

Supporting Information

Reversible Photoswitching and Isomer-Dependent Diffusion of Single Azobenzene Tetramers on a Metal Surface

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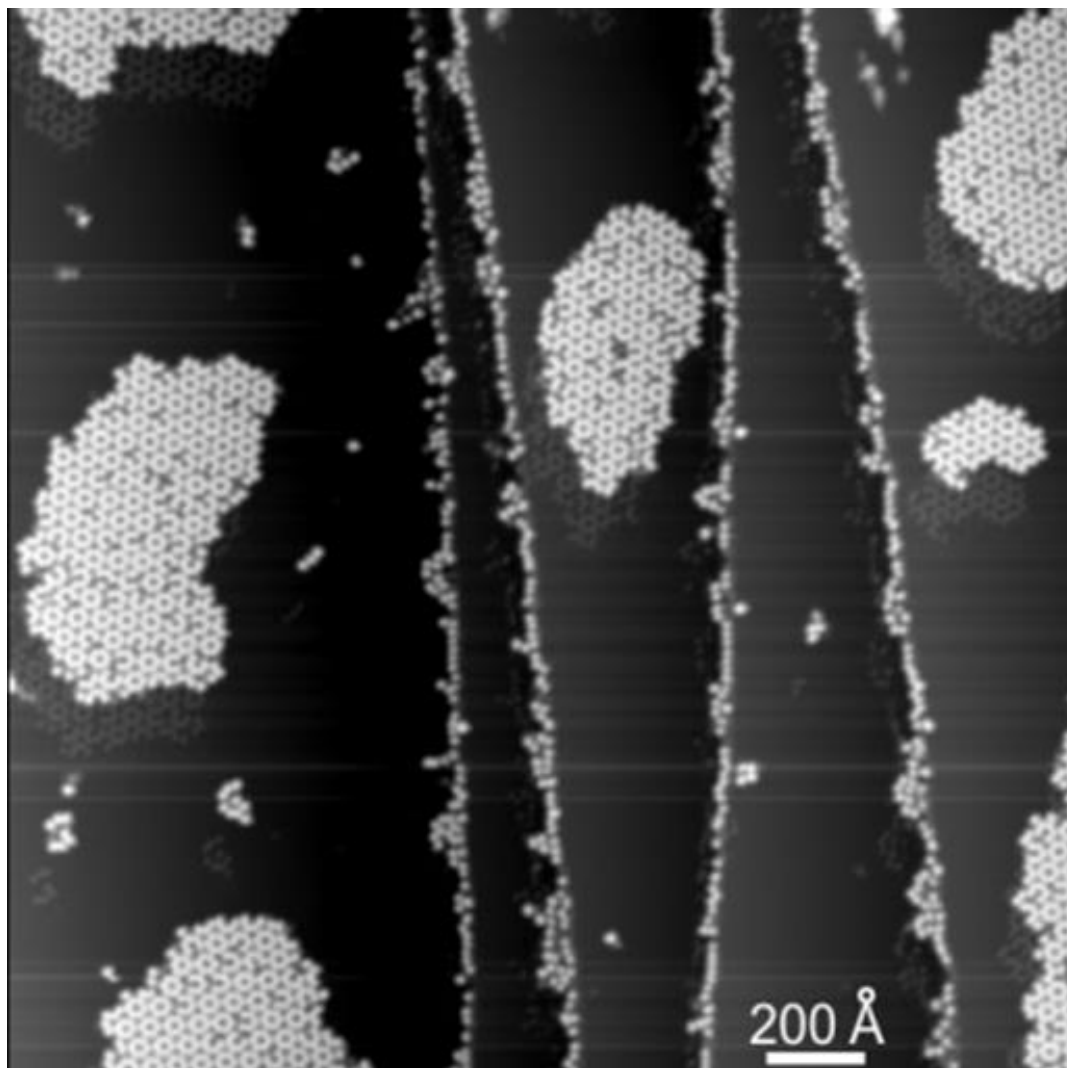
Tetra-azo islands on Ag(111)

Figure S1: Tetra-azo islands formed on Ag(111). STM overview image ($2175 \text{ \AA} \times 2175 \text{ \AA}$, 1 V, 10 pA) of tetra-azo islands on a Ag(111) surface.

Depositing tetra-azo molecules on Ag(111) kept at room temperature results in the formation of small and large islands (Fig.S1). All the surface steps are fully decorated with molecules. Molecular clusters consist mainly of 'bright' species: 'bright' ('dark') species have a relative abundance of 79% (21%).

