Supporting information for: Remote Single-Molecule Switching: Identification and Nanoengineering of Hot Electron-Induced Tautomerization

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Analysis of tautomerization switching events

For the analysis of the switching events, we distinguished between six different molecular states which are shown in Fig. S1(a): Two stable states (1 and 2), two metastable states (3 and 4) with a lifetime of about three seconds, and two cases where the metastable state

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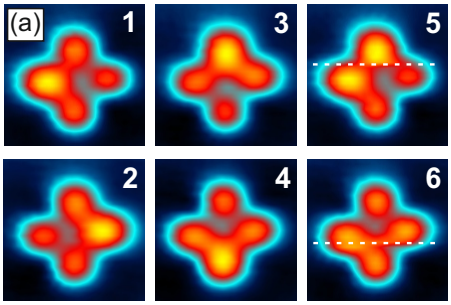

(b)

N\N+1	1	2	3	4	5	6
1	0	1	1	1	1	1
2	1	0	1	1	1	1
3	0	0	0	1	0	1
4	0	0	1	0	1	0
5	0	0	1	1	1	1
6	0	0	1	1	1	1

Figure S1: (a) Topographic images of the six different states, which were distinguished in the experiment for the analysis of the switching events: Two stable states (1 and 2), two metastable states (3 and 4) with a lifetime of about three seconds, and two cases, where the metastable states switch back to the stable state (5 and 6) while scanning the molecule (indicated by dashed white lines). (b) Successive scans ($N \rightarrow N+1$) are evaluated on the basis of this matrix. The detection of a switching event can safely be concluded only where the entry is 1. Any 0 element indicates that the molecule remained unchanged or that the switching could not safely be assigned to an STM-induced process.

switches back to a stable state (5 and 6) while scanning the molecule. Without excitation, the two stable states do not switch, whereas the metastable states switch to one of the two stable states. Based on these properties, we designed a matrix [cf. S1(b)], which is used to evaluate every two successive measurement states ($N \rightarrow N+1$). The matrix entries represent whether (1) a switching event can safely be concluded or (0) when the molecule remained unchanged or switching could not safely be assigned to an STM-induced process. The entries are derived based on the following reasoning:

- $1 \rightarrow 1$; $2 \rightarrow 2$: These observations for $N \rightarrow N+1$ are not counted as switching events since the molecule stays in the same stable state even though the occurrence of an even number of multiple switches cannot be excluded. We would like to emphasize, however, that these corrections, which scale with the square of the switching probability, will not affect the general results and conclusions for Figs. 2, 3, and 4 presented in our paper.

- $1 \rightarrow 2$; $2 \rightarrow 1$: This transition between the two stable state (1 or 2) is counted as a switching event, as this process must be induced by hot electrons and does not happen spontaneously.

- $1 \rightarrow 3,4,5,6$; $2 \rightarrow 3,4,5,6$: This transition from a stable (1 or 2) to a metastable state (3,4,5 or 6) is counted as a switching event, as this process must be induced by hot electrons and does not happen spontaneously.

- $3,4,5,6 \rightarrow 1$; $3,4,5,6 \rightarrow 2$: It does not count as a switching event if the metastable state changes to a stable state, as it is not possible to decide whether it was induced by hot electrons or occurred spontaneously due to the limited lifetime of the metastable state.

- $3 \rightarrow 3$; $4 \rightarrow 4$: It is not regarded as a switching event if the molecule is observed in the same metastable state (3 or 4) for two successive scans since we cannot exclude its survival. We would like to emphasize that these events are extremely rare and that even the complete omission of these data would not affect any of the conclusions made in our paper.

- $3 \rightarrow 5$; $4 \rightarrow 6$: Since state 5 (6) is the transition state which can not only result from a hot electron-induced process but also indicate the spontaneous decay of the metastable state 3 (4) to a stable state both observations are not counted as switching events.

- $5 \rightarrow 3$; $6 \rightarrow 4$: This observation is counted as a switching event, as the molecule is already in the stable state at the end of the measurement N (5 or 6) and has to be excited to the metastable state again for $N + 1$

- $3,5 \rightarrow 4,6$; $4,6 \rightarrow 3,5$: If a hydrogen is positioned on one of the metastable arms and switches to the other metastable arm, it is counted as a switching event, as there must have been an excitation process to switch the proton to the other metastable arm. Without excitation the metastable state switches only to stable states.

