Electronic Supplementary Material (ESI) for Chemical Communications.

Ionic-interactions-induced assembly of bimolecular "chessboard" structure

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Experimental details

Chemicals. The electrolyte used in the STM measurements is 0.1 M $HClO_4$ solution prepared by diluting 99.999% pure $HClO_4$ (Sigma-Aldrich Co.) with Milli-Q water (18.2 MΩ cm, total organic carbon < 5 ppb). The Au(111) single-crystal surface was prepared by the Clavilier method. Before each measurement, the Au(111) electrode was further annealed in a hydrogen-oxygen flame and quenched in an ultrapure N_2 atmosphere. TSPP and TTAP were purchased from Sigma-Aldrich Co. and FeTMPyP was purchased from Frontier Scientific Inc.. All chemicals are used without further purification. To prepare a TSPP, TTAP adlayers and hybrid adlayers, the molecules were dissolved in Milli-Q water to form aqueous solution at concentration of 10^{-4} M, and then, a pretreated Au(111) electrode was immersed in the as-prepared monocomponent or mixture aqueous solution for 1 minute to acquire molecular monolayer or multilayer.

STM. All STM measurements were performed in constant-current mode using a Nanoscope E STM instrument (Bruker). STM tips were electrochemically etched from W wires in 0.6 M KOH and sealed with transparent nail polish to minimize Faradic currents. All potentials were reported with respect to SCE.

Electrochemistry. CV measurements were performed on an EG&G PAR 2273 Advanced Electrochemical System (Princeton Applied Research), using the hanging meniscus method in a three-compartment electrochemical cell under an N_2 atmosphere. The commercial Au(111) single crystal was used as a working electrode.

Theoretical Simulation. Molecular assembly structures were built and optimized with Forcite modulus. Dreiding was chosen as the force field to perform geometry optimization to get the blend at the lowest energy. The structures at lowest energy can be demonstrated when the geometry

optimization is finished running, and then the molecular interaction energy consists of valence and non-bond energy can be obtained.

Table S1 | Simulated energy (in kcal mol^{-1}) of different monolayer structures in Figure 2-4

	FeTMPyP-TSPP	TTAP-TSPP	TSPP	TTAP	FeTMPyP
ΔE	−79.88	−61.55	6.21	21.87	——
Electrostatic	−73.88	−56.63	12.59	25.49	——
van der Waals	−2.71	−3.77	−8.04	−5.36	——

ΔE represents the total molecular interaction energy changes from isolated molecules to self-assembly structure, which can be generated from valence and/or non-bond energy.

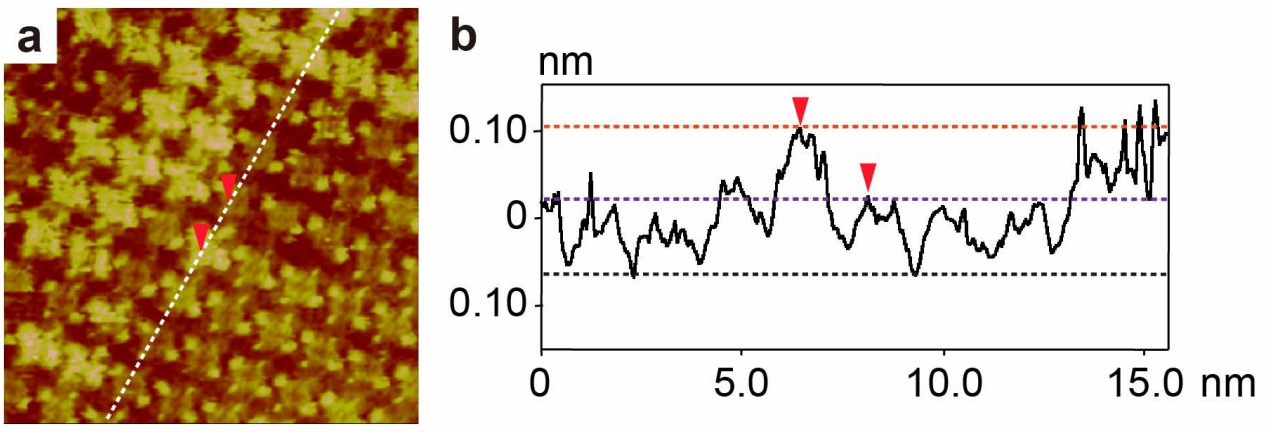

Figure S1 | (a) High-resolution STM images of TTAP adlayer in 0.1 M $HClO_4$/Au(111) interface; (b) Cross-section profiles along the white dotted line in (a); Image conditions: (a) E = 41 mV, E_{bias} = −330 mV, I_t = 1.000 nA;