Apparent height vs bias voltage

The apparent height of both species is determined from height profiles extracted from STM images (see Fig.1f in main text and Fig.S11) at different sample bias voltages. The apparent height of 'bright' and 'dark' species does not reveal any significant change over various bias voltages (Fig.S2).

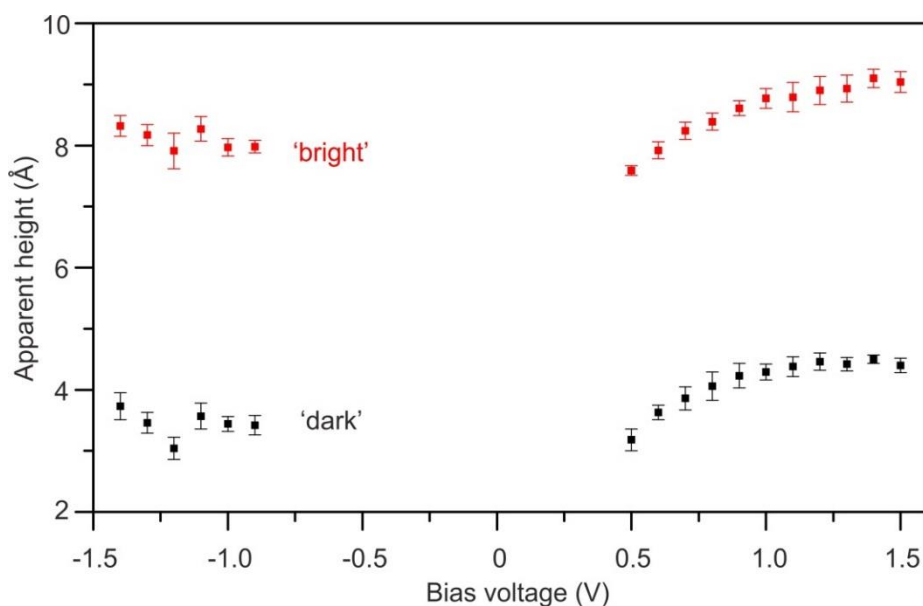


Figure S2: Tetra-azo apparent height vs. bias voltage. Apparent height of tetra-azo molecules in the 'bright' and 'dark' state as a function of the applied sample bias voltage. Each apparent height point in the plot is a value averaged over several (about 10) height measurements, the standard deviation is taken as error. A set point tunneling current of 3 pA was used.

Chirality of tetra-azo hexamers

Hexamer rings are chiral superstructures of which both handednesses are observed (Fig.1g and h, respectively), which appear with about equal abundance on the surface. After switching many molecules to the 'dark' state (Fig.S3a-b) the chirality of hexamer structures can be studied more easily. In about half of the cases it is found that the hexamers within an island all have the same chirality (indicated by arrows in Fig.S3a). On the other hand, neighboring hexamers with different chirality within the same island are also observed (see Fig. S3b), also in about half of the cases.

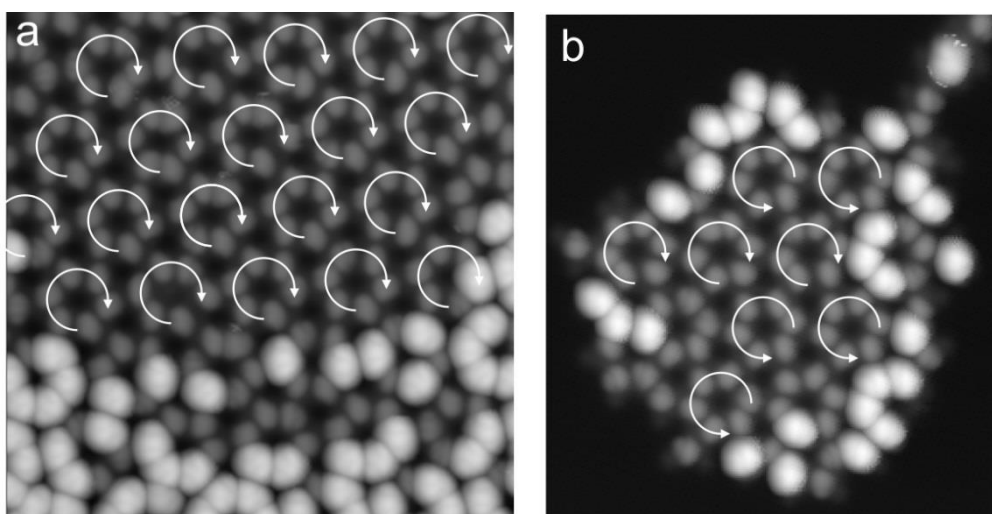


Figure S3: Chirality of tetra-azo hexamers. (a-b) STM images of tetra-azo islands where most molecules were switched before to the 'dark' state for easier characterization of the chirality. Only one handedness only is present in (a) while both are identified within the same cluster in (b).

