

Tracking Amino Acids in Chiral Quantum Corrals

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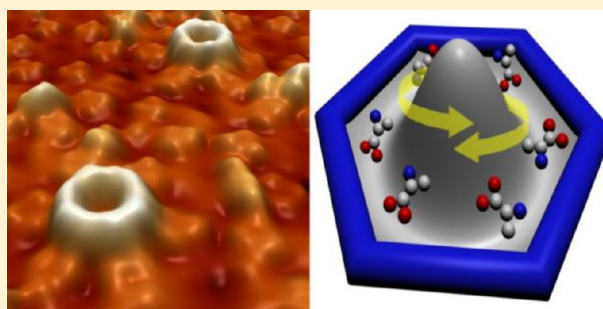
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S Supporting Information

ABSTRACT: Molecular diffusion, motion, and conformation are critical to chemical and biological processes. Concurrently, understanding how chirality affects these processes has become a critical challenge for various applications in the pharmaceutical and food industries ranging from drug catalysis to novel sensing. Here, we present a unique way of transferring the chirality of simple amino acids, L- and D-alanine, to large-scale chiral networks on Cu(111). We further utilize the unique geometry of the chiral network as a scaffolding to isolate individual molecules within a 1.2 nm hexagonal pore. These hexagonal pores act as single molecule “race tracks” where excess alanine molecules trapped at the perimeter are observed to hop between six distinct locations around the perimeter. Scanning tunneling microscopy (STM) as well as density functional theory (DFT) calculations have been utilized to directly track, influence, and probe this molecular motion confined to self-assembled, chiral, hexagonal pores which also form quantum corrals.



1. INTRODUCTION

In this article, the chirality of a simple amino acid (alanine) is transferred to large-scale, self-assembled, molecular superstructures onto Cu(111), which are subsequently utilized to confine the motion of excess molecules within 1.2 nm quantum corrals. Although studying molecular motion in a controlled environment is the final objective, the ability to create globally chiral surfaces with uniform arrays is critical for various biological processes and pharmaceutical applications, and our utilization of biological molecules further perpetuates the technological significance. Electron confinement can be traced to the first quantum corral experiment performed by Crommie et al.¹ Oftentimes, the utilization of the STM for atomic manipulation has proven a powerful tool for defining nanoscale structures with atomic precision.^{2–4} More recently, there has been a growing effort to utilize molecular self-assembly to form well-defined organic arrays on various metal substrates.^{5–10} All of these molecular superstructures demonstrate electron confinement at nanometer length scales and form repeated confined structures uniformly over the entire substrate. In addition to confining the electronic surface states, several efforts have employed various strategies to trap or selectively template organic and inorganic species that are subsequently deposited on numerous substrates.^{11–15} Although confinement of electronic states in porous networks has been demonstrated earlier, the present work utilizes this strategy to confine molecular motion within very small, chiral, quantum corrals of biologically relevant amino acids. Unlike previous reports, these

corrals are so small that the first two energy states are spaced by almost 1 eV and are placed within standard operating voltages of modern electronics, which makes them interesting for potential molecular electronic logic and memory technology.

In this system, individual alanine molecules organize into chiral trimers, which self-assemble to form hexagonal pores. These pores subsequently form a chiral, homogeneous, hierarchical, supramolecular network across the Cu(111) surface (illustrated in Figure 1a). Each pore acts as a quantum corral with an approximate diameter of 1.2 nm, meaning that on an “ideal” 1 cm² Cu substrate, approximately 10¹⁴ identical quantum corrals with the same geometry and confined energy states form within minutes. Additionally, we observed that excess alanine can become trapped within the hexagonal pores of the molecular superstructure. If the excess molecule is moving within the hexagonal pore, it appears as a protruding toroid or “ring” as it moves around the inner perimeter of the pore, as indicated by arrows in Figure 1a, where the local density of states (LDOS) is a minimum for the ground-state energy of the quantum corral. The remainder of this paper will examine the specific details at each step of the experiment, which were heavily supported by two theoretical efforts that computationally define the chemical structure and binding of

