

Electronic supplementary information

**Molecular planting of a single organothiol into a “gap-site” of a
2D patterned adlayer in an electrochemical environment**

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Experimental

Materials Ovalene was purchased from Chiron AS (purity: 99.5%). Benzene (Spectroscopy Grade) and perchloric acid (ultrapure grade, Cica-Merck) were purchased from Kanto Chemical Co. Ltd. (Tokyo, Japan). 3-Mercaptopropionic acid (99.9%) and aldrithiol-4 (4,4'-dipyridyldisulfide; 98%) were purchased from Sigma–Aldrich Japan, and 4-mercaptopyridine (97%) was acquired from Tokyo Chemical Industry (Tokyo, Japan). 2-Mecaptopyrazine (2-PyzSH) was obtained from Angene International (98%; China). All chemicals were used without further purification.

Sample Preparation The Au(111) single-crystal electrode was prepared as described in our previous papers.^{s1} Prior to immersion, the Au(111) substrate was annealed in a hydrogen flame and cooled down in a ultrapure water to prevent any contaminations.^{s1} An ovalene adlayer was formed by immersing a Au(111) substrate in a benzene solution saturated with ovalene at room temperature for 15–20 min. The ovalene adlayer thus produced was transferred into an electrochemical STM cell filled with 0.05–0.10 M HClO₄ after it was washed thoroughly with ultrapure water. A 10–50 μM aqueous solution of 3-MPA, 4-PySH, and 2-PyzSH was added to EC-STM cell under potential control at potentials between 0.25 and 0.20 V vs. RHE to form a special ovalene adlayer on Au(111). The final concentration of each solution was less than approximately 0.1 μM in the EC-STM cell.

EC-STM Measurements Electrochemical STM measurements were performed in 0.1 M HClO₄ by using either a Nanoscope E (Digital Instruments, Santa Barbara) or Nanoscope V (Bruker, Billerica) systems with a tungsten tip etched in 1 M KOH. To minimize residual faradaic currents, the tips were coated with either nail polish.^{s2} STM images were obtained in constant-current mode with a high-resolution scanner (HD-0.5I). All potential values (both substrate and tip) refer to the reversible hydrogen electrode (RHE).

References

- s1 J. Clavilier, R. Faure, G. Guinet and R. Durand, *J. Electroanal. Chem. Interfacial Electrochem.*, 1980, **107**, 205–209.
- s2 S. Yoshimoto and K. Itaya, *Annu. Rev. Anal. Chem.*, 2013, **6**, 213–235.

