Supplementary information for

Directed Assembly of Fullerene on Modified Au(111) Electrodes

Zhen-Feng Cai,[ab] Wei-Long Dong,[a] Ting Chen,[a] Hui-Juan Yan,[a] Dong Wang,[*a] Wei Xu,[*c] and Li-Jun Wan[*a]

[a] CAS Key Laboratory of Molecular Nanostructure and Nanotechnology and Beijing National Laboratory for Molecular Sciences, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100190, People's Republic of China;

[b] University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China;

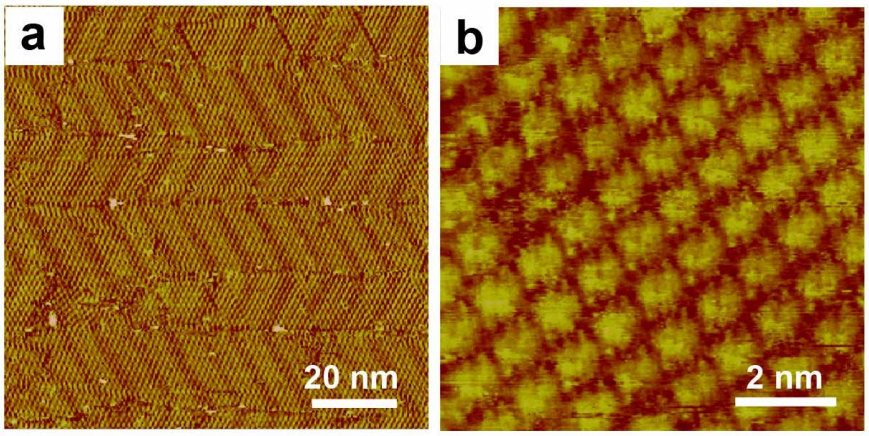
[c] CAS Key Laboratory of Organic Solids, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100190, People's Republic of China.

Correspondence and requests for materials should be addressed to D.W., W.X. or L-J.W, (email: wangd@iccas.ac.cn; wxu@iccas.ac.cn; wanlijun@iccas.ac.cn)

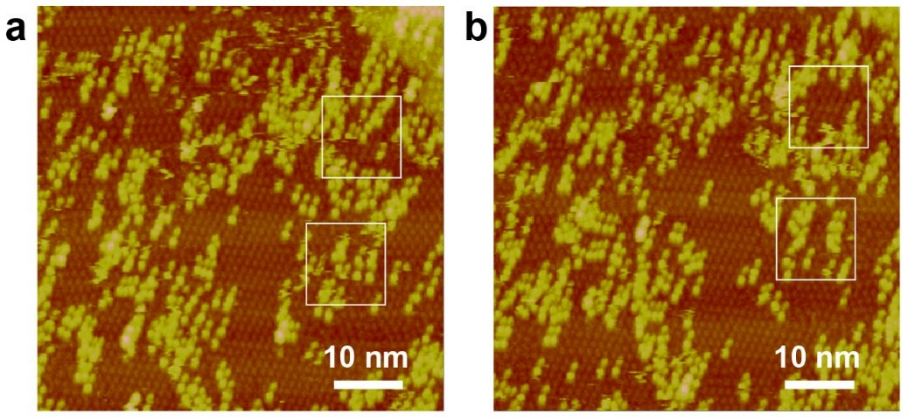
Experimental Section

STM measurements. 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 RHE.

