 to 8.2×10^{-9} /electron and the error is estimated to be about $\pm 10\%$ (see Supplementary Fig.S3). (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 mV and voltage

pulses of 300 mV). The tip position during the measurement is at the position indicated in (a).

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 different adatom positions as 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. Note that the tautomerization rate changes with the adatom as it is (for the transition from the “high” to the “low” state) 0.69 ± 0.15 Hz for the isolated molecule and for large atom-molecule distances (a-d) and decreases to 0.29 ± 0.08 Hz for the molecule with a single adatom close to the molecule (e). (h-j) Sequential STM images and schematics of the adatom manipulation 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 center).

Figure 4: Potential well deformation by a single copper atom. (a-c) Schematic potential energy curves of the tautomerization double well where the two minima correspond to the two cis-1 configurations (“high” and “low”) as indicated by the calculated images on top. Note the slight molecular displacement of 0.02 nm to the left/right of the copper row underneath (marked by a dashed line). (d) Calculated energy difference ΔE of the two tautomers (i.e. ΔE is the difference in barrier heights for the “high” and “low” states) as a

function of the adatom distance from the molecular centre. Note that adatom configurations I and II, plotted in (e,f) and (g,h), respectively, correspond to the experimental configurations in Fig.3E and 3F. 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 Cu row beneath the adsorbed molecule. The calculated interaction energies are given below the images (e-h).

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) Scheme of the dimer. (c-d) STM images of a trimer ($1.47 \times 4.33 \text{ nm}^2$), tetramer ($1.47 \times 5.70 \text{ nm}^2$) and pentamer ($1.47 \times 7.10 \text{ nm}^2$) nearby an oxygen row (which does not influence the tautomerization; see Supplementary Fig.S7). Images were acquired at 300 mV and 1 nA to induce continuous switching. (f-i) STM images (100 mV and 1 nA) of one and the same trimer in various orientations of the termini molecules with (j) corresponding current histograms acquired at 300 mV (the tip position is indicated by a star in (f-i), set point: 100 mV and 10 pA). Note that in (f) and (i) P_H and P_L are simply inverted, due to the mirror-symmetric arrangement of the termini molecules, which proves the experimental method.