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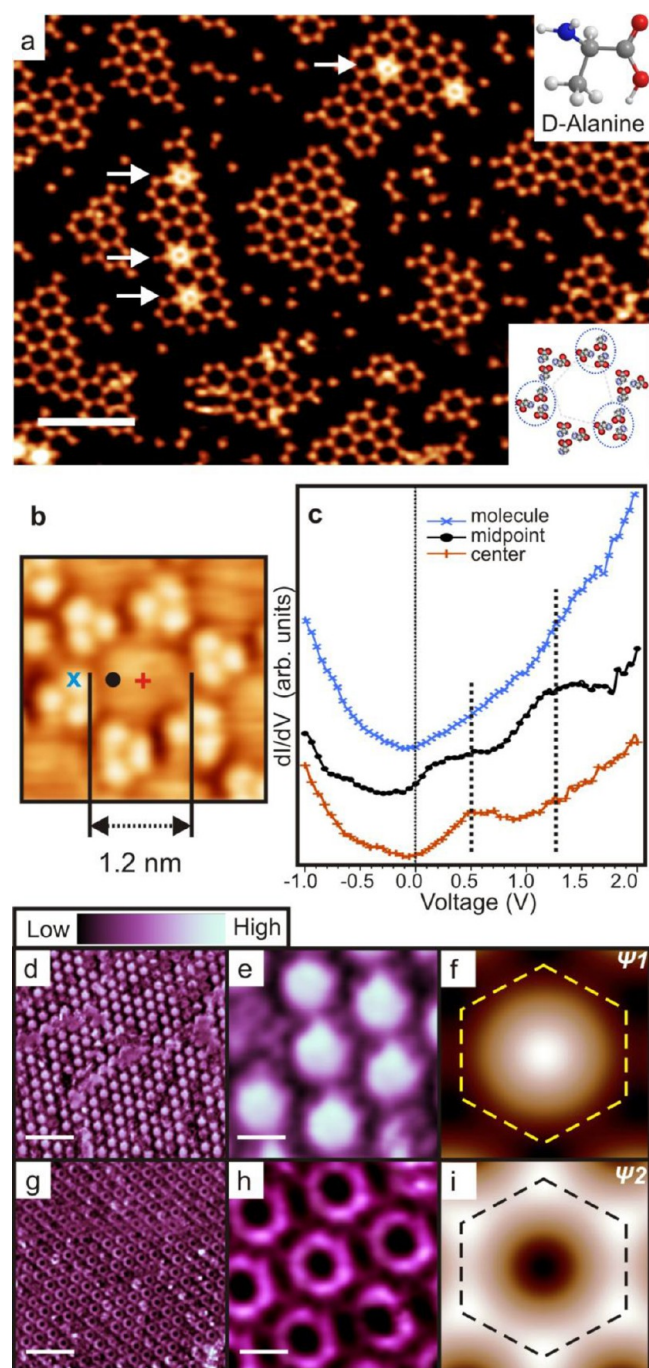


Figure 1. Probing the confined states of the quantum corrals formed in the hexagonal pores of the molecular superstructure. (a) Topographic image of the molecular superstructure of alanine on Cu(111), forming a hexagonal porous network; occasionally, bright rings will be observed as an indication of molecular motion inside the hexagonal pores. Top inset: model of alanine molecule; bottom inset: reconstruction of hexagonal pore from DFT calculations highlighting the trimer formation for D-alanine. (b) Filled state image of a single D-alanine unit cell (sample bias -2.0 V, set point current 2 nA). The symbols (blue \times , black dot, and red $+$) overlaid on the image depict the different positions at which the dI/dV spectra were taken. (c) dI/dV spectra showing tip position dependence on the confined local density of states, where a state at $+0.5$ and $+1.3$ V have been highlighted with a dashed line. (d) Spatial conductance (dI/dV) map of the D-alanine molecular superstructure at the lower energy state (scale bar 5 nm, sample bias $+500$ mV, set point current 5 nA). (e) Zoomed-in image showing the hexagonal pores with a maximum

