Electronic supplementary information:

Molecular tuning of amino acid to form two-dimensional molecular network driven by conformational preorganization

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1. Experimental and computational details

STM measurements were performed in a UHV chamber equipped with an OMICRON VT-STM instrument at a base pressure below 1.0×10^{-10} Torr. The Au(111)/mica substrate (Agilent Technologies, N9805B) was cleaned by submitting the substrates to several sputtering cycles using 0.5 keV Ar$^+$ ions (20 min) followed by annealing at 680 K for 10 min, resulting in a characteristic herringbone reconstruction of the clean Au(111) substrate.[1] The cleanliness of the Au(111)/mica substrate was checked with STM. Depositions of α- and γ-phenylalanine on the substrate were performed using a home-built doser which is composed of a glass tube wrapped with a heating wire, a kovar glass for insert of the sample powdered at room temperature, and a gate valve for the connection of the glass tube and the kovar glass. For sublimation of α- and γ-phenylalanine, the glass tube and the kovar glass are heated at 420 and 320 K, respectively, which relatively are low temperature compared with temperature for decomposition of α-Phe and for formation of a ring-like cluster in the gas-phase via sublimation shown in α-Ser.[2, 3] For purification of α- and γ-phenylalanine, repeated sublimation was executed to remove all dissolved gasses prior to dosing. After exposing the phenylalanine molecules to the Au(111)/mica surface at room temperature, the substrate was cooled to 150 K to minimize the surface mobility of α- and γ-phenylalanine molecules.

All STM images were recorded using an electrochemically etched tungsten tip at various sample bias voltages (V_s) with a tunneling current of I_t= 0.07 or 0.1 nA. Because the amplitude of herringbone corrugation on the reconstructed Au(111) was reported as 0.1 – 0.2 Å, the underlying herringbone structure may give rise to intensity modulation of the overlayer molecules.[1] STM image is affected by height and electron density of the molecules adsorbed on the surface. Therefore, the statistical analysis was executed to minimize an inevitable height error arising from the corrugation of the reconstructed Au(111). All values measured from the line profile analysis had an error rate that provided a 95% confidence interval.

α-Phe (L-phenylalanine; $C_6H_5CH_2CH(NH_2)COOH$, 99.0% purity) was purchased from Aldrich. β-Benzyl γ-aminobutyric acid (γ-Phe) was synthesized in a straightforward manner from (1R,5S)-bicyclic lactone by following our protocol reported.[4]

To investigate the self-assembly configurations of γ-Phe on the Au(111) surface, we performed ab initio calculations within the generalized gradient approximation (GGA) using the Vienna ab initio simulation package (VASP).[5] The ionic pseudopotentials were described via the project-augmented wave (PAW) method.[6] Plane waves with energy up to 400.0 eV were included to expand the wave functions, and the atoms were represented by ultrasoft pseudopotentials, as provided by VASP.[7] In the surface calculations, the theoretical lattice constant of 4.17 Å was determined for gold, which compares well to previously- reported value of 4.175 Å.[8] The Au(111) surface with adsorbed γ-Phe was modeled as a slab with a proper surface unit cell such as p(4×4), p(6×2), p(7×2), p(8×3), or p(10×10) that was composed of four Au layers and adsorbed γ-Phe molecules. The topmost two layers of the slab and the adsorbed molecules were relaxed until the calculated Hellmann-Feynman forces were smaller than 0.02 eV/ Å, and the two remaining Au layers were kept frozen during the structure optimization. By using self-consistent Kohn-Sham eigenvalues and wavefunctions, the constant-current STM images were simulated within the Tersoff-Hamann scheme.[9, 10]
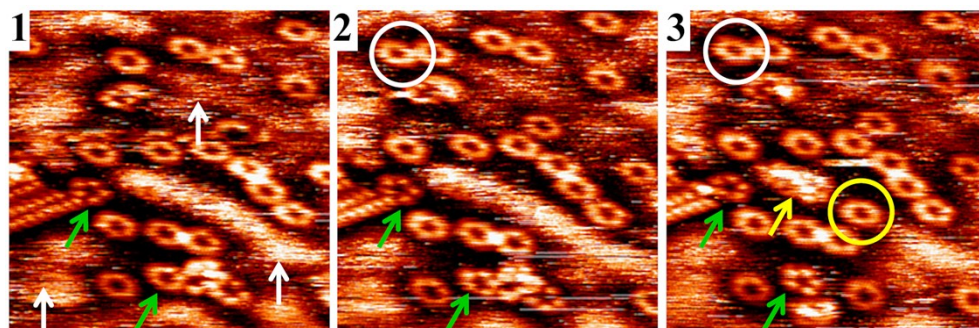
Fig. S1 A sequence of filled-state STM images (19.3 × 19.3 nm², V_s= –2.0 V, I_t = 0.07 nA) of the Au(111) surface at 150 K after exposure to γ-Phe until an intermediate coverage. The white and yellow circles indicate the newly formed the RSCs. The white arrows indicate several blurs associated with mobile γ-Phe molecules. The yellow arrow indicates a confined area in which the mobile γ-Phe molecules were enclosed by the RSCs due to the formation of a RSC (indicated by a yellow circle). The feature of a RSC was changed from a ring-like structure to the cluster exhibiting individual protrusions when the RSC interacts with mobile γ-Phe molecule, another RSC, PLC, or 2D molecular domain, indicating the destruction of the RSC configuration. The green arrows indicate the destroyed RSCs which are imaged as the cluster with individual protrusions.
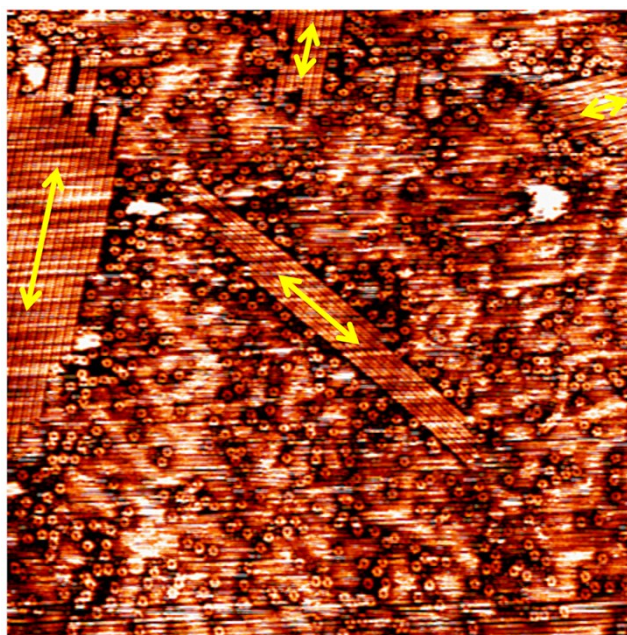