Adsorption geometry

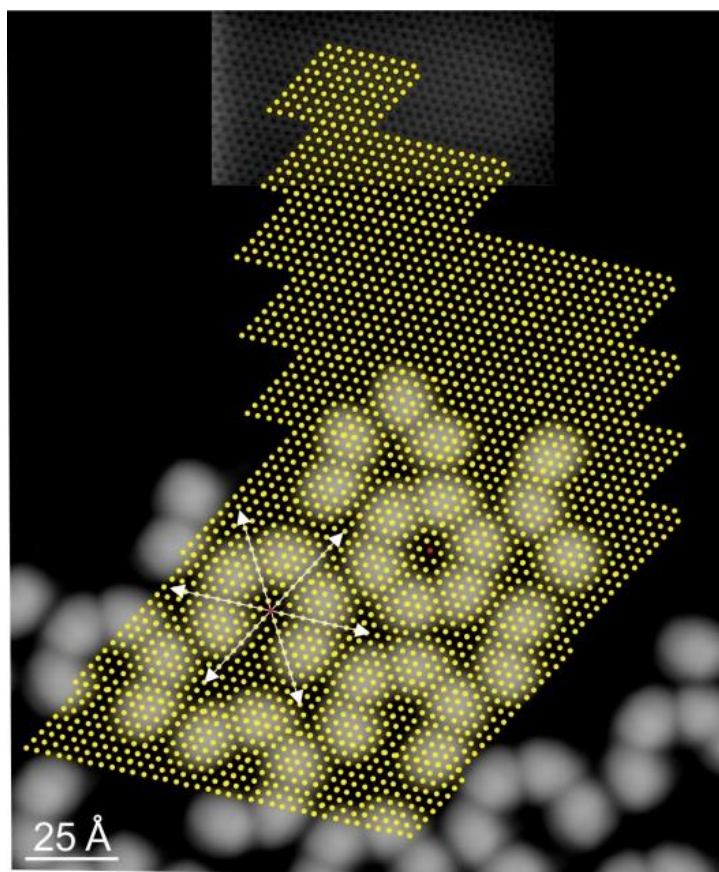


Figure S4: Adsorption geometry of tetra-azo molecules on Ag(111). STM image of a molecular island on Ag(111). A clean Ag(111) surface area nearby a tetra-azo cluster is atomically resolved (on top of the image). This surface lattice is then used to determine the adsorption geometry of tetra-azo molecules in the lower half of the image. High-symmetry directions of the surface are indicated by arrows.

The precise adsorption geometry of tetra-azo molecules is determined with the help of atomically resolved images of the Ag(111) surface. Figure S4 shows a larger area of the same surface area as in Fig.1c. After identifying a tetramer cluster and its surrounding area, a small area ($92 \text{ \AA} \times 47 \text{ \AA}$) far from the tetramer cluster – on top of Fig.S4 - has been imaged with atomic resolution (set point: 50 mV, 2.1 μA). Starting exactly from the same point, a larger image (Fig.S4) has been taken subsequently at larger tip height (set point: 0.7 V, 20 pA). Superimposing both images allows extending the resolved Ag lattice to the area occupied by the tetramer cluster and accordingly, to identify the adsorption geometry of individual molecules and the hexamer orientation with respect to the underlying substrate surface.

Tripod linkers

The tripod linkers, i.e. the tetramer arms that are adsorbed on the surface, become visible by using an enhanced contrast for the STM images. Figure S5 shows an STM image (similar to Fig.1e in the main text) of a molecular island of hexamers where these linkers are visible as green lobes. Their arrangement is in agreement with the suggested assembly (Fig.1d).

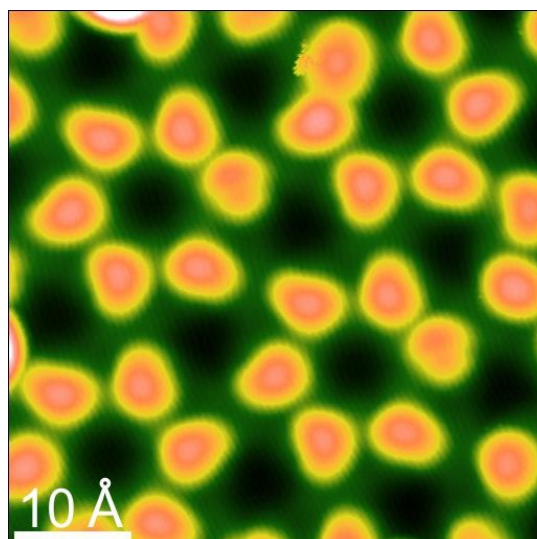


Figure S5: Tripod linkers in a molecular island. STM image ($92 \text{ \AA} \times 92 \text{ \AA}$, 0.7 V , 20 pA) of an internal area of a molecular cluster with enhanced contrast to visualize the tripod linkers.