Figure 1. continued

LDOS at the center of the pore (scale bar 1.2 nm, sample bias $+500$ mV, set point current 5 nA). (f) Calculated LDOS map of the first eigenstate (Ψ_1) at $+0.5$ V for a 1.2 nm pore. (g) Spatial conductance map of the L-alanine molecular superstructure probing the higher energy state (scale bar 5 nm, sample bias $+1.0$ V, set point current 5 nA). (h) Zoomed-in image showing the donut structure of the higher energy confined state (scale bar 1.2 nm, sample bias $+1.0$ V, set point current 5 nA). (i) Calculated LDOS map for the higher energy eigenstate (Ψ_2).

the molecular superstructure, the energetics of our quantum corrals, and the molecular motion within the corrals.

The present article explores the study of alanine [$\text{NH}_2\text{--CH}(\text{CH}_3)\text{--COOH}$], the simplest chiral amino acid which exists as either an L- or D-enantiomer, where D-alanine is schematically illustrated in the inset of Figure 1a. Both enantiomers are being explored for various applications in nonlinear optics, liquid crystal technology, asymmetric catalysis, and protein studies.^{16–18} Previous studies have thoroughly examined the adsorption of L- and D-alanine on Cu(001) and Cu(110).^{19–25} On both of these surfaces, the self-assembled monolayers result in close-packed ordering of the molecules. In contrast, the adsorption on Cu(111) has not been fully explored.²⁶ Therefore, we performed systematic studies of the room temperature deposition from low (<0.1 ML) to high (>1 ML) surface coverage (Figure S1) for both L- and D-alanine sources independently on a Cu(111) single crystal. For both enantiomers, subsequent annealing (~ 500 K for 15 min) of the higher coverage samples resulted in the formation of a monolayer of a well-ordered, self-assembled, molecular superstructure with hexagonal pores, whose dimensions are ~ 1.2 nm in size (Figure 1b).

2. EXPERIMENTAL SECTION

Prior to alanine deposition, the Cu(111) crystal was sputter-annealed using Ar^+ ions at 1 kV at an annealing temperature of ~ 973 K. All sample preparation and molecular deposition was performed in an UHV chamber operating at 5×10^{-11} Torr. The samples were transferred *in situ* to the microscope chamber without ever leaving a UHV environment. The D- and L-alanine source materials were commercially purchased from Sigma-Aldrich (purity 4N) and were subsequently loaded into two different cells within a four cell molecular doser. The alanine molecules were thermally sublimated onto the clean Cu(111) crystal at room temperature. In order to form the molecular superstructure, the alanine source was heated to approximately 426 K for dosing, which typically lasted 7 min. The distance of the source to the sample is approximately 15 cm. Following room temperature deposition, the sample was annealed close to 473 K for 15 min to induce molecular ordering. The temperatures for both the molecular dosing and thermal annealing are approximate as mounted thermocouples are within proximity of the sample and molecular source. Following deposition, the samples were then transferred to the analysis chamber, which housed a commercial Omicron VT- AFM/STM. The imaging was performed at a sample temperature of 55 K.

3. RESULTS AND DISCUSSION

The characterization of this porous, molecular superstructure was performed utilizing a UHV-STM, with the sample cooled

to ~ 55 K during imaging. As confirmed by DFT calculations (Supporting Information Section 4, Figures S4–S6) and previous reflection absorption infrared spectroscopy (RAIRS) studies,^{20–23} alanine molecules fall on the Cu(111) surface in their deprotonated form which is very similar to the adsorption mechanism of alanine on Cu(110) or glycine on Cu(111),^{20–23,27} where the nitrogen and oxygen stick to the surface, the methyl group stands up, and the C–C axis lies parallel to the surface (Figure S2). The molecules combine to form two possible trimer substructures that are connected through hydrogen bonding and linked to subsequent trimers forming the boundaries of the hexagonal pores, as illustrated in the two-dimensional schematic of Figure S2b. Because of the transfer of chirality from the single molecules to the final, molecular superstructure, these pores form a hexagonal chiral hierarchical porous network.