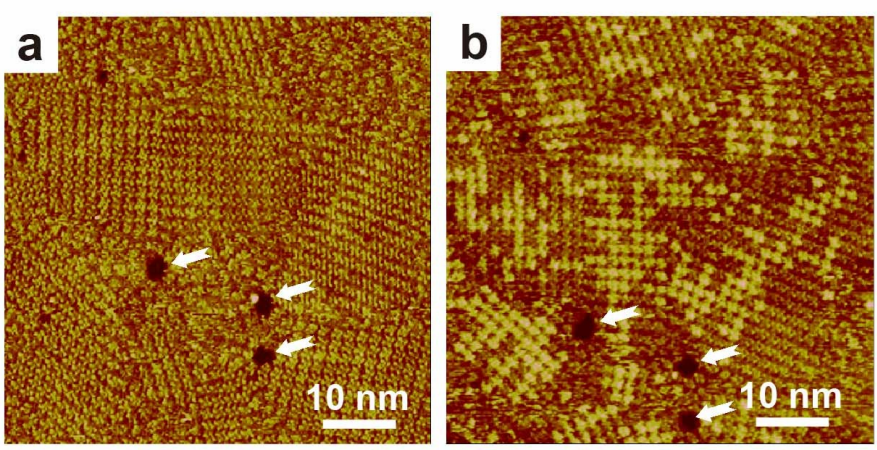

Figure S2 | Sequential STM images taken under different potentials recorded the formation of the TTAP bilayer structure. Image conditions: (a) E = 350 mV, E_{bias} = −369 mV, I_t = 1.000 nA; (b) E = 41 mV, E_{bias} = −330 mV, I_t = 1.000 nA;