Apparent height profiles

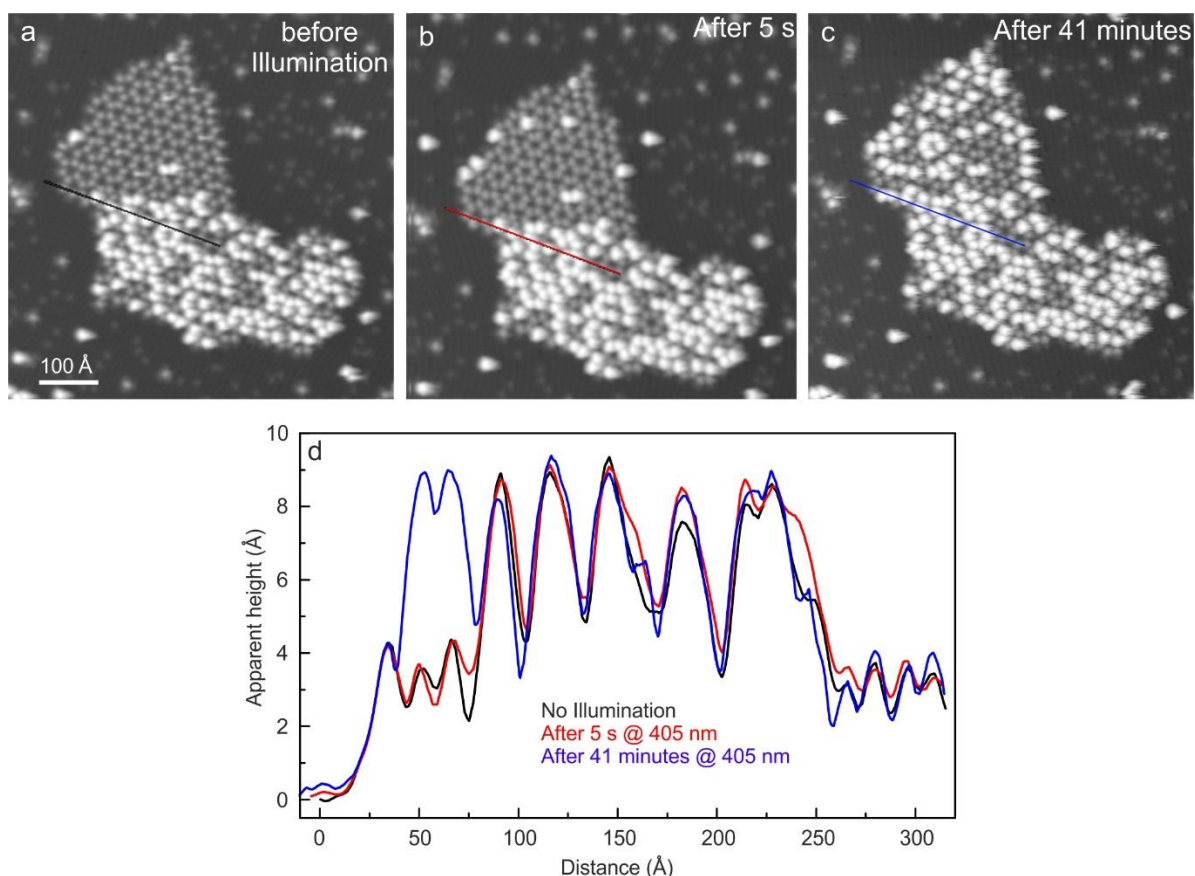


Figure S6: Tetra-azo apparent height after illumination. STM images (all 1 V , 5 pA , $650 \text{ \AA} \times 650 \text{ \AA}$) of tetra-azo molecules on Ag(111). (a) After molecule deposition (before illumination) and after switching the molecules in the upper half of the island in a controlled manner to the 'dark' state by the STM tip. (b-c) The exactly same surface area after exposure with 405 nm laser light for $t = 5 \text{ seconds}$ (b) and 41 minutes (c). (d) Apparent line profiles taken before and after illumination along the lines indicated in a-c.