Particular effort was made to experimentally characterize the quantum corrals formed by this molecular network as they define the molecular motion within the hexagonal pores. The molecular trimers making up the hexagonal superstructure are most clearly visible in filled-state imaging (Figure 1b), while inside the hexagonal pore is the bare Cu(111). The strong contrast in topography as a function of sample bias is a result of the tunneling current's strong dependence upon the LDOS of the sample. This sensitivity can be utilized to extract electronic information via scanning tunneling spectroscopy (STS). Using a lock-in amplifier, dI/dV point spectra were measured at various points on the surface. Three representative spectra are plotted in Figure 1c, and their corresponding spatial position is illustrated by points overlaid on the STM image of Figure 1b. Spectra taken directly over the molecular structure are fairly featureless; however, spectra taken within the pore reveal distinct electronic states as a function of position within the pore. When measured at the center of the pore, a state is clearly visible at $\sim +0.5$ V sample bias, while a measurement at the midpoint reveals both the lower energy state and a higher energy state at $\sim +1.3$ V sample bias (Figure 1c). These peaks within the dI/dV spectra represent energy states of the confined, two-dimensional, electron gas of the Cu(111) surface within the hexagonal pore, such that each hexagonal pore on the surface forms a small quantum corral.

The surface state for bare Cu(111) being around -440 meV, previous quantum confinement studies report states at much lower energies, but for much larger confined structures.^{1,6,8,9} The energy states are inversely proportional to the size of the corral. In this study, some of the smallest quantum corrals ever reported were characterized, and it is not surprising that the smaller dimensions result in a larger separation between states and an overall shift of the states to higher energies.

To further explore this electronic confinement, two-dimensional conductance maps were recorded over a D-alanine hexagonal network. These conductance maps give a spatial snapshot of the LDOS for a particular energy applied to the surface. For a sample bias of $+0.5$ V, corresponding to our lowest, confined, energy state, the pores of the hexagonal network light up with a maximum value at the center of the pore (Figure 1d). Figure 1e shows a higher resolution conductance map of six pores. We approximated the confinement in the hexagonal pore to a particle in a 2D hexagonal quantum well with a diameter of 1.2 nm and solved for the eigenstates Ψ_n .^{28–30} The first eigenstate, Ψ_1 , is plotted in Figure 1f and corresponds well to what is observed in the conductance maps.

The confined states do not appear to be influenced by the chirality of the molecular network and are solely dictated by the shape and size of the pore. Similar conductance maps taken on a molecular network comprised of L-alanine show identical confinement. In this case, while probing the higher energy state at a sample bias of $+1.0$ V, a donut-like structure is observed around the inner perimeter of the corral (Figure 1g). A high-resolution conductance map is illustrated in Figure 1h, which also has schematic of the molecular network overlaid on a single pore. Solving for the next eigenstate, Ψ_2 , of our approximated corral, we confirm a hexagonal donut shape, which is again consistent with the two-dimensional conductance maps for the given energy (Figure 1i). Overall, these self-assembled networks form very robust, quantum corrals that demonstrate a large-scale uniformity in size and energy states across the surface.

At slightly higher coverage we start to observe excess alanine becoming trapped within the quantum corrals of the hexagonal molecular superstructure. At extremely high coverage, new phases of ordering can be observed. For the moderate case, excess alanine is always adsorbed or trapped within a hexagonal pore. More importantly, it is not trapped anywhere within the pore, but specifically at the inner perimeter, as illustrated in the schematic of Figure 2a. This seems reasonable, considering the electronic landscape within the hexagonal quantum corral, where the profile of the LDOS for the lowest energy eigenstate, Ψ_1 , is a minimum at the inner perimeter of the pore.