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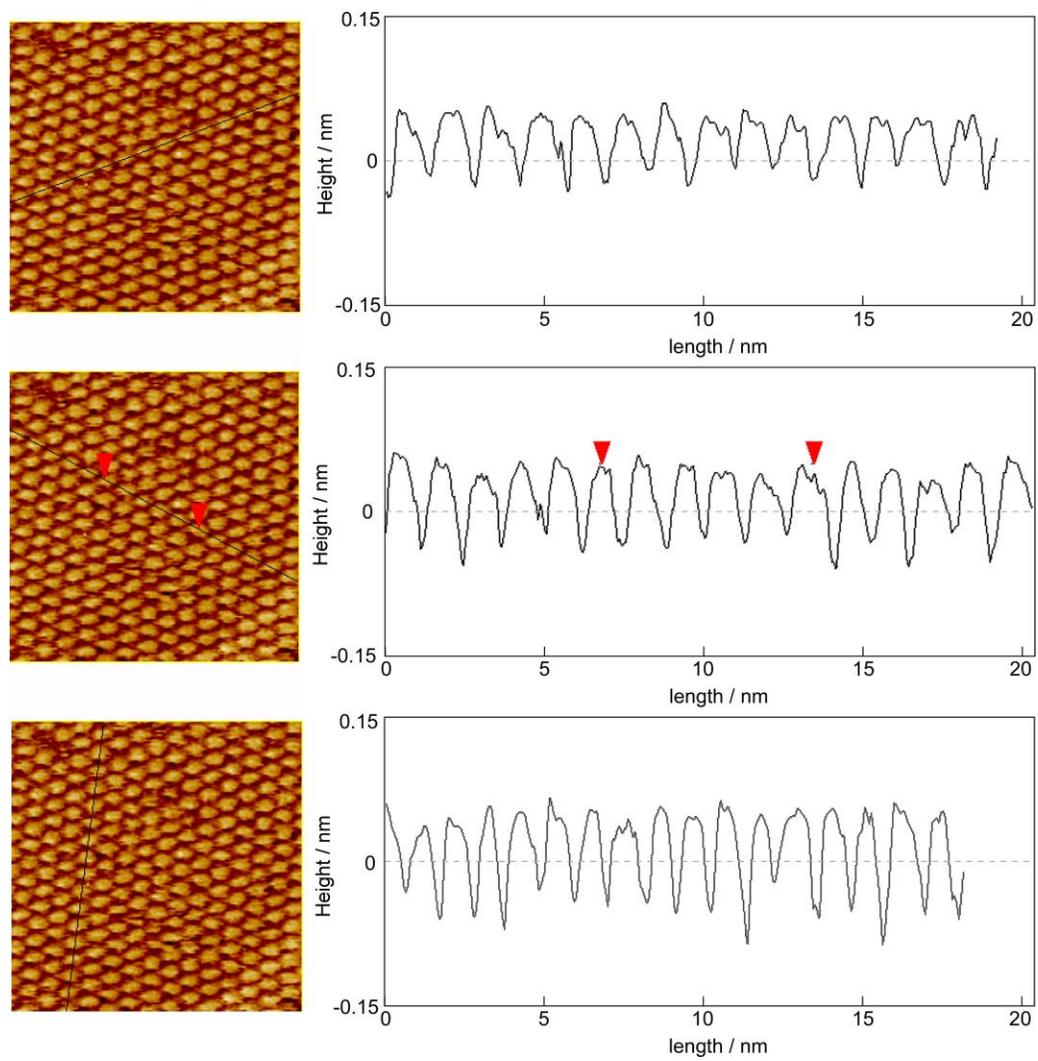


Fig. S1 Cross-sectional profiles for three directions