Spatial periodicity in molecular switching

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The ultimate miniaturization of future devices will require the use of functional molecules at the nanoscale and their integration into larger architectures[1,2]. Switches represent a prototype of such functional molecules because they exhibit characteristic states of different physical/chemical properties, which can be addressed reversibly[3]. Recently, various switching entities have been studied and switching of single molecules on surfaces has been demonstrated[4–13]. However, for functional molecules to be used in a future device, it will be necessary to selectively address individual molecules, preferentially in an ordered pattern. Here, we show that azobenzene derivatives in the *trans* form, adsorbed in a homogeneous two-dimensional layer, can be collectively switched with spatial selectivity, thus forming a periodic pattern of *cis* isomers. We find that the probability of a molecule switching is not equally distributed, but is strongly dependent on both the surrounding molecules and the supporting surface, which precisely determine the switching capability of each individual molecule. Consequently, exactly the same lattices of *cis* isomers are created in repeated erasing and re-switching cycles. Our results demonstrate a conceptually new approach to spatially addressing single functional molecules.

Molecular switches located on surfaces have been investigated extensively over recent years, particularly isolated molecules[4,5,12] and two-dimensional (2D) molecular aggregates[6–11,13]. These studies have mostly focused on azobenzene derivatives undergoing characteristic *trans–cis* isomerization triggered by light[7,8], tunnelling electrons[4,5,13] or an electric field[6]. In some cases, multiple switching events seem to be influenced by adjacent molecules[9,10]. The use of bulky *tert*-butyl side groups has proved to be useful because they weaken the interaction between the central azobenzene core with the substrate while, at the same time, allowing convenient monitoring of the switching event by scanning tunnelling microscopy (STM)[6,8,13].

By attaching a single methoxy group to the previously studied 3,3′,5,5′-tetra-*tert*-butylazobenzene (TBA) molecule, we have been able to generate asymmetry in the resulting M-TBA (4-methoxy-3,3′,5,5′-tetra-*tert*-butylazobenzene) molecules (Fig. 1a), inducing a net dipole moment in the *trans* configuration. Furthermore, such methoxy groups are known to donate electron density into the aromatic core of the molecule[14]. This minute structural modification results in various stable surface structures that exhibit a fundamentally different switching behaviour, which has not been observed before.

In STM images (taken at a low temperature, 7 K), individual M-TBA molecules appear as four protrusions associated with the *tert*-butyl groups (Fig. 1b). The molecular asymmetry of the M-TBA is reflected by the fact that the image shows two pairs of lobes of slightly different intensity (see Supplementary Information), which allows the relative molecular orientation to be determined (arrow in Fig. 1b). Four different molecular arrangements (with various relative orientations of the molecular dipole), denoted I–IV (Fig. 1c–f), are found after adsorption on Au(111). Note that TBA[6,8,13] and also diM-TBA (4,4′-dimethoxy-3,3′,5,5′-tetra-*tert*-butylazobenzene; see Supplementary Information) adopt just one structure, which is similar to structure I (Fig. 1c). From the unit cells of the four structures, the molecular densities on the surface turn out to be rather similar: 1.70 ± 0.06, 1.69 ± 0.08, 1.69 ± 0.03 and 1.67 ± 0.02 molecules per nm^2 for structures I, II, III and IV, respectively. The relative abundance of these structures can be controlled thermodynamically by the substrate temperature during deposition (see Supplementary Information).

Trans→*cis* isomerization was induced by voltage pulses above ~1.7 V, leading to switched molecules, *cis* M-TBA, with lobes of strongly enhanced intensity due to the 3D molecular structure, as described previously for TBA molecules[6,8,13]. This is probably caused by the upwards motion of one phenyl ring[13], with a high preference for the brighter molecular half, likely due to the asymmetry of the molecule (see Supplementary Information). Similarly to the isomerization of TBA molecules, the switching process can be induced at small tip heights, but also at large tip–sample distances (where the tunnelling current vanishes) by the electric field[6]. Note that the rate of isomerization events is rather low, similar to TBA molecules[6], leading to saturation (a constant number of *cis* isomers within an island) after voltage exposures of ~1 min.