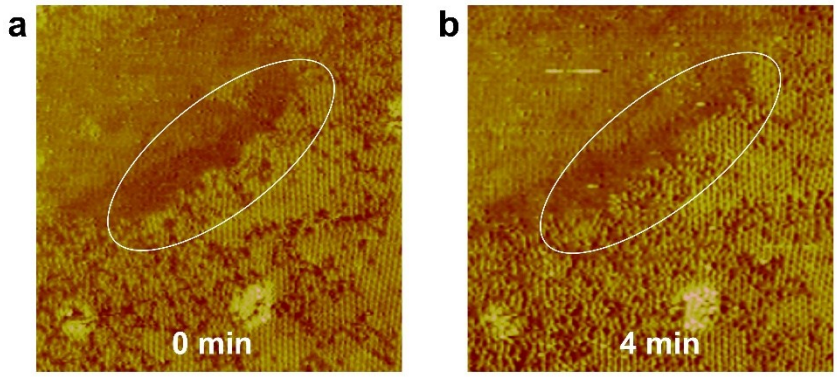
Materials. The electrolyte used in the STM measurements is 0.1 M $HClO_4$ solution prepared by diluting 99.999% pure $HClO_4$ (Sigma-Aldrich Co.) with Milli-Q water (18.2 MΩ cm, total organic carbon < 5 ppb). The Au(111) single-crystal surface was prepared by the Clavilier method[1]. Before each measurement, the Au(111) electrode was further annealed in a hydrogen-oxygen flame and quenched in an ultrapure N_2 atmosphere. DPTTA was synthesized as per the literatures[2]. To prepare a DPTTA adlayer, the molecules were dissolved in dimethyl formamide (Sigma-Aldrich Co.) to form saturated solution. Fullerenes-C_{60} (97%) was purchased from Suzhou Dade Carbon nanotechnology Corporation and used without further purification. The C_{60} molecules were dissolved in chlorobenzene (Sigma-Aldrich Co.) to form saturated solution and then diluted 10 times. To prepared C_{60} adlayer on DPTTA modified Au(111) surface, some C_{60} solution was dropped into the electrochemical cell.



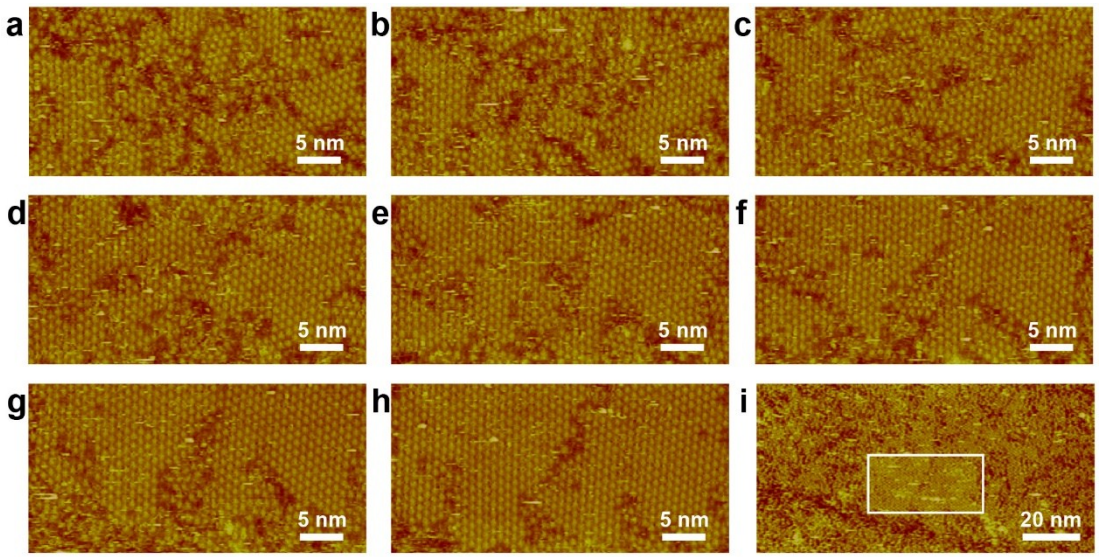
Supplementary Figure 1 | DPTTA monolayer on 0.1 M $HClO_4$/Au(111) interface. (a) Large-scale and (b) high-resolution STM images of DPTTA monolayer on Au(111) surface. Tunneling conditions: (a) Scan area = 100 × 100 nm^2, E_{bias} = −197.0 mV, I_t = 1.000 nA. (b) Scan area = 20 × 20 nm^2, E_{bias} = −100.0 mV, I_t = 1.096 nA.