A comparison of the apparent height profiles (d) taken across the directions shown in panels a-c does not reveal any significant change of the apparent height of ‘dark’ and ‘bright’ species before and after illumination. While the azobenzene unit protruding away from the surface is photo-isomerized, the adsorbed azobenzene tripod legs do not switch as the molecular order within the islands is unaffected by light (Fig.S6).

Laser light sources

Laser parameters: (1) $\lambda = 405$ nm, CW, 3.72 mW, ~ 0.18 mm² spot size; The power density is 2.07 W/cm² corresponding to a total photon density of 4.21×10^{18} s⁻¹cm⁻². (2) $\lambda = 532$ nm, CW, 4.11 mW, 0.22 mm² spot size. The power density is 1.87 W/cm² corresponding to a total photon density of 4.82×10^{18} s⁻¹cm⁻².

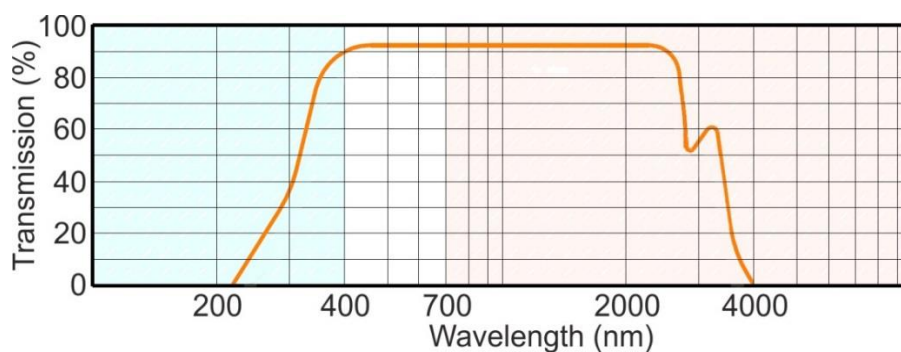


Figure S7: Kodial UHV viewport – Transmission curve. Transmission curve as a function of the wavelength of the viewport laser entrance (Vab GmbH). The transmission factor is about 93% at 532 nm and 90 % at 405 nm.

Laser illumination was performed in situ with optical access to the sample for both incident and reflected beams (angle of incidence approximately 60° to the surface normal) through outer Kodial viewports (Fig.S7) and internal STM lens made of MgF₂-coated quartz (transmission coefficient T= 98 % within 400-700 nm).

Light-induced switching

The tetra-azo clusters consist of bright (*trans*) and dark (*cis*) species that reversibly switch either remotely by light or locally by the STM probe. Figure S8 shows a detailed analysis of one and the same island during a complete switching cycle (similar to the light-induced switching shown in Fig.2 of the main text). After irradiation at 532 nm only few tetra-azo remain in the *trans* state (Fig.S8b). Upon illumination at 405 nm the tetra-azo molecules are switched back to the *trans* state (Fig.S8c). Not all of them, however, reach the *trans* state, presumably because 405-nm light can also trigger the *trans*-to-*cis* transformation; in other words, a *trans/cis* photostationary mixture is obtained (with a ration of about 90:10 for N_{trans}/N_{cis} as visible in Fig.2e), as usually observed for azobenzene derivatives. Note that many of the molecules that are switched to the *trans* state in this second step

were already in the *trans* state at the beginning (Fig.S8a). However, some of them were initially in the dark *cis* state as indicated by red arrows in Fig.S8a and c.

By analyzing many experiments we find that about 25% of the molecule never switch but always remain in the dark (*cis*) state. These species (which are excluded from the statistics of Fig.2d-e) could either have undergone an irreversible chemical transformation (e.g., reduction or oxidation of the azo moiety) or interact with the surface in a different way. Unfortunately our present data prevent us from elaborating further on this aspect.

Furthermore, we do not have any evidence for light-induced molecular decomposition on the surface. We repeated several illumination experimental runs, each one consisting of several tens of irradiation cycles with exposures from few seconds up to several hours. We also used different wavelengths within the same experimental run (405 nm and 532 nm) for the reported reversible light-induced isomerization and found that the molecules keep isomerizing by light (and also by STM manipulation) in a constant manner during these cycles and the molecular appearances remain always the same. On the other hand, we did not observe significant isomerization at 630 nm, 680 nm and 780 nm.