- $5 \rightarrow 5$; $6 \rightarrow 6$: These two observations are counted as switching events as the decay of a metastable state has been imaged (N). The detection of the same state in the subsequent scan ($N + 1$) implies that there occurred a hot electron-induced excitation process in the time between the two scans.

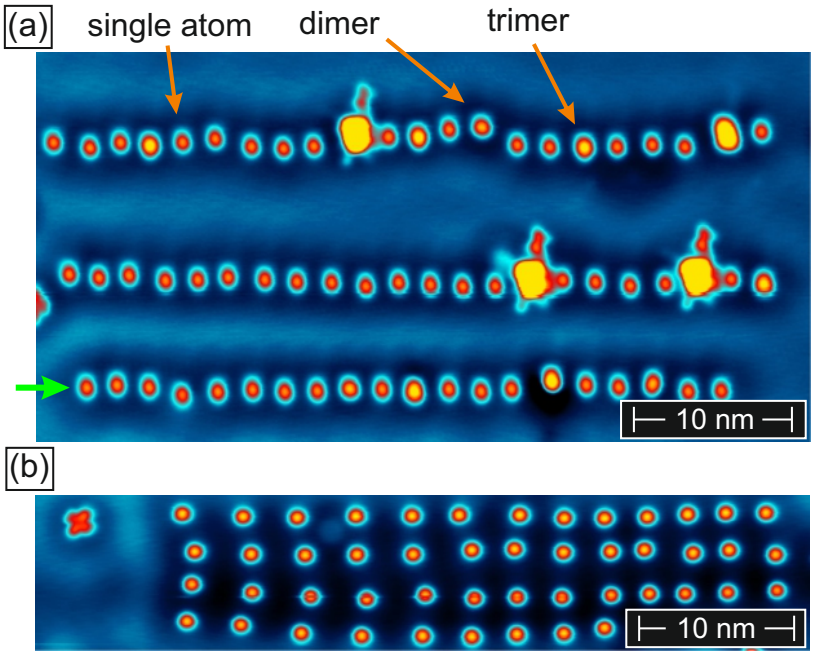

Figure S2: (a) Topographic image of the silver atom production showing lines of single silver atoms, dimers, trimers and bigger clusters, which were produced by an automatized dipping procedure. (b) Silver atom storage built by moving single silver atoms to a clean surface location.

Production of silver adatoms

To produce single silver atoms we used an automatized procedure similar to the one proposed by Limot and co-workers,[1] based on the following steps:

1. Positioned the STM tip over a clean area on the surface at the stabilization parameters $U = 1.0\,\mathrm{V}$ and $I = 0.5\,\mathrm{nA}$.

2. Save the actual z-position (z_i) of the tip.

3. Approach the STM tip by $z_{\mathrm{step}} = 550\,\mathrm{pm}$ towards the Ag(111) surface after deactivation the feedback loop. Stay here for 500 ms.

4. Turn on the feedback loop and measure the new z-position at the same stabilization parameters mentioned above.

(a) If the new z-position (z_{i+1}) as compared to the previous value z_i fulfills the requirement $|z_{i+1} - z_i| < 20\,\mathrm{pm}$ the penetration depth is increased by 5 pm, i.e., $z_{\mathrm{step,new}} = z_{\mathrm{step,old}} + 5\,\mathrm{pm}$), and the iteration starts again at point 3.

(b) If $|z_{i+1} - z_i| \geq 20\,\mathrm{pm}$: The tip has dropped at least one single atom.

To produce more than one single atom, the tip is laterally moved 2 nm away and the atom production procedure described above is repeated, resulting in a line of single atoms and some silver clusters as can be seen in Fig. S2(a) (marked by green arrow). Afterwards, the single atoms were moved with the STM tip to a new place on the surface to form a silver atom storage [cf. Fig. S2(b)]. For moving the atoms we used a bias voltage $U = 20\,\mathrm{mV}$ and a tunneling current $I \approx 1.3\,\mu\mathrm{A}$.