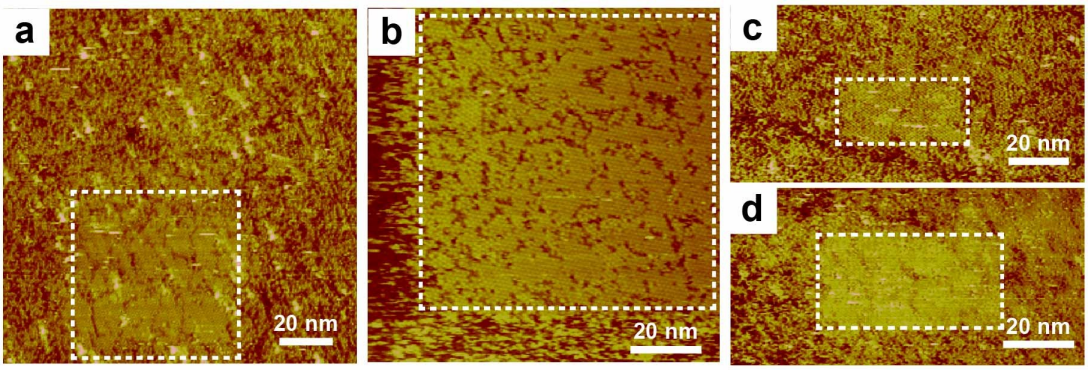
Supplementary Figure 2 | Real time STM measurements of C_{60} adlayer on DPTTA modified Au(111) surface with a function of time. Tunneling conditions: (a − b) Scan area = 60 × 60 nm^2, E_{bias} = −238.0 mV, I_t = 1.000 nA.



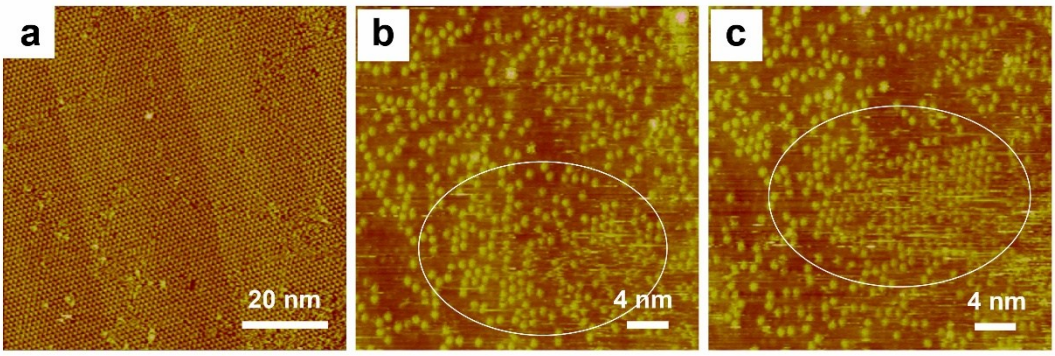
Supplementary Figure 3 | Real time STM measurements of C_{60} adlayer on Au(111) surface with a function of time. (a) Typical STM images (Scan area = 61 × 61 nm^2, E_{bias} = −260.0 mV, I_t = 1.000 nA) of C_{60} adlayer adsorbed on Au(111) electrodes. (b) The same region of a after continuing scanned by STM tip for 4 minutes. Tunneling conditions: Scan area = 65 × 65 nm^2, E_{bias} = −260.0 mV, I_t = 1.000 nA.