Similar to TBA, switching is not restricted to the area underneath the tip and can occur over large distances from the tip, exceeding 40 nm. However, in the present case, switching occurs exclusively in certain structures (III and IV), the molecules in structures I and II never being observed to isomerize. This unexpected selectivity is evident in Fig. 2, where, after applying a voltage pulse over the island composed of structure I, switching is completely inhibited in structures I and II, and occurs only in the areas of structure III, even when farther from the tip (for example, at the right border of the image of Fig. 2b). By applying another voltage pulse of 1.6 V while approaching the tip by at least 0.5 Å towards the surface, the *cis* M-TBA molecules can be switched back to the *trans* isomer, precisely restoring their initial appearance (see Supplementary Information). Note that parallel-lying molecules associated with structure I switch only in the case of TBA[6,13], but not for M-TBA and diM-TBA (see Supplementary Information).

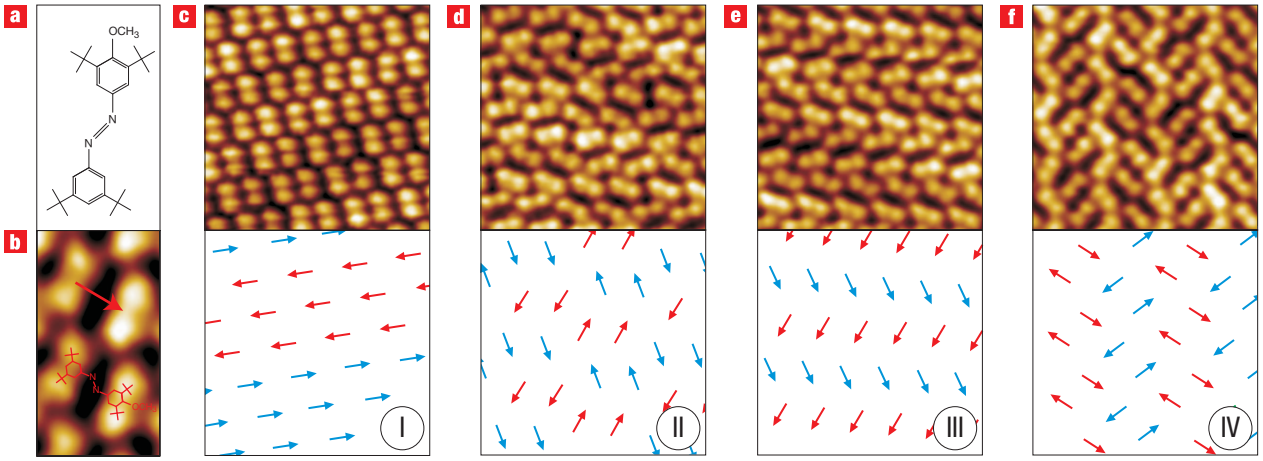

Figure 1 Different surface structures caused by the molecular asymmetry of M-TBA. a, Chemical structure of M-TBA (4-methoxy-3,3′,5,5′-tetra-*tert*-butylazobenzene). **b**, STM image of two M-TBA molecules (2.9×1.6 nm^2 in size, tunnelling current 0.1 nA and bias voltage 1 V), showing the asymmetrical appearance (marked by an arrow, pointing towards the part of higher intensity) of the four molecular lobes of each molecule. The chemical structure is superimposed: the methoxy group is likely located at the brighter pair of legs (see Supplementary Information). **c**–**f**, STM images of the four highly ordered molecular structures adopted by M-TBA on Au(111), denoted I–IV. The upper panels are STM images (all 6.4×6.4 nm^2; $I = 0.1$ nA, $U = 1.2$ V (**c**) and 1 V (**d**–**f**)) and the lower panels show the corresponding models. Structure I: all molecules are oriented parallel in rows. Structures II and III coexist in the same islands, but structure II consists of alternating domains (double rows) of structure III. Structure IV: no parallel dipoles in adjacent molecules. The arrows indicate the asymmetry of the molecules, with red and blue indicating different orientations.

These results unambiguously demonstrate the importance of the molecular structure, which not only determines the intrinsic electronic properties of the molecules but also directs their organization into larger self-assembled aggregates. It turns out that the switching capability of each M-TBA molecule is determined by the island structure and therefore its surrounding molecules. This is particularly evident in the contrasting switching behaviour of the very similar structures II and III, in which isomerization is prevented and allowed, respectively. Hence, the specific local environment, that is, molecule–molecule interactions, within these assemblies causes crucial differences between chemically identical molecules in terms of their switching abilities.

