Supplementary Information

Scanning tunneling microscopy/spectroscopy on self-assembly of glycine/Cu(111) nanocavity array

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1. Comparison of glycine-trimer STM image with the result of calculation

To confirm the molecular arrangement of the glycine trimer, we examined high-resolution STM images in more detail. As shown in Fig. 1(b), the STM image of a single glycine molecule in a trimer structure exhibits a bright spot surrounded by dark regions. According to a previous IR study, the brightest point corresponds to the geographically highest methylene (-CH_2-) group.[1] The amino group in each molecule is considered to face outward from the trimer structure, enabling the formation of hydrogen bonds between the amino and carboxyl groups and the structure to form a nanocavity network through intra- and intertrimer couplings, as described later. In consideration of these findings, models of the trimer structure, which has three possible relationships with the substrate, are shown in Fig. S1(a), namely, the center of the trimer is located ontop of the Cu(111) substrate surface or in two hollow sites on the surface. In the array of nanocavities with the $2\sqrt{13}\times2\sqrt{13}$-R13.9° structure, two adjacent trimers have their centers at ontop and hollow sites, which, however, are imaged with almost the same brightness. This result suggests that the difference between the positions of the center of the trimer does not affect the electronic structure of the nanocavity. Therefore, in the following calculation, we assumed a molecular arrangement with the center of each trimer located at site ontop of the Cu(111) surface.

We performed a simple density functional theory calculation using the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) with the ABINIT code with plane-wave-based norm-conserving pseudopotentials.[2] The

$(6\times3\sqrt{3}\times6)$ slab model with three Cu(111) layers is shown in Fig. S1(b). The energy cutoff of the calculation was 50 Ry. From the spatial distribution of the local density of states (LDOS) near the Fermi energy in the surface region (-0.5 eV $< E < E_F$), we can obtain results that can be compared with STM images.[3]

Fig. S1(c) left shows a simulated STM image of the trimer structure on Cu(111). As expected, the methylene group is imaged as the brightest point, and the Cu areas near the carboxyl groups are imaged darker than the original substrate region indicating a region of depression. These results are consistent with the experimental STM image shown on the right.

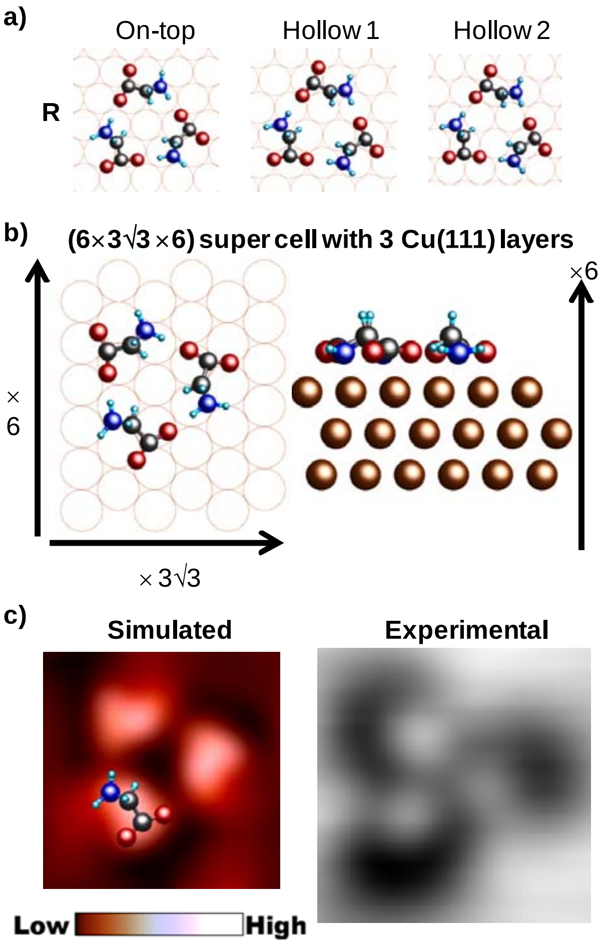

Fig.S1 (a) Schematic illustrations of glycine trimer structures where the center of the trimer is located at ontop and in hollow sites of the substrate (only type R is shown). (b) Schematic structure used for theoretical calculation. (c) Trimer images obtained by simulation and STM experiment (V_s = -0.5 V, I_t = 1.0 nA).