Fig. S2 Filled-state STM image (150 × 150 nm², V_s = –1.2 V, I_t = 0.07 nA) of the Au(111) surface recorded at 150 K after exposure of γ-Phe until an intermediate coverage. Shown is the coexistence region of the RSCs and the 2D molecular networks. In the STM image, the 2D molecular domains grew along three directions with three-fold symmetry on the Au(111) surface (indicated by yellow arrows).
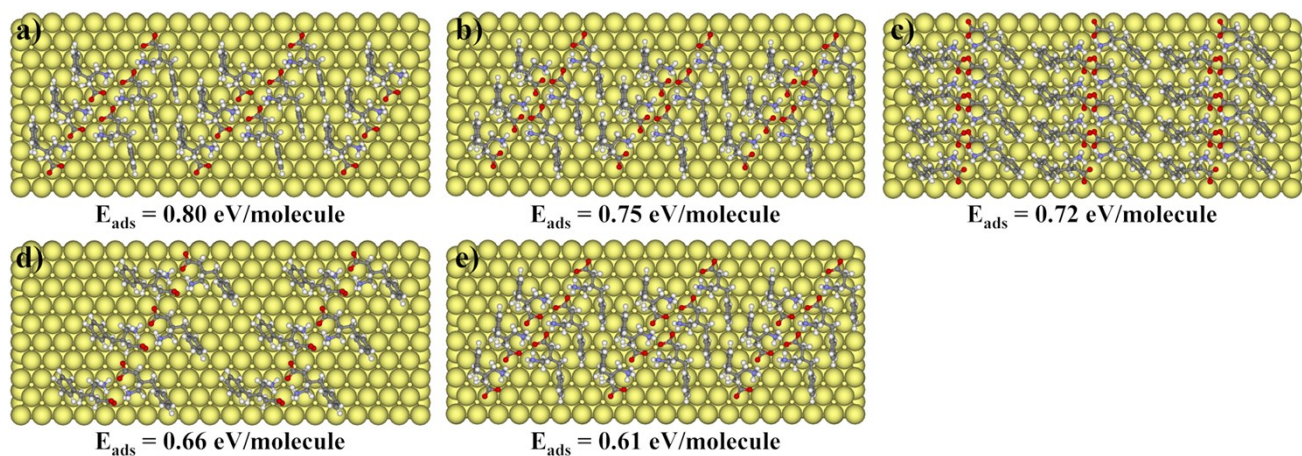
Fig. S3 The calculated structures with adsorption energies for 2D molecular network. Considering the adsorption energies, (a) is more favorable than the others, the simulated STM image of which is exhibited in Fig. 5c.

References

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