However, in addition, the surface atoms are expected to play an important role, as any local modification of the topographic or electronic molecular environment by the substrate could influence the switching properties. Thus, preferred switching sites should result at locations where either a particular surface arrangement is present or the geometrically inequivalent lattices of the molecular assembly and the underlying substrate match (shown schematically in Fig. 2c). In both cases, a periodic order of switched molecules could be expected.

By switching many molecules within the same island of structure III, it turns out that the isomerization events do not occur arbitrarily, but only certain M-TBA molecules can be switched from the *trans* to the *cis* isomer and therefore a distinct spatial periodic distribution of *cis* isomers is observed. As the intermolecular interactions are probably equivalent for all molecules in the layer, it is indeed the substrate that defines the local conditions for successful isomerization. Figure 3a shows an island of molecules in structure III after scanning at increased bias voltage. It can be clearly seen that isomerization does not occur at random, but that a rectangular superstructure is found within the molecular island. The thus created lattice of *cis* molecules exhibits a 2D periodicity with characteristic distances in both directions: every second molecule switches in the direction across the molecular rows (structure III consists of molecular rows with parallel molecules in each row, Fig. 1e). Furthermore, within a molecular row, fundamental differences are present in the switching abilities. Even though the molecules in such a row are equivalent, only every third molecule can be isomerized (with a high probability) to the *cis* configuration. Based on these observations, a unit cell of *cis* isomers can be defined, consisting of one *cis* and five *trans* isomers (Fig. 3b). Detailed analysis shows that ~86% of the created *cis* isomers are found in the corner site 1, but only very few (5% at most) are present in any other site (see Supplementary Information), revealing dramatic local differences for the individual isomerization events in the densely packed layer (Fig. 3c). Accordingly, a very precise periodic arrangement of the *cis* isomers after isomerization is observed and, consequently, a 'switching lattice' with characteristic dimensions is created.

In order to understand this strong site preference for the molecular switching, we have repeatedly performed isomerization experiments on the same island. It turns out that the creation of the switching lattice is completely reversible and does not depend on the initially isomerized molecule, as *cis* isomers in an island can be erased by voltage pulses and subsequently re-switched. Figure 4 shows a switching series of one particular surface area, where a number of molecules have previously been isomerized to the *cis* form. By applying voltage pulses, all molecules are repetitively switched back, that is, erased to their initial *trans* form (Fig. 4b,d,f,h). Subsequent *trans*→*cis* isomerization events (Fig. 4c,e,g,i) show that the newly created *cis* isomers are found exactly at the preferred switching sites of the initial pattern, meaning that only molecules on the original switching lattice can be isomerized efficiently to the *cis* form. In this way, precisely the same *cis* pattern can be created over several switching cycles, which unambiguously shows that the switching lattice of structure III is an initial property of the molecular island. Hence, this is not a cascade effect, where isomerized molecules facilitate switching of their nearest neighbour[9], but a periodic