It is not uncommon, even at 55 K, to observe molecular motion of the alanine around the perimeter of the pore. For a typical scan speed (~ 113 ms per hexagonal unit cell), the molecule within the pore is moving too fast for singular motion from one specific position to the next to be resolved by STM, but instead a time-averaged look at all positions is generated. Molecular motion around the perimeter of the hexagonal pore results in ring-like features centered within the pore, as illustrated in the 3-dimensional rendering of the STM image in Figure 2a. The apparent height of the molecular network is ~ 0.8 nm, while the height of the ring-like features is ~ 1.2 nm. Figure 2b shows no evidence of molecular motion, but after a few scans of the same area, empty pores become occupied with an alanine molecule moving around the perimeter (Figure 2c). It should be noted that all motion within a corral is limited to single molecules. This hopping motion ceases when more than one molecule is present within a given hexagonal pore, which can be seen by looking closely at neighboring pores in Figure 2b,c, as these now appear as bright dots clustered together.

It is possible to intentionally manipulate the molecular motion with the STM tip, if it is moved closer to the surface through the use of higher currents (typically changing the set point current from 500 pA up to 5 nA at a constant voltage). The most obvious result is knocking the alanine from one quantum corral to another, as illustrated in Figure 2d. The blue and black arrows in Figure 2d track the movement of two different alanine molecules as they are displaced from one hexagonal pore to another. The STM image captures partial ring-like structures that begin when the molecule enters a pore and abruptly end when it is displaced into another pore. The black arrows show how the alanine moves to a neighboring pore and then back to the original. A high-resolution image of a ring-like feature shows that it is confined to the perimeter of a pore within the molecular network (Figure 2e). The alanine molecules appear to stay in motion within the molecular pore at 55 K, and conditions used to induce this motion have been

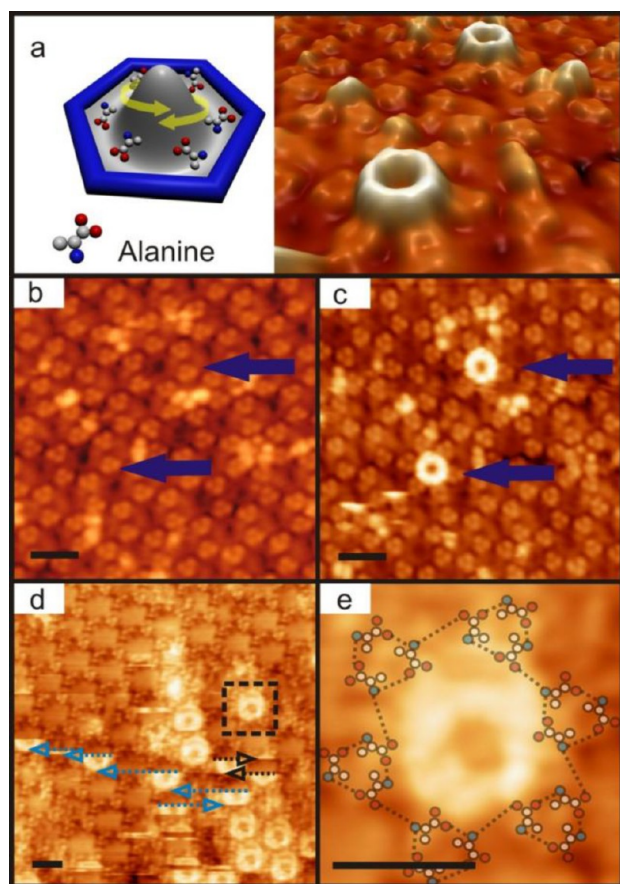


Figure 2. Molecular motion confined to the perimeter of hexagonal pores within the self-assembled molecular network. (a) Schematic representation of the energy landscape within the hexagonal pore for the ground state, where the minimum in the LDOS is at the perimeter of the pore, making it a preferential site for alanine adsorption. However, excess alanine does not necessarily remain stationary, as illustrated by the ring-like features in the 3-dimensionally rendered STM image. (b) STM image of the D-alanine molecular superstructure (scale bar 1.2 nm, sample bias +2 V, set point current 1 nA), where the blue arrows focus on empty quantum corrals, which after multiple scans are (c) subsequently filled by bright circular rings. (d) The blue and black arrows detail tip-induced motion of single adsorbates hopping from one well to the other on the surface (scale bar 1.2 nm, sample bias +250 mV, set point current 5 nA). (e) Zoomed-in image of a ring-like feature (black dashed box in (b)) with a schematic overlay of the underlying molecular network (scale bar 1.2 nm, sample bias +250 mV, set point current 5 nA).

very reproducible. The effect of temperature on the molecular motion was also studied at 150 K (Figure S3). We are still trying to determine the effect of the tunneling current on the hopping rate of trapped molecules, but even at the lowest currents, down to 5 pA, the excess adsorbates still hop within the corral.