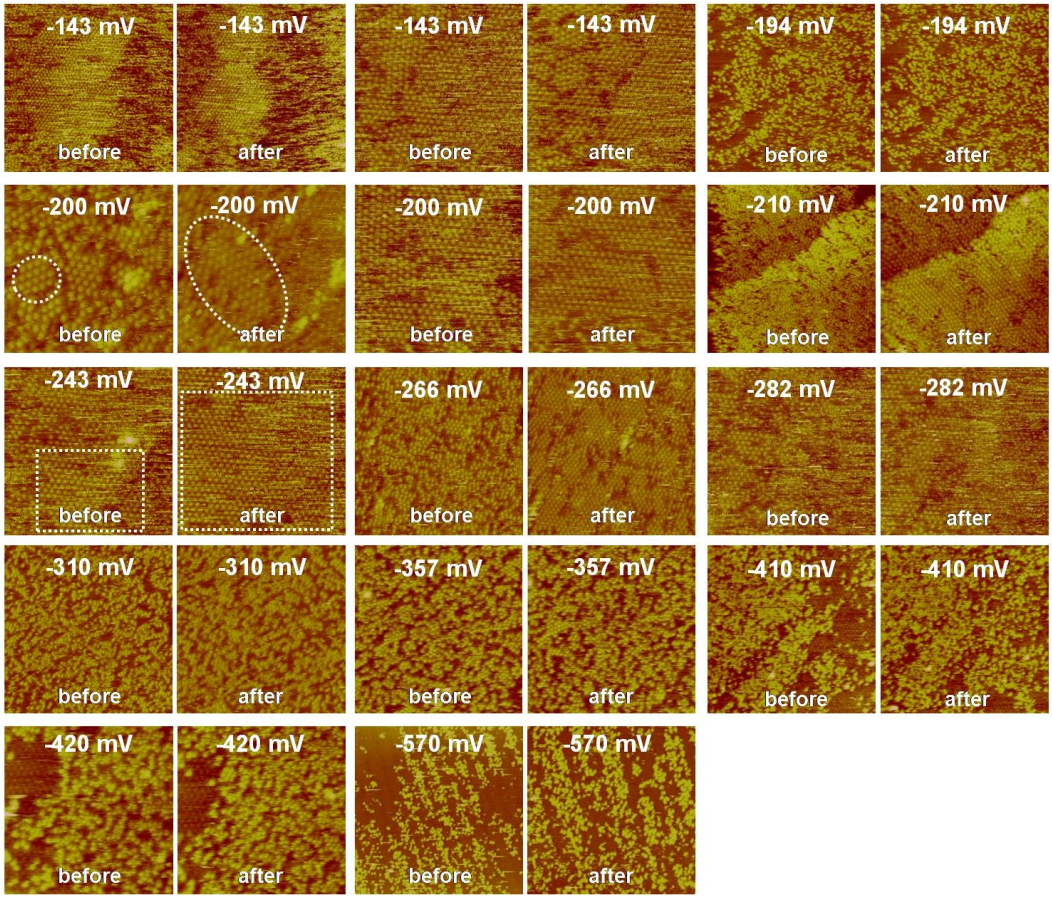
Supplementary Figure 4 | Real time STM measurements of induced-assembly C_{60} adlayer on DPTTA modified Au(111) surface. (a-h) Typical STM image (Scan area = 40 × 20 nm^2, E_{bias} = −310.0 mV, I_t = 2.500 nA) of C_{60} adlayer induced by STM tip. (i) The zoomed out image of **a**. Tunneling conditions: Scan area = 118 × 59 nm^2, E_{bias} = −310.0 mV, I_t = 2.500 nA.



Supplementary Figure 5 | Assembly patterns of C_{60} adlayer induced by STM tip. (a, b) STM images of square patterns of C_{60} adlayer on DPTTA modified Au(111) surface; (b, c, d) STM images of rectangle patterns; Aspect ratio of the patterns: (a, b) 1:1; (c, d) 2:1.