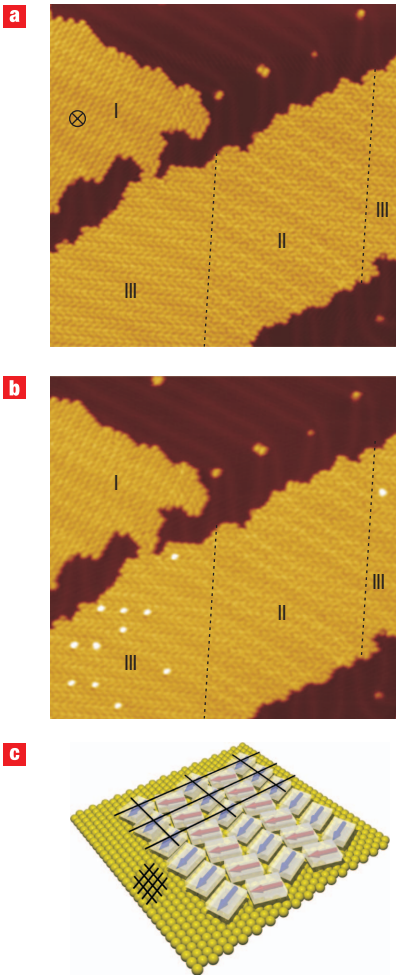

Figure 2 Selective molecular switching for different structures. a,**b**, STM images ($I = 0.1$ nA and $U = 1$ V) showing the same surface area (52×52 nm^2) before (**a**) and after (**b**) applying a voltage pulse with the STM tip. In **a** all the molecules are in the *trans* state, and the crossed circle marks the tip position during the voltage pulse (2 V for 30 s, average tunnelling current 0.33 nA). It can be seen that only M-TBA molecules in structure III are switched to the *cis* state (white spots), while those in structures I and II remain in the *trans* state (dashed lines separate the molecular structures). **c**, Schematic of an ordered molecular layer adsorbed on a surface. The arrows indicate the dipole moments, and the black grids represent the two unequal lattices associated with adsorbate and substrate.

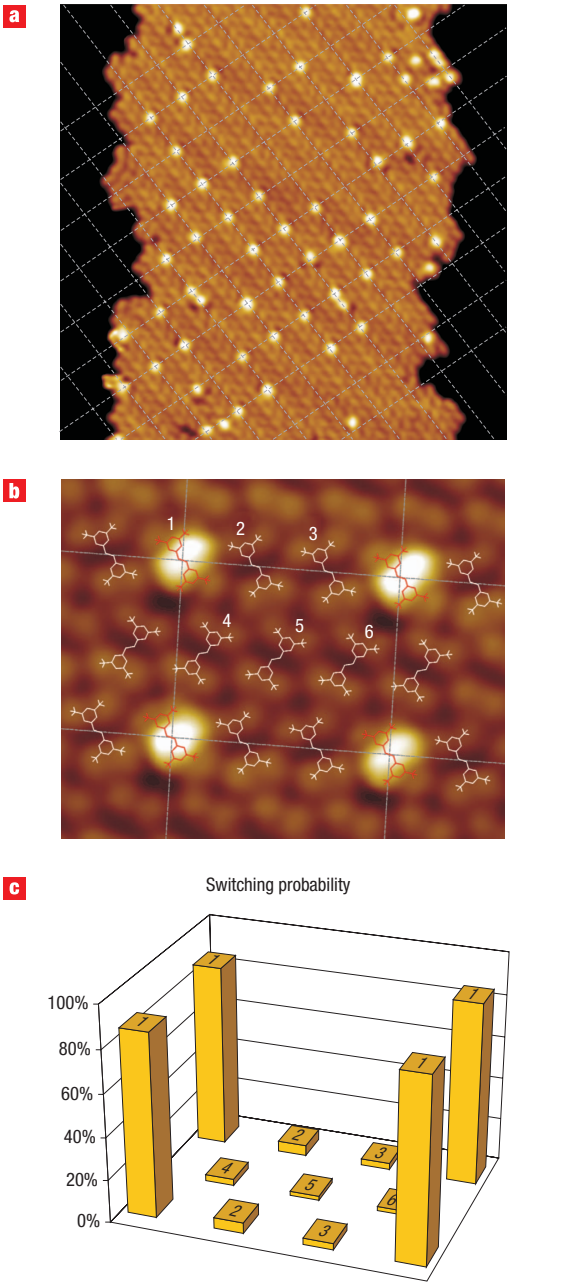

Figure 3 Molecular switching in periodic arrays. a, STM image (29.2×28.5 nm^2, $I = 0.08$ nA and $U = 0.1$ V) of structure III after switching many molecules to the *cis* state by scanning at a sufficiently elevated bias voltage (-1.7 V sample bias; the entire image area is scanned in 38 s at 80 pA tunnelling current). This method provides a more efficient means to induce the *trans* → *cis* isomerization than applying voltage pulses at fixed lateral tip positions and ensures equal exposure of the chosen surface area. The *cis* isomers are created in a periodic order, forming a lattice (indicated by a grid). **b**, STM image (7.1×5.8 nm^2, $I = 0.1$ nA and $U = 1$ V) of the *cis* isomer unit cell, where the numbers indicate the different molecules. **c**, Fraction of *cis* molecules observed in each unit cell site (numbered according to **b**), determined from ~200 *cis* molecules (see Supplementary Information). These values reflect the high precision of the *cis* ordering. Furthermore, by taking into account the intrinsic efficiency of the switching process itself under the exposure conditions used here, the overall probability for any *trans* molecule to be switched to the *cis* isomer is ~60% for position 1 and <3% for all other sites.

pattern is created, which is predetermined by the molecule-substrate system.