of the STM image observed at 0.78 V vs. RHE.

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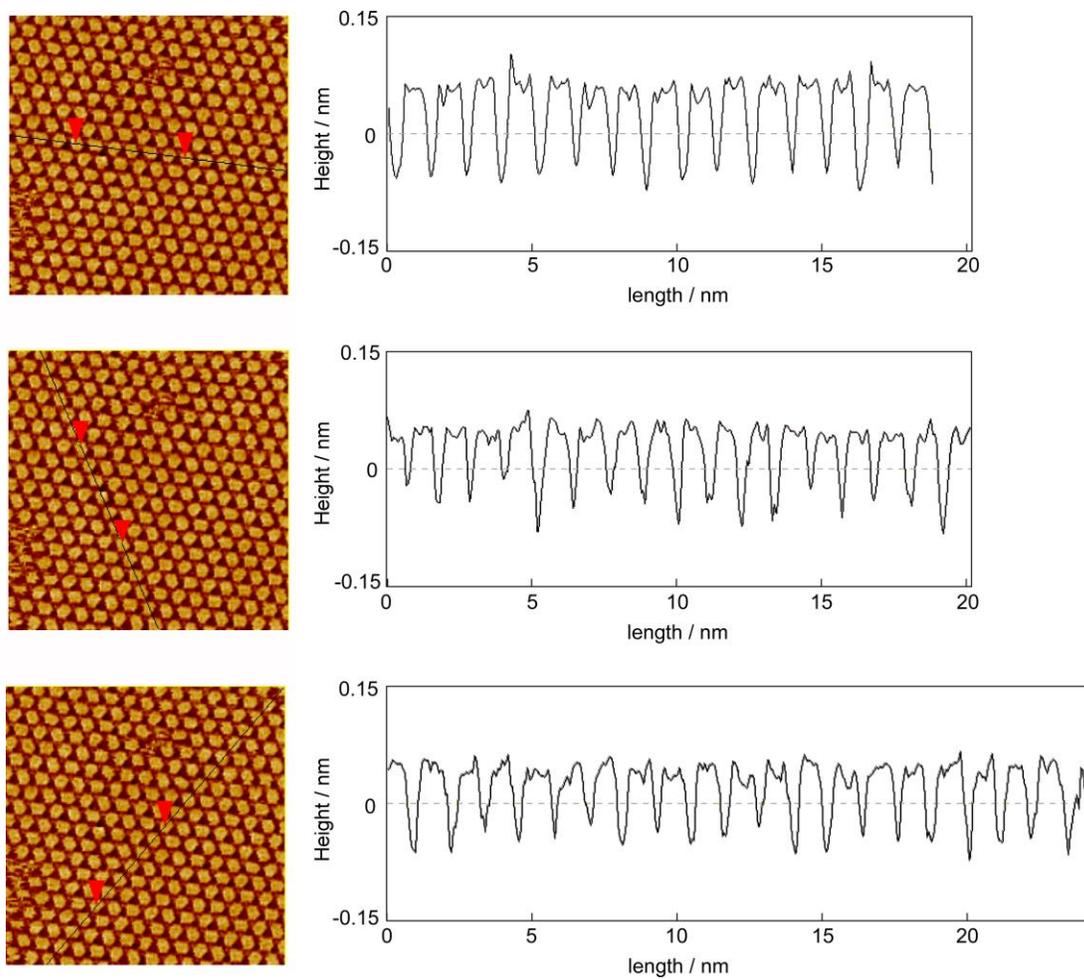