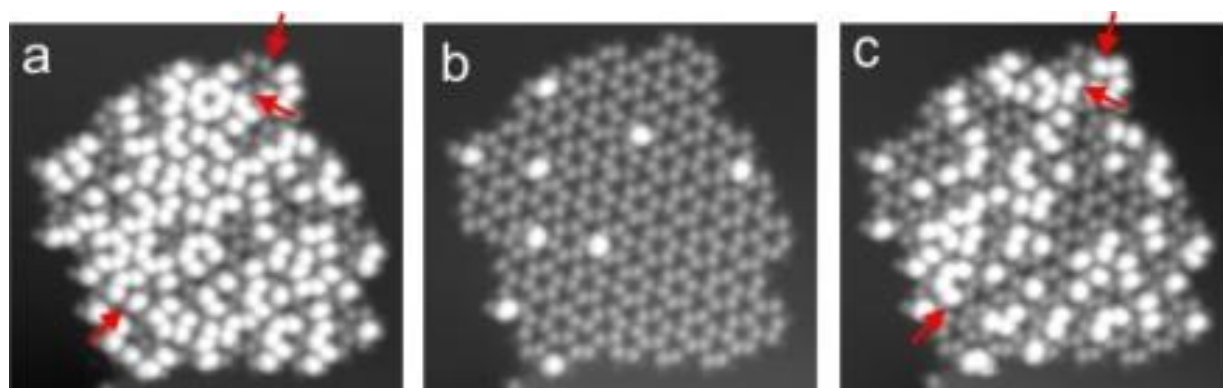


Figure S8: Light-induced tetra-azo switching cycle *trans-cis-trans*. (a-c) STM images of one and the same tetra-azo island on Ag(111). (a) Before illumination. (b) Molecules are switched after illumination at 532 nm for 30 minutes. (c) Illumination at 405 nm for 10 minutes results in isomerization of many molecules back to the bright *trans* state. The arrows indicate particular molecules (see text).

Switching by STM manipulation

The upright standing azobenzene units can be reversibly isomerized by applying voltage pulses with the STM tip. Taken an area within a cluster with all molecules in dark (*cis*) state (panel a), the tip is positioned on top of a single tetramer (see cross in panel a) and a bias voltage (of max. ± 2 V) is applied. By this procedure, the upright standing azobenzene unit of the same tetramer has been first switched from dark-to-bright (Fig.S9a-b) and then switched back (see cross in panel b) to the dark state (Fig.S9b-c). Hence, a complete reversible *cis – trans – cis* isomerization cycle is realized with one and the same molecule.

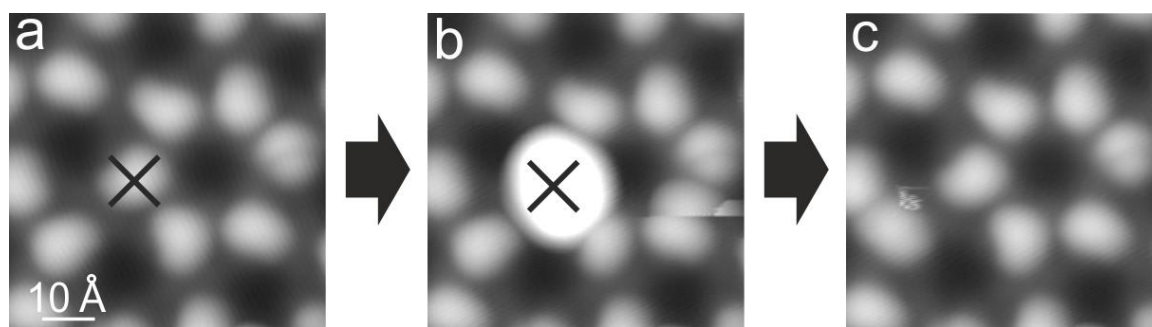


Figure S9: Complete cycle of tetra-azo switching by STM manipulation. (a-c) STM images ($60 \text{ \AA} \times 60 \text{ \AA}$, 1 V, 6 pA) of an internal area of a molecular island. Initially all molecules are 'dark' (a), then one molecule (marked by a cross) is switched with a voltage pulse to the 'bright' state (b) and subsequently switched back to the 'dark' state (c) by another pulse.

Diffusion of *trans* species at different tip heights

Figure S10 shows STM images taken at different tunneling currents (between 1 and 25 pA) while keeping the bias voltage (1 V) constant, thus changing the tip height over the surface and thus its potential tip influence on the molecular motion by direct interatomic forces. It can be seen that the bright *trans* species can always diffuse across the surface when they are adsorbed as isolated entities or at an island edge and they move roughly from top to bottom, thus following the scanning direction. For higher currents (Fig.S10a-b) these lines of diffusing molecules become rather straight (i.e. vertical in the images), which indicates the increased interaction with the tip. Hence, these molecules move under the influence of the STM tip.