The dimensions and the orientation of the 'switching lattice' neither reflect the Au(111) lattice nor the herringbone reconstruction and can only be explained in terms of commensurability between the molecular layer and the underlying substrate (Fig. 2c). Along the basis vector directions of the 'switching lattice' unit cell (determined by the corner *cis* isomers, Fig. 3b), the substrate Au(111) lattice exhibits a periodicity of 30.3 and 27.5 Å, respectively (see Supplementary Information). These values are in very good agreement with the 'switching lattice', because they match the observed intermolecular distances of the molecular layer: the distances between the *cis* isomers are 31.5 ± 3.2 Å in one and 27.9 ± 2.5 Å in the other direction. Hence, it is clear that the commensurability of the two lattices,

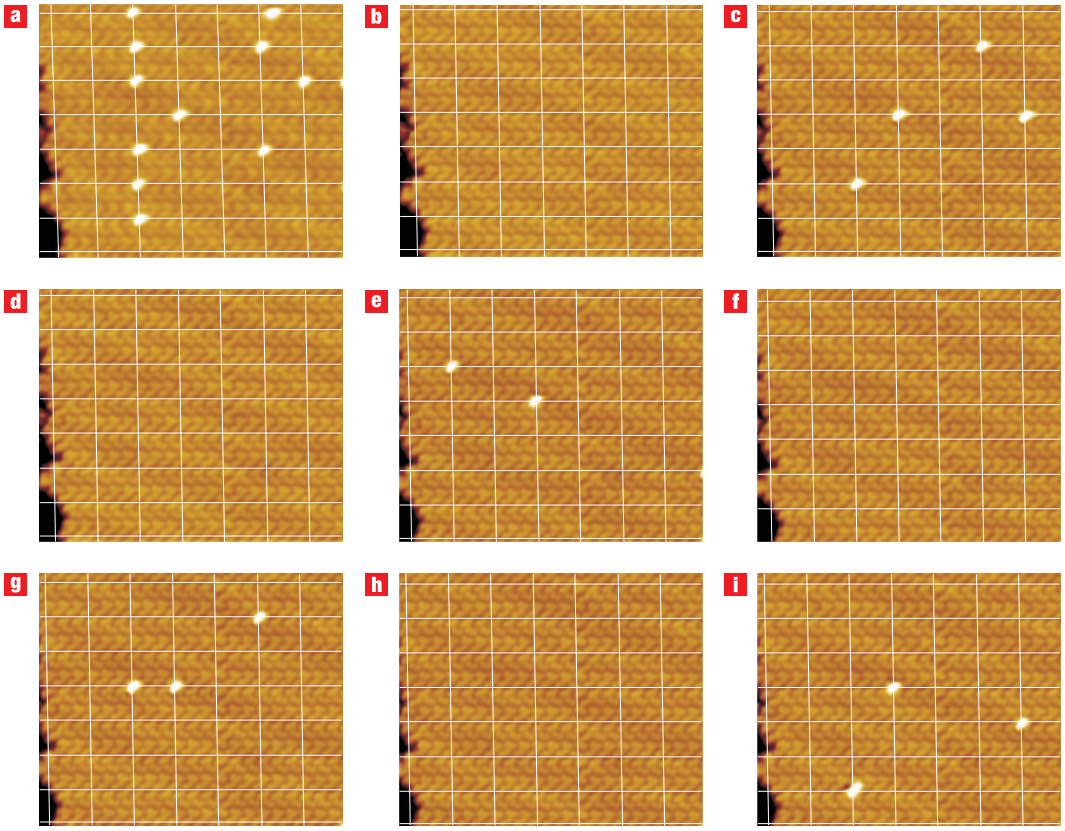

Figure 4 Erasing and re-switching. a–i, Isomerization series of STM images ($I = 0.1$ nA and $V = 0.5$ V) of the same surface area (25×21 nm^2), as is apparent from the island edge at the left border. Between the images, voltage pulses were applied to erase (*cis* → *trans* isomerization) or to re-switch (*trans* → *cis* isomerization) the molecules. Erasing (**a** → **b**, **c** → **d**, **e** → **f**, **g** → **h**) was carried out using pulses of 1.6 V induced over each isomer individually after approaching the tip by 1 Å. Re-switching (**b** → **c**, **d** → **e**, **f** → **g**, **h** → **i**) was carried out using pulses between 1.6 and 1.8 V induced in the centre of the image. The grid marks the 'switching lattice' (determined from **a**) on which all switched *cis* isomers are precisely located. Note that, by applying single voltage pulses instead of scanning at elevated voltages (Fig. 3a), a smaller number of *cis* isomers is created in these experiments, which are intended to prove the *cis* locations in various erasing/re-switching attempts rather than to create a complete pattern.

associated with the 2D molecular layer and the Au(111) surface, defines the local switching abilities of the molecules on the surface.

Furthermore, periodic order is also observed in the switching events if molecules in structure IV are isomerized (see Supplementary Information). The created *cis* isomers are not distributed at random, but follow the $22 \times \sqrt{3}$ herringbone reconstruction of the Au(111) substrate. In contrast to the matching with the substrate atoms shown above, a phenomenon that might be present for various flat surfaces, in this case the substrate reconstruction is transferred to the switching properties of a molecular film. This effect is probably caused by the vertical corrugation in the transition regions between f.c.c. and h.c.p. areas[15] that can cause steric and electronic alterations of the molecules adsorbed on top of these regions[16,17].

For both structures (III and IV), the fundamentally different switching properties depend on the precise adsorption site of the molecules on the gold surface. The isomerization capability of each individual molecule is therefore determined by one or more of the following criteria: adsorption energy, charge transfer with the substrate, and (de-)stabilization of certain configurations.