In an effort to track the motion of excess alanine between these positions, we utilized the STM tip as a local probe. Similar to STS, the tip is positioned at a desired location and changes in the tunneling current are monitored (initially established at 1 nA) as a function of time with the feedback turned off and the set-point voltage held constant. Our time resolution is limited by the control electronics software to 200 μ s.

Positioning the tip over excess alanine molecules, that exhibit molecular hopping, resulted in the observation of reproducible

switching between two distinct reproducible states of tunneling current (~ 0.4 and ~ 3.0 nA) compared to an empty pore that remains constant at 1 nA for the same time duration, as illustrated in Figure 3a. Previous STM studies have utilized this technique to study the motion of molecular rotors.^{31–35} When utilizing the STM tip to monitor the molecular motion, we

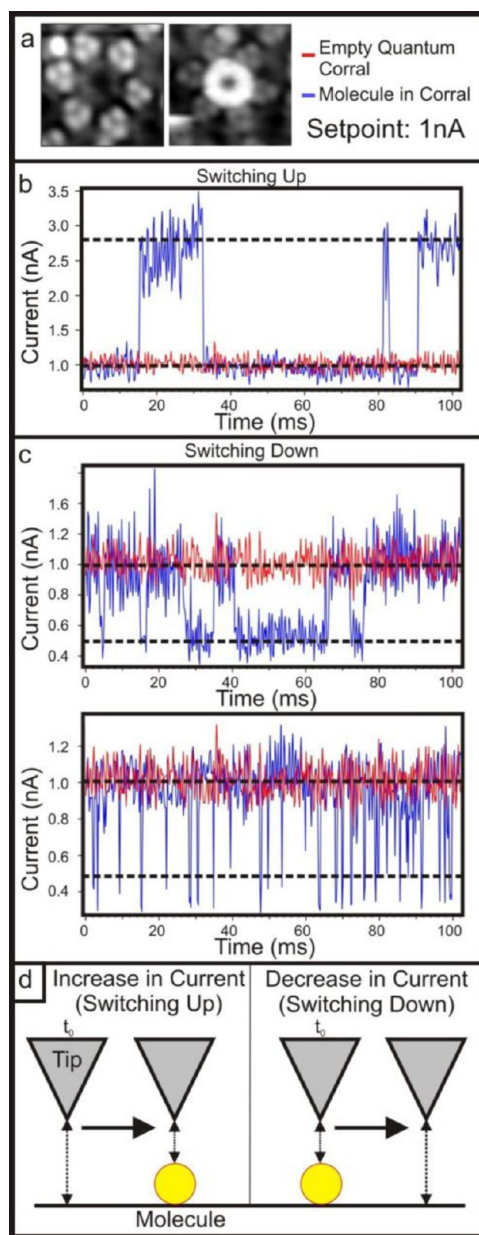


Figure 3. Monitoring the molecular motion. (a) Two STM images of an empty corral and a corral with a rotating molecule measured near the perimeter. (b) Switching up: measuring changes in the tunneling current vs time reveal molecular switching between two states, from 1 up to 2.8 nA. (c) Switching down: the tunneling current vs time data reveal molecular switching between two states, from 1 down to 0.4 nA, in a slow and later more rapid motion (bottom image) when the tip is closer to the center of the ring. (d) Schematic explaining the changes recorded in the tunneling current vs time measurements: during a “switching up” event, there is an increase in current as the molecule moves under the tip; while during a “switching down” event, there is a current decrease as the molecule moves away from underneath the tip, during its movement around the corral.