On the other hand, the dark *cis* species were never found to move, even if they are located at island edges. Since this behavior (mobile *trans* and immobile *cis*) is valid for all used tip heights (i.e. tunneling currents), we believe that it is mainly the molecule-surface interaction that causes the different in the isomer-dependent mobility. However, the tip-molecule interaction certainly plays a role for the dislocation of the *trans* species, but it is not clear whether this is sufficient to cause the isomer-dependent difference. In other words: It appears reasonable to conclude that also without a tip the different isomers would diffuse differently, but a proof of this conclusion requires experiments without a local probe.

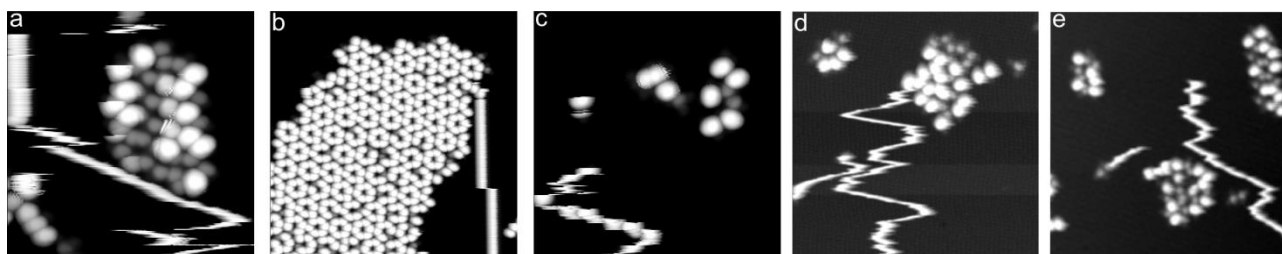


Figure S10: Tetra-Azo diffusion as a function of the tunneling current. STM images taken at different set points (bias voltage is always 1 V): 25 pA (a), 10 pA (b), 6 pA (c), 2 pA (d) and 1 pA (e). The STM images were taken by scanning in horizontal lines from top to bottom.

State of the surface-adsorbed tetra-azo legs

Various reasons let us conclude that the surface-adsorbed tetra-azo legs are likely in the *trans* state. First, the *trans* state is the energetically most stable form in the gas phase [1] and in the solid state [2]. Second, azobenzene derivatives adsorb on various metal surfaces at room temperature in the *trans* state [3-6] and only recently we found *cis* isomers on a metal surface directly after deposition if the sample is cooled during deposition to 10 K [7]. Third, planar tri-azobenzene systems adsorb on Ag(111) with all branches in the *trans* state [8], which is a configuration that is probably very similar to the azo-tripod linker in the present case.

Another argument why the surface-adsorbed azobenzene legs are probably in the *trans* state comes from the regularity of the molecular appearance. We observe that the hexamer pattern within each tetra-azo cluster is very regular. If one or more surface-adsorbed legs of a tetra-azo molecule were in the *cis* state (instead of *trans*) this would probably introduce (lateral and vertical) deviations from this high order. Instead, the hexamer pattern appears very homogeneous with high order (Fig.S11).