The observed modes of *cis* pattern formation indicate that the switching is mediated by the surface only and not by intermolecular, that is, adsorbate–adsorbate, interactions (however, the island structure must enable isomerization, Fig. 1). Thus, by fine-tuning the molecular structure it should be possible to control the self-assembly process and consequently the switching behaviour, which is determined by the relative position of the molecules with respect to the substrate. Although the structure of the molecular islands is given by intermolecular interactions, the switching process is determined by the substrate through the lattice commensurability for structure III and the herringbone reconstruction for structure IV. Hence, by modifying the surface properties using ordered step edges or kinked structures in a controlled way, patterns of predefined periodicity could in principle be created. Note that the conditions for isomerization of these molecules are likely to be different at elevated temperatures where thermal effects become important.

The fact that two different species (*trans* and *cis*) are present on the surface in a well-defined pattern can be used for the selective removal of only one of the components (the *cis* isomer). This process, induced by exposing the surface to ~ -1.7 V (see Supplementary Information), could in principle be used to transfer the pattern of the switched molecules to an equivalent pattern of holes in the molecular monolayer. In analogy to lithographic techniques, the controlled removal of *cis* isomers could provide the unique opportunity to transfer the switching pattern of the monolayer to the underlying substrate by means of another chemical process (for instance by thiol binding of

additional molecules, occurring only in these small Au(111) areas[18]). Note that, as the spatial addressing is achieved as a result of the local atomic-scale environment of each molecule, pattern formation should in principle be possible in large, macroscopic areas by means of photo-isomerization.

METHODS

Experiments were carried out under ultrahigh vacuum conditions (base pressure of 10^{-10} mbar) with a homebuilt low-temperature STM[19]. The Au(111) sample was cleaned before molecular deposition by ion sputtering and subsequent annealing at 800 K. Molecules were deposited from a Knudsen cell onto the surface, kept at ~220 K (unless otherwise noted), before transferring the sample into the STM at cryogenic temperatures. All STM images were taken at 7 K sample temperature (unless otherwise noted) in constant-current mode, applying the bias voltages to the sample (while the STM tip was grounded).

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Author contributions

S.H. and L.G. conceived the experiments. C.D. and L.G. performed the experiments and analysed the data. M.V.P., J.S. and S.H. synthesized the molecules. L.G. wrote the paper. C.D., S.H. and L.G. discussed the results and commented on the manuscript.

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