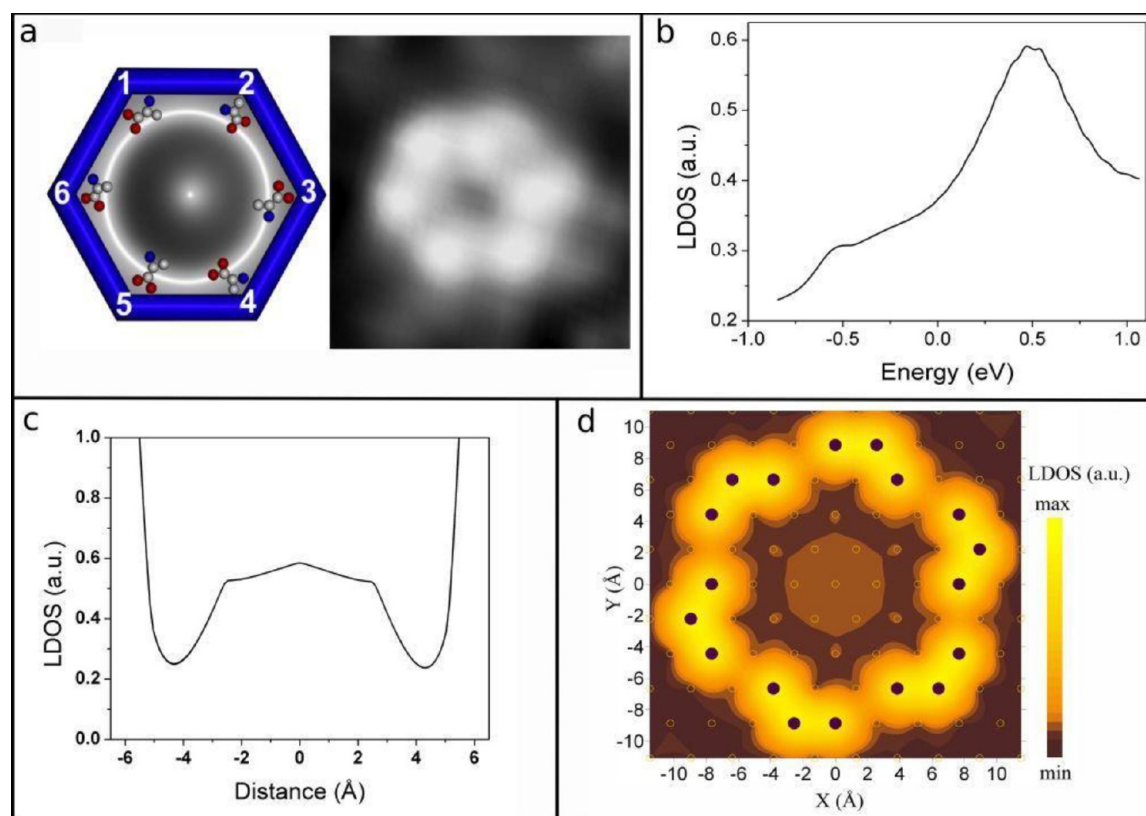


Figure 4. Effect of quantum confinement on excess alanine adsorbate motion. (a) Schematic representation of the hexagonal corral showing the six possible “random” molecular positions; a corresponding STM image shows six lobes within the ring-like feature indicating those distinct positions. (b) LDOS showing a strong peak at $E = 0.5$ eV. (c) LDOS distribution along $y = 0$. (d) LDOS ($E = 0.5$ eV) inside corral showing six special positions. Dark purple circles denote the corral wall, while open circles denote underlying Cu(111) surface as well as the brown perimeter.

observed a few different dynamics that were reproducible. As the excess molecule hops inside the quantum corral, the time resolution of the STM prohibits the accurate measurement of discrete movements, even at our instruments lowest temperature of 55 K. When positioning the tip directly over a molecular hopping site we observe two different switching events. In one scenario the current jumps to a higher value (2.8 nA), as illustrated in the time sweep of Figure 3b. Alternatively, we observe a switching event in which the current drops to a value 0.4 nA (Figure 1c). The time sweeps are either exclusively up or down and we never have a combination of both in a single sweep. Our interpretation of these two switching events is related to whether or not the molecule is under the tip when we start the measurement, as schematically illustrated in Figure 3d. When we start the sweep, the tip–sample distance is frozen and the feedback is off. To first order, if no molecule is present and then moves under the tip, it will lead to an increase in current as the tip–sample spacing is decreased. Alternatively, if the molecule is present when the set point is established, its movement out from under the tip will lead to a decrease in current.