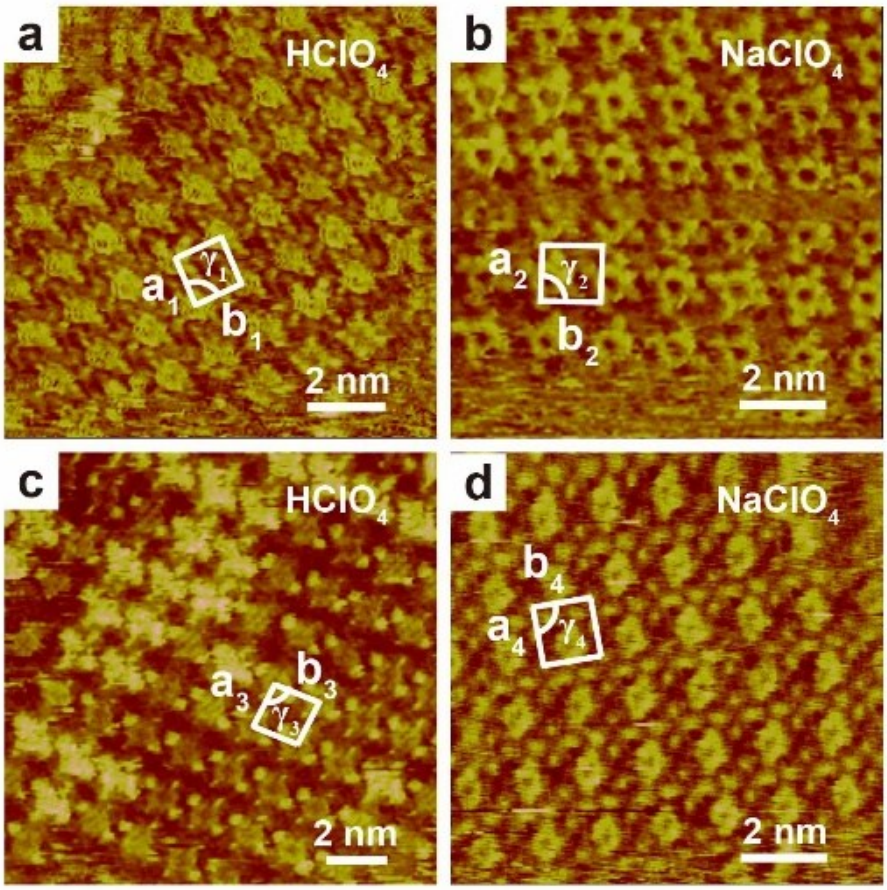

Figure S3 | (a – b) STM images of TSPP monolayer in 0.1 M $HClO_4$/Au(111) interface and 0.1 M $NaClO_4$/Au(111) interface; (c – d) STM images of TTAP monolayer in 0.1 M $HClO_4$/Au(111) interface and 0.1 M $NaClO_4$/Au(111) interface; Image conditions: (a) E = 350 mV, E_{bias} = −593 mV, I_t = 6.000 nA; (b) E = 350 mV, E_{bias} = −355 mV, I_t = 2.388 nA; (c) E = 41 mV, E_{bias} = −330 mV, I_t = 1.000 nA; (d) E = 350 mV, E_{bias} = −572 mV, I_t = 2.500 nA;

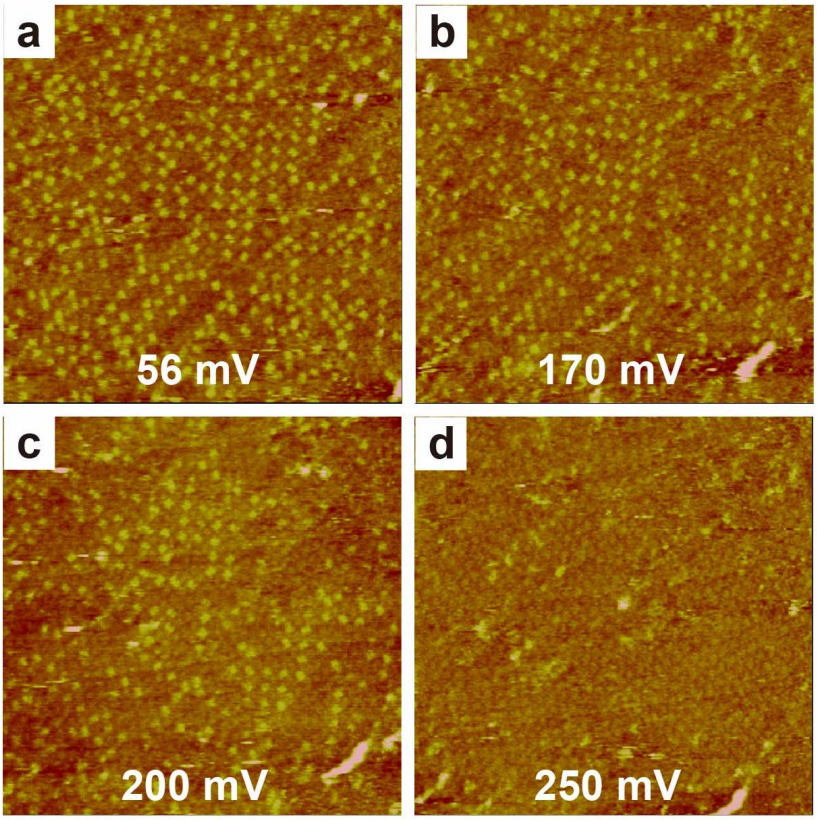

Figure S4 | Sequential STM images taken under different potentials recorded the desorption process of the TTAP molecules on the 2D bimolecular chessboard structure. Image conditions: (a) E = 56 mV, E_{bias} = −380 mV, I_t = 2.200 nA; (b) E = 70 mV, E_{bias} = −380 mV, I_t = 2.200 nA; (c) E = 170 mV, E_{bias} = −380 mV, I_t = 2.200 nA; (d) E = 200 mV, E_{bias} = −380 mV, I_t = 2.200 nA; (e) E = 250 mV, E_{bias} = −380 mV, I_t = 2.200 nA;