$\mathrm{d}I/\mathrm{d}U$ analysis of the double slit

In order to analyze if the standing wave pattern formed by the surface electrons might be responsible for the experimentally observed trend in the switching probability [cf. Fig. 4(e)], we measured a topographic STM image [Fig. S3(b)] and the corresponding $\mathrm{d}I/\mathrm{d}U$ map [Fig. S3(a)] around a double slit. A molecule was positioned on the right side of the double slit, which scatters electronic states and leads to a circular interference pattern, thereby emulating the effect of hot electrons injected by an STM tip. A line profile of the $\mathrm{d}I/\mathrm{d}U$ signal (green line) was extracted from the area on the left side of the double slit, i.e., far away from the wall and the molecule. In Fig. S3(c) this $\mathrm{d}I/\mathrm{d}U$ signal (green data points) is compared with the switching probability already presented in Fig. 4(e) of the main text. Obviously, the $\mathrm{d}I/\mathrm{d}U$ signal cannot account for the features observed in the experiment. The switching probability shows a minimum at a distance of $s \approx 2\,\mathrm{nm}$ and a maximum at $s \approx 4\,\mathrm{nm}$, whereas the $\mathrm{d}I/\mathrm{d}U$ signal has its minimum at a distance of $s \approx 3\,\mathrm{nm}$ and a maximum at $s \approx 6\,\mathrm{nm}$. Therefore we conclude that the local density of states behind the double slit is not responsible for the main trends observed for the switching probability.

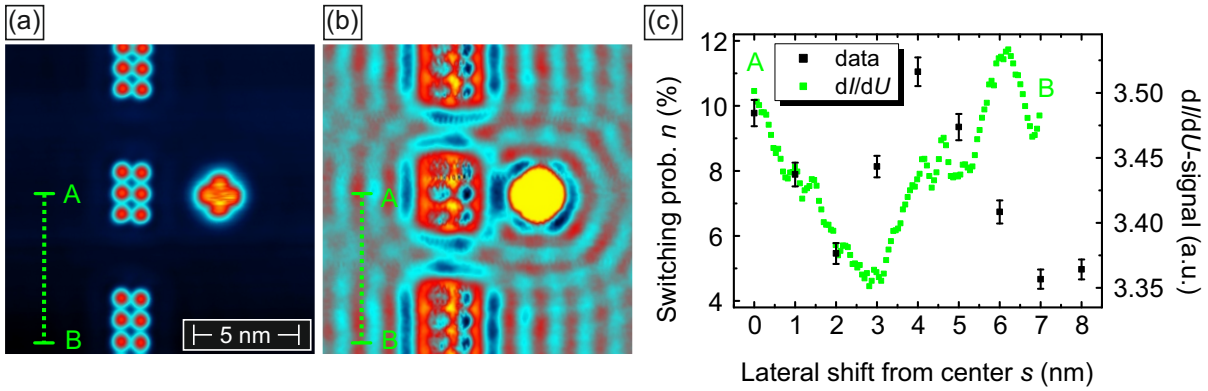

Figure S3: (a) Topographic image of the double slit and (b) $\mathrm{d}I/\mathrm{d}U$-map taken at the same location as (a) (scan parameters: $U = 0.5\,\mathrm{V}$, $U_{\mathrm{mod,rms}} = 20\,\mathrm{mV}$, $I = 0.5\,\mathrm{nA}$). (c) A line profile of the $\mathrm{d}I/\mathrm{d}U$-signal [green line in (a),(b)] is compared with the switching obtained for the molecule sitting at different positions behind the double slit.

Nevertheless, a certain influence of the $\mathrm{d}I/\mathrm{d}U$ signal on the switching probability cannot strictly be excluded.

Adsorption site of the dehydrogenated H_2Pc molecule

We analyzed the adsorption site of the dehydrogenated H_2Pc molecule by utilizing an elliptical quantum corral (cf. Fig. S4), where we adjusted an atom lattice over the complete image so that all the adsorbed silver atoms are lying on fcc or hcp sites. The lateral spacing of this lattice was furthermore checked by atomic resolution images (not shown). By this method, we could show that the dehydrogenated H_2Pc molecule sits on bridge site, with the arms pointing into the $[0\bar{1}1]$ and $[2\bar{1}\bar{1}]$ direction.