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2. Electronic structures of quantum corral

(1) To investigate the electronic structure, we performed STS measurements. Figure 2S(b) shows the results of differential conductance curves (d*I*/d*V*-*V*), which are proportional to the local density of states (LDOS) of the surface, obtained at the substrate Cu(111) area and the center of a nanocavity, indicated by S (substrate) and G (glycine) in Fig. S2(a), respectively. STS was conducted under an open-feedback loop condition with lock-in techniques (lock-in moderation: 14 mV rms, 3.00 kHz). Although both regions consist of bare Cu atoms, the two curves are different near the Fermi energy level (V_s = 0). The value of V_s ~ -0.4 V, from which the differences between the two curves originate, is close to the minimum energy of the free-electron-like dispersion relationship of the Shockley states on the Cu(111) surface (= -0.39 eV from the Fermi energy). As shown in the series of bias-dependent STM

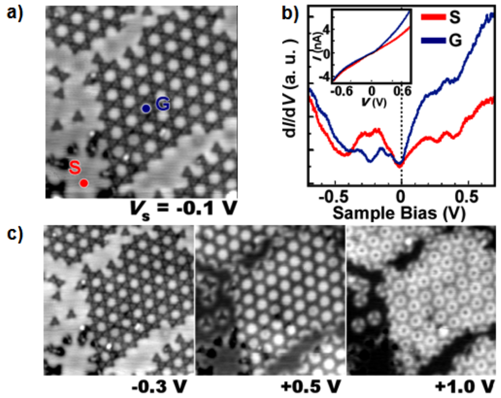

Fig. S2 (a) STM image of nanocavity network (V_s = -1.0 V, I_t = 1.0 nA). (b) d*I*/d*V* and *I*-*V* (inset) spectra measured on S and G in (a) (set point: V_s = -0.5 V, I_t = 0.5 nA). (c) Bias-dependent STM images obtained for V_s = -0.3, +0.5 and +1.0 V, I_t = 1.0 nA.

images (Fig. S2(c)), the inside region of the nanocavity became much brighter than the outside region, with the increase in sample bias voltage in the positive bias region, which corresponded to larger d*I*/d*V* values. However, in the STM images obtained for further high bias voltages (~ +1.0 V), the center of the nanocavity turned darker than the surface outside. The diameter of this depressed area was estimated to be less than 0.8 nm, which is obviously smaller than that of the Cu area in the nanocavity (~1.3 nm).

These results suggest the existence of a new electronic structure formed by a modification of LDOS in the nanocavity. To clarify the electronic states in detail, we performed d*I*/d*V* mapping, which is more sensitive to the spatial distribution of LDOS on the surface. The results are shown in Fig. 3 in the text.

(2) For mapping analysis shown in Fig. 3 in the text, we measured the d*I*/d*V* curve at each grid point (128×128) in an STM image. During d*I*/d*V* measurement, tunneling gap should be kept constant. However, owing to the presence of electronic states in the nanocavity, tunneling probability, which corresponds to the tunnel resistance of the gap, may vary with the tip location or sample bias voltage. To remove these effects, we chose the STS set point of V_s = -0.25 V and I_t = 1.0 nA, because all the areas of the nanocavity show an almost flat geography for this bias voltage.

Figure 3 in the text shows the results of d*I*/d*V* images obtained at various sample bias voltages, reflecting the electronic states similar to the characteristics of quantum corrals with the electronic states of the confined two-dimensional free electronic gas (2DEG). In consideration of the electron confinement of the Cu(111) 2DEG state by the nanocavity of 1.3 nm diameter, we can explain the molecular quantum confinement as follows. In the energy region of –0.4 V ~ 0 V, since the wavelength of the original Cu(111) 2DEG state is longer than twice the nanocavity diameter, the 2DEG state is absent in the cavity and the LDOS decreases. At V_s = +0.1 V, the 2DEG state is allowed to exist in the nanocavity as the ground state with half-wavelength (n = 1, 2.6 nm). The node of the wave function should be near the molecular ring with the loop at the center. On the other hand, for the second state (n = 2, 1.3 nm), the wavelength becomes similar to the diameter of the nanocavity; therefore, the edge and center of the cavity become the node of the confined wave function. Since dI/dV represents the square of wave function intensity, the center of the nanocavity becomes local maximum and minimum for the ground state and second state, respectively. Since the ground state obtained by dI/dV measurement is +0.1 eV above the Fermi level E_F, the energy level for the second state is expected to appear at about +1.0 eV. However, the second state was clearly observed even at V_s = +0.8 V. The first state was also observed at -0.05 V, which is lower than the n = 1 state of +0.1 V.