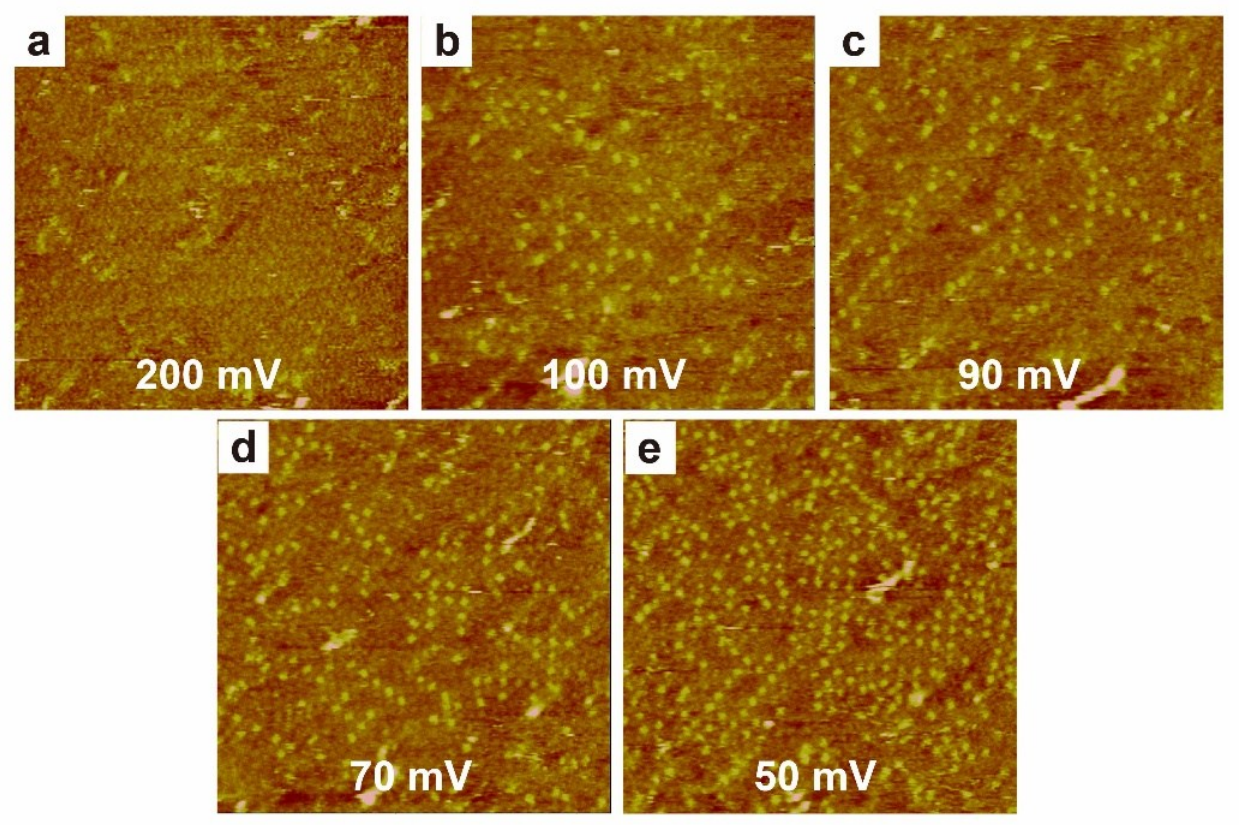

Figure S5 | Sequential STM images taken under different potentials recorded the formation process of the bilayer chessboard structure formed by TTAP and TSPP. Image conditions: (a) E = 200 mV, E_{bias} = −550 mV, I_t = 2.200 nA; (b) E = 100 mV, E_{bias} = −550 mV, I_t = 2.200 nA; (c) E = 90 mV, E_{bias} = −550 mV, I_t = 2.200 nA; (d) E = 70 mV, E_{bias} = −550 mV, I_t = 2.200 nA; (e) E = 50 mV, E_{bias} = −550 mV, I_t = 2.200 nA;