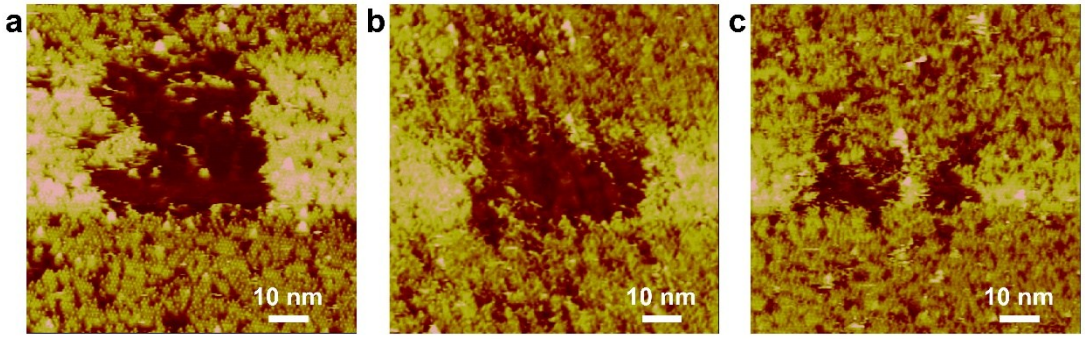


Supplementary Figure 6 | Coronene monolayer on Au(111) surface and C_{60} adlayer on coronene modified Au(111) surface. (a) Typical STM image (Scan area = 80 × 80 nm^2, E_{bias} = −200.0 mV, I_t = 1.000 nA) of coronene monolayer adsorbed on Au(111) electrode. (b − c) Typical STM images of C_{60} adlayer adsorbed on coronene modified Au(111) surface with the function of time. (c) The same region of b after continuing scanned by STM tip for 2 minutes. Tunneling conditions: (b − c) Scan area = 33 × 33 nm^2, E_{bias} = −179.0 mV, I_t = 1.000 nA.

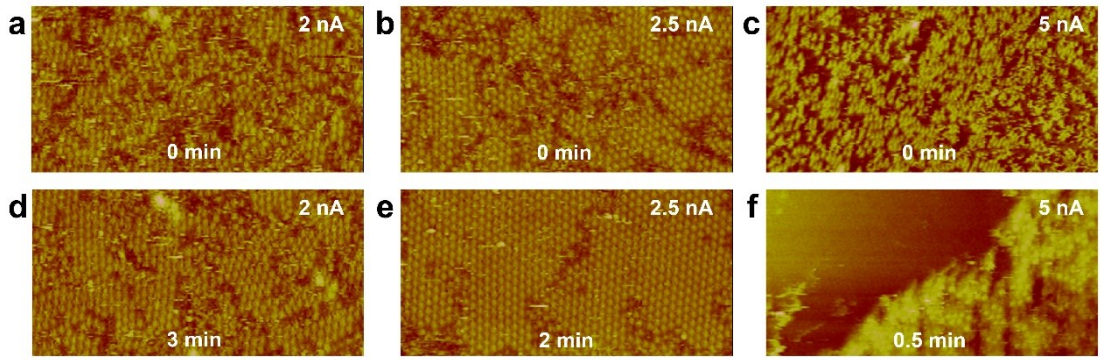


Supplementary Figure 7 | STM measurements of C_{60} adlayer with a function of E_{bias}.

Typical STM images of C_{60} adlayer adsorbed on DPTTA modified Au(111) electrodes under different bias voltage.



Supplementary Figure 8 | The reassembly process of C_{60} adlayer. (a−c) The sequential STM images of the reassembly process C_{60} adlayer after the effect of positive bias voltage. Tunneling conditions: (a−c) Scan area = 82 × 82 nm^2, E_{bias} = −200.0 mV, I_t = 1.000 nA.



Supplementary Figure 9 | STM measurements of C_{60} adlayer with a function of I_t. Typical STM images of C_{60} adlayer adsorbed on DPTTA modified Au(111) electrodes with a function of tunneling current. Tunneling conditions: (a, d) Scan area = 40 × 20 nm^2, E_{bias} = −200.0 mV, I_t = 2.000 nA. (b, e) Scan area = 40 × 20 nm^2, E_{bias} = −200.0 mV, I_t = 2.500 nA. (c) Scan area = 84 × 42 nm^2, E_{bias} = −200.0 mV, I_t = 5.000 nA. (f) Scan area = 52 × 26 nm^2, E_{bias} = −200.0 mV, I_t = 5.000 nA.

Reference:

[1] J. Clavilier, *J. Electroanal. Chem.* **1980**, *107*, 211-216.

[2] K. Singh, A. Sharma, J. Zhang, W. Xu, D. B. Zhu, *Chem. Commun.* **2011**, *47*, 905-907.