In the case of electron confinement, the molecular edge works as a fixed end for the reflection of the 2DEG wave function. Therefore, the standing wave should have a node at the edge; however, since the height of the barrier for the reflection or scattering of electrons is finite, the 2DEG waves would not have a node exactly at the edge. This is the so-called phase-shift effect, which may cause the observed loose conditions for the allowed wavelength. To examine the effect of electron confinement in more detail, we analyzed how the electrons are scattered by the adsorbed molecules by comparing the wave patterns of 2DEG between the Cu surface of the outside region of the nanocavity and the area of the molecules forming the nanocavity. Figure S3(a) shows a dI/dV map simultaneously obtained with a STM topographic image for V_s = +1.0 V. The cross sections of the wave patterns along X-Y in Fig. S3 (a) obtained for V_s = +0.8 and +1.0 V (red lines) are shown in Fig. S3(b). The standing waves with the original 2DEG wavelengths of Cu(111) for the two energy states in the form of decay from the edge of the molecular structure are also shown (green dotted lines).[1,2] The edge of the molecular structure determined by the STM image taken at -0.8 V, which is shown in the lowest part in Fig. 3(b), is indicated by a black dotted line.

In our dI/dV images, for both states, the first loop is at an almost the same distance, which is about 0.3 nm away from the edge, as indicated by a black dash-dotted line in Fig. S3 (b). Using the position of the first loop as the basis for the measurement, phase shift was estimated. The position of the node of the standing wave is near the edge of the molecule for V_s = +1.0 V, while there exists a phase shift of ~ 30 ° for V_s = +0.8 V. In consideration of the phase shift of ~ 30 °, the observed loose condition for the wavelength may be allowed. In addition, some electrostatic interactions between molecules and the Cu substrate, such as the charge transfer observed in the $p(2\times4)$ structure in the glycine/Cu(100) system,[3] may cause the change by shifting the bottom of 2DEG to some extent.

References

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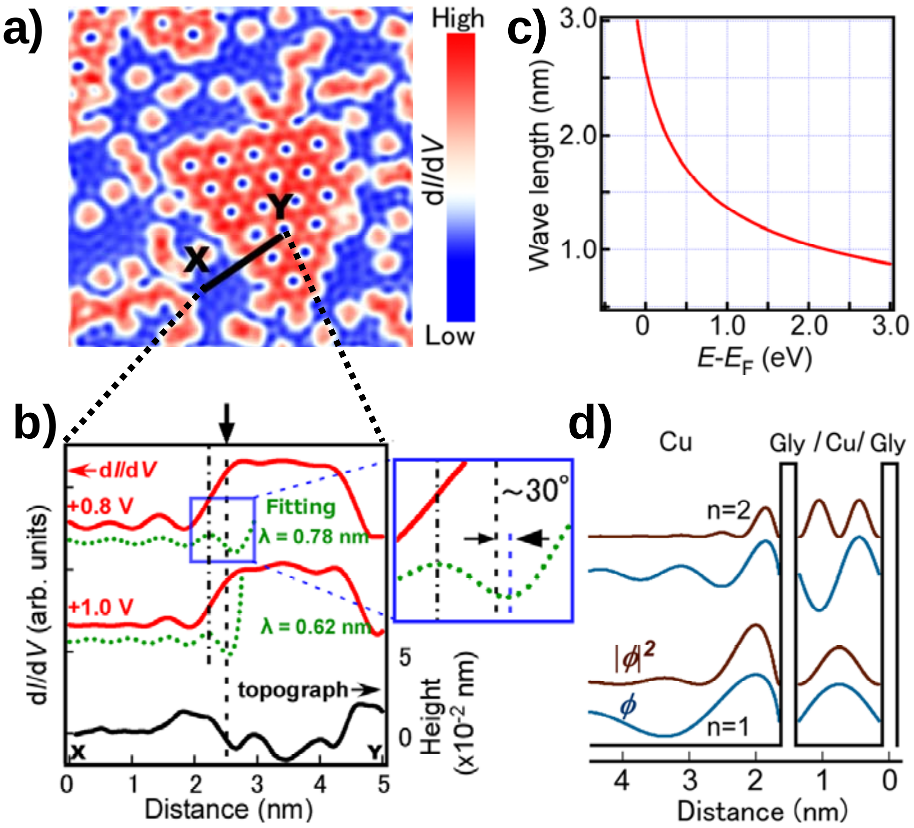

Figure S3. Analysis of electronic states in nanocavity by d*I*/d*V* mapping. **a**, d*I*/d*V* map obtained over surface including bare Cu areas with standing wave patterns (V_s = +1.0 V, I_t = 1.0 nA). **b**, Cross sections of d*I*/d*V* images along X-Y in (a) for V_s = +0.8 and +1.0 V (red lines) and their fitting curves (green lines) with the wavelengths obtained from (c) for the corresponding energies. The solid black line represents the cross section of the STM image along X-Y in (a) obtained for V_s = -0.8 V. Black dotted and dash-dotted lines indicate the edge of the supramolecular network and the first loop of the standing wave from the edge, respectively. **c**, Wavelength as function of energy from Fermi level.[1] **d**, Schematic models for electronic states in quantum corral. Brown and blue lines represent the spatial distributions of wave functions and their density of states, respectively.