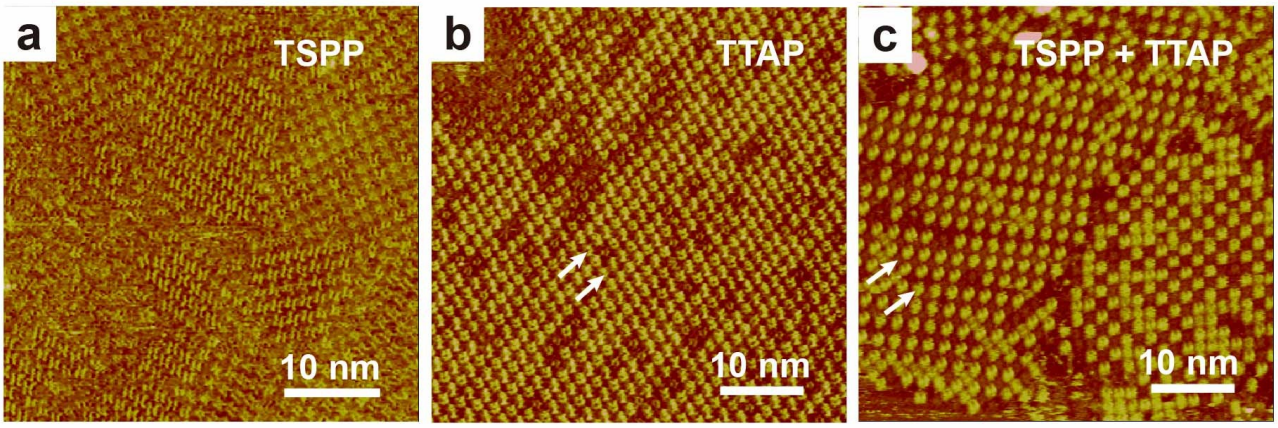

Figure S6 | Large-scale STM images of (a) TSPP monolayer, (b) TTAP bilayer and chessboard bilayer structure on Au(111) surface; Image conditions: (a) E = 350 mV, E_{bias} = −383 mV, I_t = 0.983 nA; (b) E = 50 mV, E_{bias} = −231 mV, I_t = 2.272 nA; (c) E = 50 mV, E_{bias} = −699 mV, I_t = 1.236 nA.

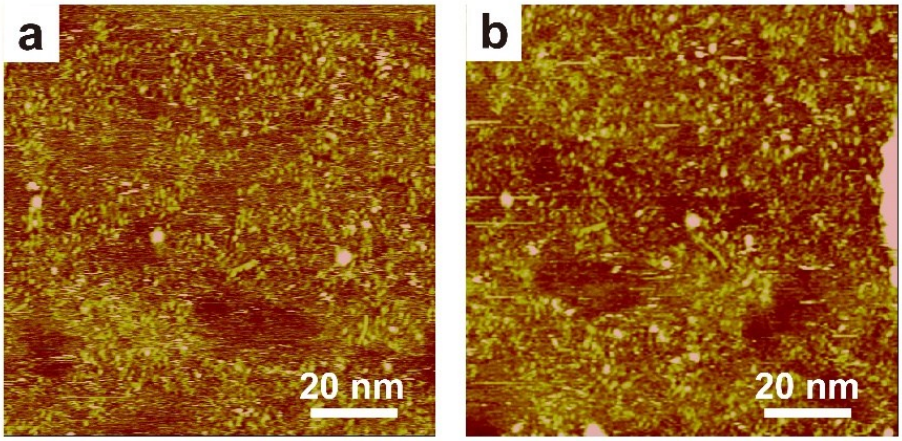

Figure S7 | FeTMPyP monolayer. (a – b) Large-scale STM images of FeTMPyP monolayer on Au(111) surface. Image conditions: (a – b) E = 350 mV, E_{bias} = −422 mV, I_t = 1.000 nA.