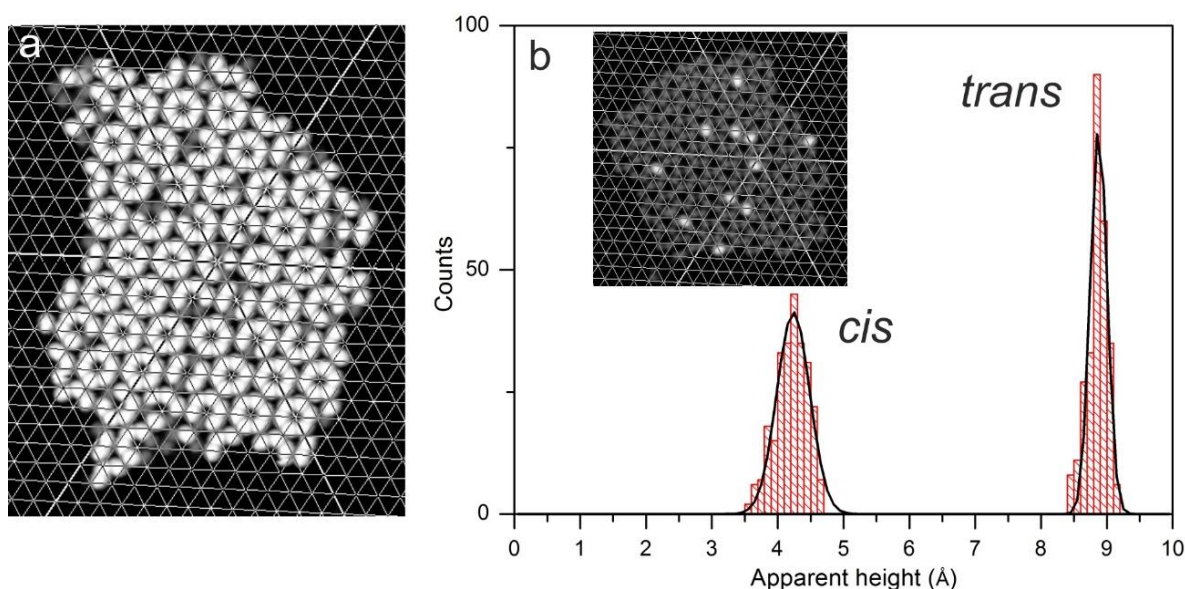


Figure S11: Lateral and vertical order inside a tetra-azo island. (a) STM images of a tetra-azo island with the upwards pointing azo-group in most cases in the *trans* state. (b) Height distribution of tetra-azo molecules with the upright standing azo-group either in *trans* (obtained from (a)) or *cis* (obtained from the STM image in the inset with an island composed mainly of dark tetra-azo molecules) state. Hexagonal grids are superimposed over the two STM images to prove the regularity of the hexamer pattern. STM image tunneling parameters: 1 V and 6 pA (a); 0.9 V and 8 pA (inset of b).

In view of lateral order, a hexagonal grid - superimposed over an island (Fig.S11a) – matches nicely the hexamer distribution and highlights its regularity. On the other hand, the vertical order (perpendicular to the surface) becomes evident from the height distribution within an island (Fig.S11b) where multiple peaks would be expected if the surface-adsorbed legs were not all in the *trans* state. Instead, the histogram shows only two clear peaks $4.19 \pm 0.24 \text{ \AA}$ (*cis* state of the upwards pointing azobenzene unit) and $8.87 \pm 0.12 \text{ \AA}$ (*trans* state of the upwards pointing azobenzene unit).

In combination with previous studies of similar molecules (mentioned above), this high regularity indicates that the surface-adsorbed azobenzene legs of the tetra-azo molecules are in the *trans* state.

Note that the experimentally determined height difference (absolute apparent STM heights of organic molecules on metal surfaces are always smaller than their real heights) is in very good agreement with the dimensions of molecular structures in the gas phase (Fig.S12).

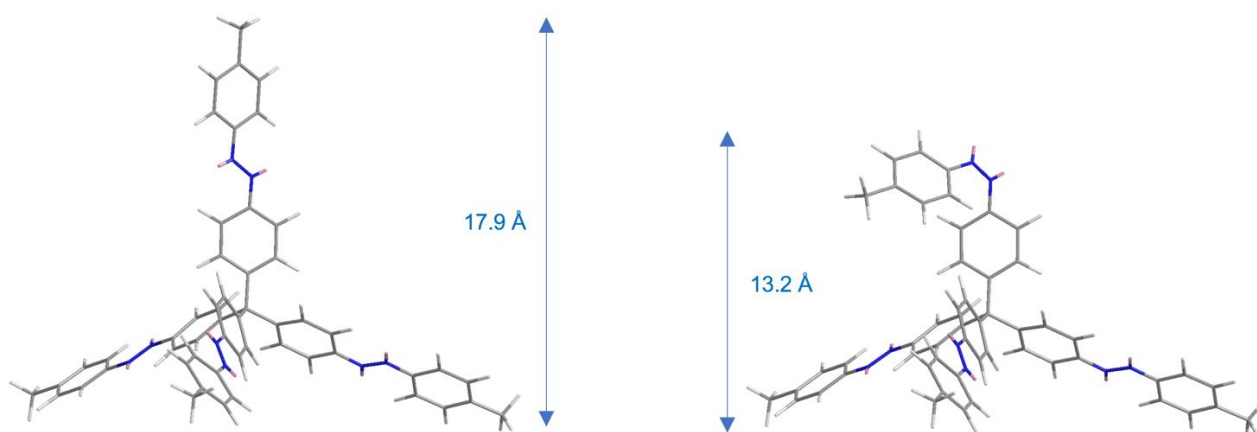


Figure S12: Dimensions of tetra-azo molecules with the upwards pointing arm either in *trans* (left) or *cis* (right) state. The three tripod arms at the bottom are in the *trans* state. Both structures were obtained by molecular modelling (Chem3D, MM2 force field) without a surface.

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