References

(1) Limot, L.; Kröger, J.; Berndt, R.; Garcia-Lekue, A.; Hofer, W. A. *Phys. Rev. Lett.* **2005**, *94*, 126102.

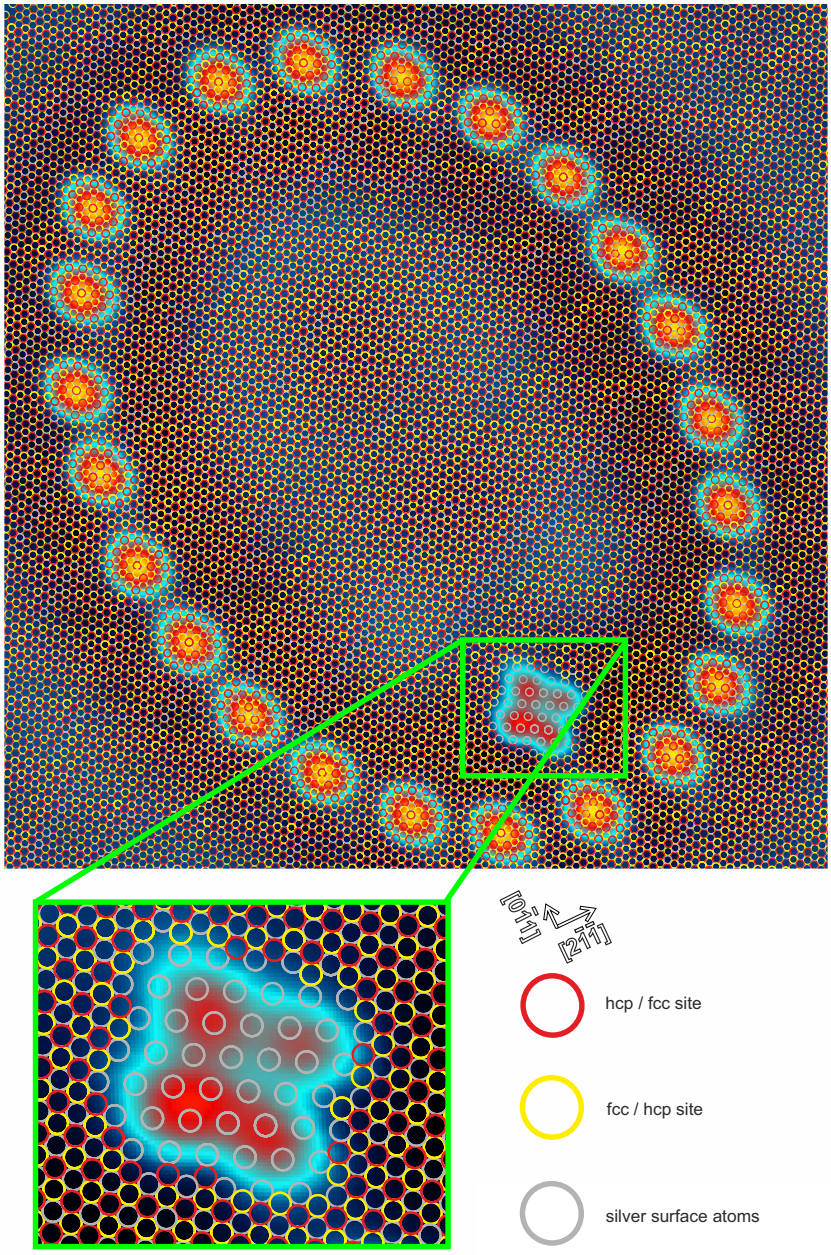

Figure S4: Elliptical nanostructure build from single Ag Atoms overlaid with the lattice, showing surface silver atoms (gray rings) and the different adatom sites (red & yellow rings). Note that hcp and fcc sites cannot be definitely identified in our experiments. A magnification of the area around the molecule (green rectangle) reveals that the molecule sits on bridge site, with the arms pointing into the $[0\bar{1}1]$ and $[2\bar{1}\bar{1}]$ direction.