These measurements are also very sensitive to the tip’s position. If the tip is positioned close to the center of the ring, it seems to sample all the sites and the hopping motion becomes rapid and difficult to monitor, as illustrated by the rapid spikes in the second time sweep of Figure 1c. The same quick motion has also been recorded in the “switching up” cases.

Upon inspection, there are six distinct positions within the hexagonal pore in which the alanine can reside, whether moving or stationary, as depicted in the schematic of Figure 4a. In some

cases, the ring-like feature develops six lobes corresponding to these individual positions, as clearly seen in the STM image of Figure 4a. To get a detailed insight into the physics underlying the aforementioned effects, we have performed *ab initio* calculations of the electronic states in the quantum corrals. Our approach is based on density functional theory in the local density approximation. Multiple scattering of surface-state electrons in corrals is treated by means of the Korringa–Kohn–Rostoker Green function method.³⁶ We treat a surface as a 2D perturbation of an ideal crystal bulk. Taking into account the translational symmetry of the surface geometry, the Green’s functions are formulated in momentum space.

A corral is considered as a perturbation of the clean surface. These calculations are performed in configurational space. Our approach based on the multiple-scattering theory is well-suited for calculations of electronic states in confined geometries. Details of this method and its applications can be found in previous works.^{37–39}

As aforementioned, during adsorption of alanine on Cu(111), the nitrogen and oxygen stick to the surface. In other words, the scattering of surface-state electrons is mainly determined by these light atoms. Therefore, we have studied the scattering of surface electrons from corral walls made up of N, C, and O. The size of the corrals was chosen to be 1.2 nm, as observed in the STM images. Our studies have revealed that in all corrals the quantum interference between the electron waves traveling toward the corral wall and the backscattered ones leads to the confinement of the surface-state electrons inside the corral. As an example, the energy-resolved LDOS at the center of the N corral is shown in Figure 4b: one can see a well-

resolved peak at $E = 0.5$ eV, which perfectly corresponds to the experimental finding.

A spatial variation of the LDOS at this energy along the $y = 0$ direction inside the corral is depicted in Figure 4c. The LDOS exhibits an oscillatory behavior with strong minima near the corral wall. The above results clearly demonstrate the quantum confinement of surface electrons. To address the experimental observation about minima of LDOS at special areas on the inner perimeter of corrals, we have calculated a spatial distribution of the LDOS at $E = 0.5$ eV. Figure 4d demonstrates that there are six positions where the LDOS exhibits strong minimum, which also coincides with the experimental findings. It is interesting to note that we have studied the energy of different adatoms (N, C, O, and 3d adatoms) inside the N corral. For all adatoms it appears to be energetically favorable for them to sit in regions where the LDOS are at a minimum near the corral wall.

4. CONCLUSION

In summary, a novel, hierarchical, and chiral network was formed on Cu(111) via a molecular superstructure comprised of the biologically relevant amino acid alanine. The individual molecular constituents, subunits, and resulting self-assembled molecular superstructure all exhibit homogeneous chirality uniformly across the surface. The superstructure forms a network of hexagonal pores that act as quantum corrals by confining the two-dimensional electron gas of the surface. The electronic landscape of the surface has been modified in a controlled manner, where the confined states of the corrals have a strong influence on subsequent adsorption. After the complete formation of the hexagonal network, any excess alanine is found to adsorb exclusively at six distinct positions around the perimeter of a hexagonal pore where the ground-state energy of the corral is at a minimum as verified by theoretical predictions. Molecular motion between these six positions was observed, induced, probed, and manipulated with the STM.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details; Figures S1–S6 and Table S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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