Fig. S2 Cross-sectional profiles for three directions of the STM image observed at 0.25 V vs. RHE.

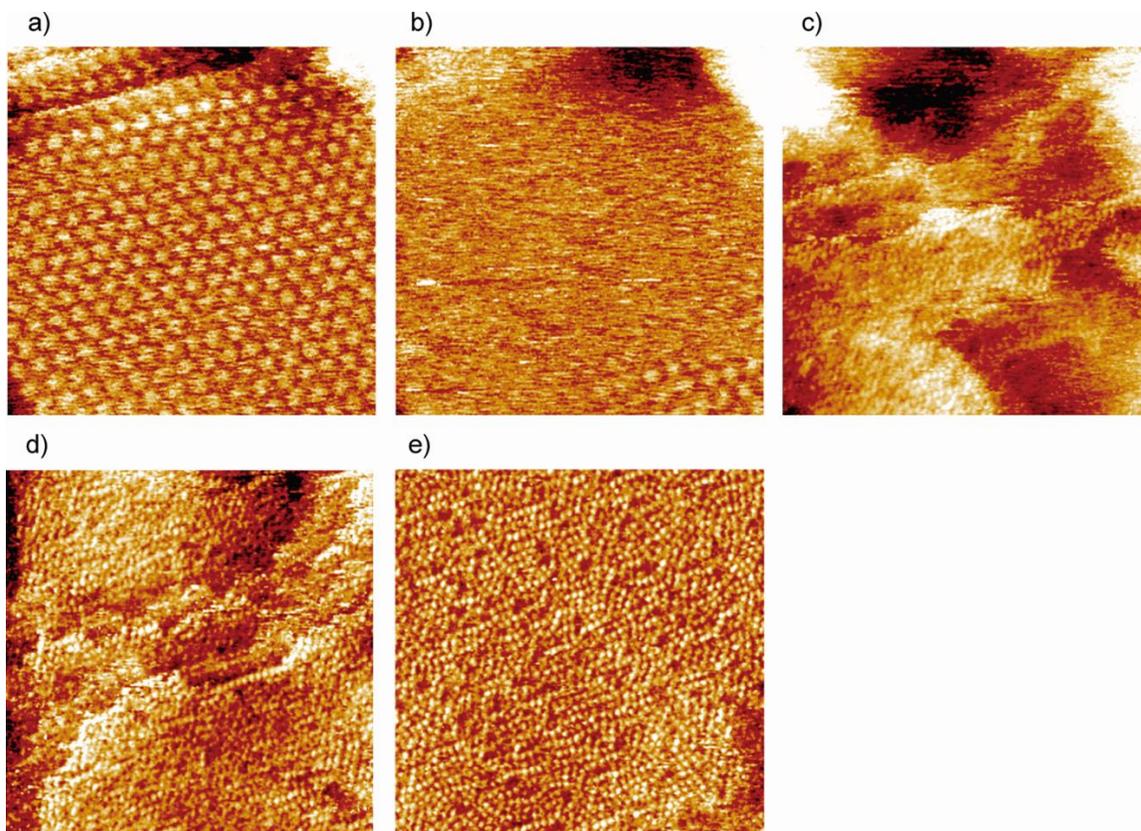


Fig. S3 | Time-dependent ECSTM images of ovalene adlayer on Au(111) in 0.1 M HClO₄ in the presence of 50 μM 3-MPA. STM image was taken in b), 13 min, c), 23 min, d), 36 min, and e), 90 min, respectively, after panel a) was observed at 0.25 V versus RHE in 0.1 M HClO₄. The tip potential and tunneling current were 0.39 V and 0.50 nA, respectively.

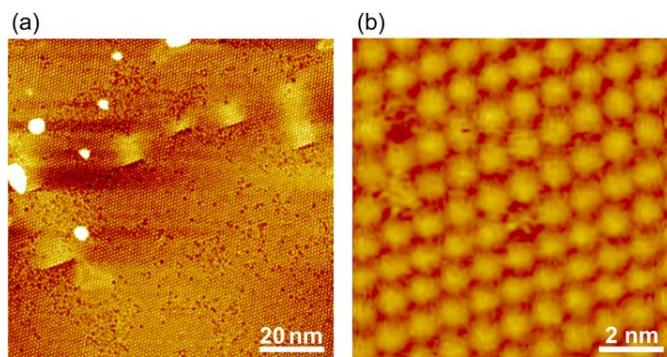


Fig. S4 | Coronene adlayer in the presence of 3-MPA. EC-STM images of a) Large-scale ($100 \times 100 \text{ nm}^2$) and b) high-resolution ($10 \times 10 \text{ nm}^2$) STM images of coronene adlayer on Au(111) on Au(111) at 0.25 V versus RHE in 0.1 M HClO_4 in the presence of 3-MPA. The tip potential and tunneling current were 0.40 V and 3.0 nA, respectively.

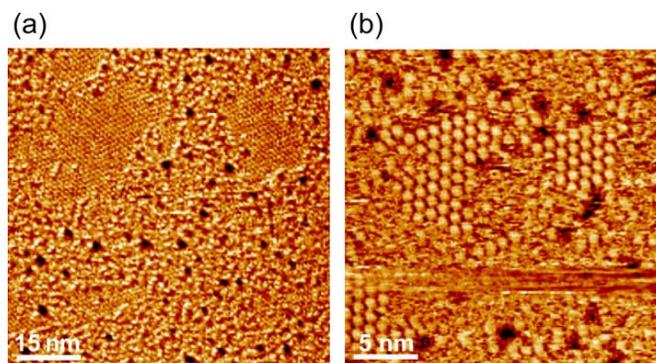


Fig. S5 | Replacement of coronene adlayer with 3-MPA. a) Large-scale ($75 \times 75 \text{ nm}^2$) and b) high-resolution ($25 \times 25 \text{ nm}^2$) STM images of coronene adlayer on Au(111) at 0.60 V versus RHE in 0.1 M HClO_4 in the presence of 3-MPA. The tip potential and tunneling current were 0.40 V and 2.0 nA, respectively.

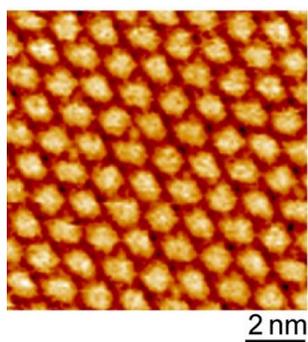


Fig. S6 | Ovalene adlayer in the presence of PySSPy. High-resolution STM image of ovalene adlayer on Au(111) at 0.25 V versus RHE in 0.1 M HClO₄. The tip potential and tunneling current were 0.40 V and 2.5 nA, respectively.