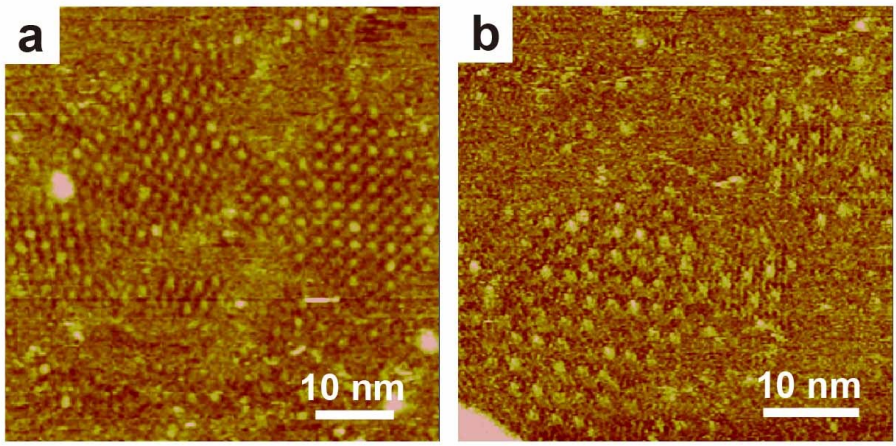

Figure S8 | Large-scale STM images of single-layer bimolecular chessboard structure. (a – b) Large-scale STM images of 2D bimolecular chessboard monolayer formed by FeTMPyP and TSPP on Au(111) surface. Image conditions: (a) E = 50 mV, E_{bias} = −193 mV, I_t = 1.000 nA; (b) E = 50 mV, E_{bias} = −214 mV, I_t = 1.000 nA.

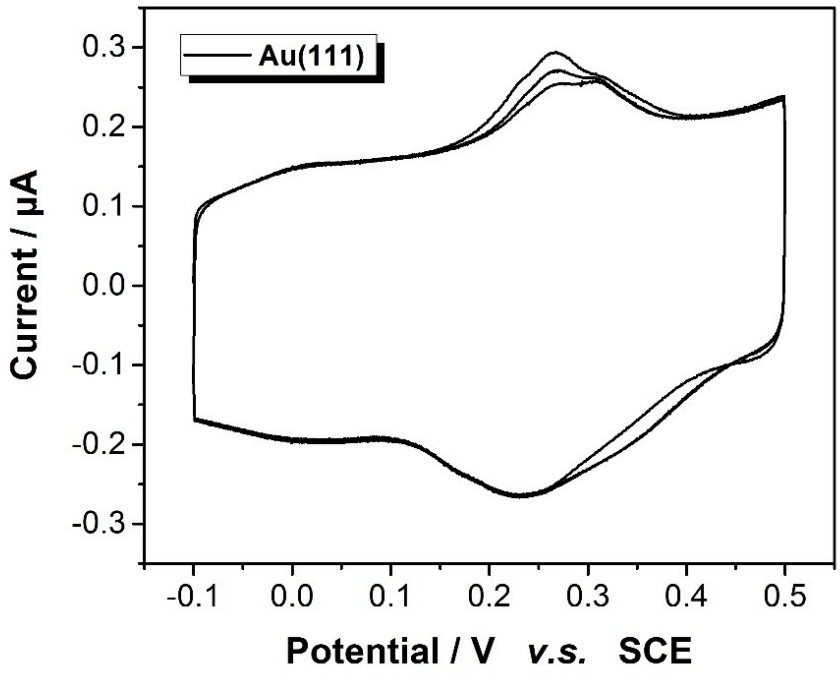

Figure S9 | Cyclic voltammogram of bare Au(111) electrode in 0.1 M $HClO_4$. CV was recorded in a N_2 atmosphere at a scan rate of 50 mV s^{-1}.

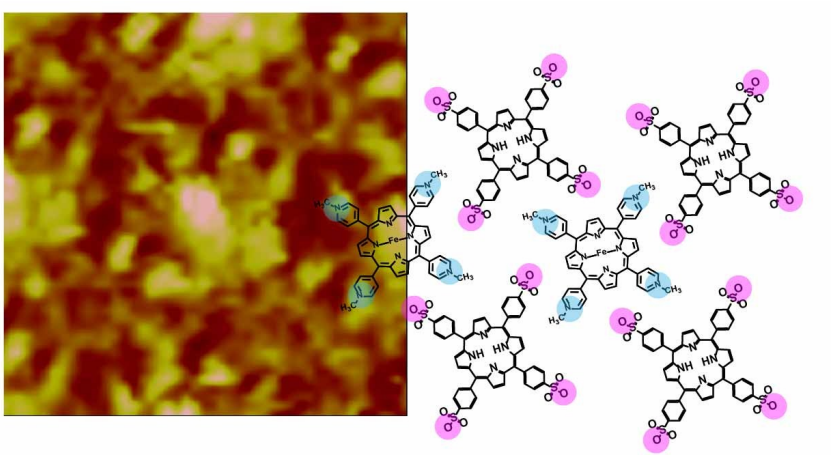

Figure S10 | High-resolution STM image and proposed structural model of the 2D bimolecular chessboard monolayer formed by FeTMPyP and TSPP on Au(111) surface. Image conditions: E = 350 mV, E_{bias} = −214 mV, I_t = 1.000 nA.