Potential and concentration-dependent self-assembly structure at solid/liquid interface

Zhen-Feng Cai\textsuperscript{a,b}, Hui-Juan Yan\textsuperscript{a,b}, Dong Wang\textsuperscript{*a,b}, and Li-Jun Wan\textsuperscript{*a}

\textsuperscript{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

\textsuperscript{b} University of Chinese Academy of Sciences, Beijing 100049, People’s Republic of China
Figure S1. Series STM images of DDBDT rhombus structures on Au(111) surface at different potentials. Image conditions: (a) Scan area = $43 \times 43$ nm$^2$, $E_{\text{bias}} = -200$ mV, $I_t = 1.000$ nA; (b – c) Scan area = $43 \times 43$ nm$^2$, $E_{\text{bias}} = -1030$ mV, $I_t = 1.000$ nA; (d) Scan area = $42 \times 42$ nm$^2$, $E_{\text{bias}} = -200$ mV, $I_t = 1.000$ nA; (e – f) Scan area = $42 \times 42$ nm$^2$, $E_{\text{bias}} = -529$ mV, $I_t = 1.000$ nA.
Figure S2. Series STM images of DDBDT two phase adlayer on Au(111) surface at different potentials. Image conditions: (a) Scan area = 32×32 nm$^2$, $E_{\text{bias}} = -200$ mV, $I_t = 1.000$ nA; (b – c) Scan area = 32×32 nm$^2$, $E_{\text{bias}} = -771$ mV, $I_t = 1.000$ nA; (d) Scan area = 42×42 nm$^2$, $E_{\text{bias}} = -200$ mV, $I_t = 1.000$ nA; (e – f) Scan area = 42×42 nm$^2$, $E_{\text{bias}} = -404$ mV, $I_t = 1.000$ nA.
Figure S3. Series STM images of DDBDT herringbone structure on Au(111) surface at different potentials. Image conditions: (a) Scan area = 46×46 nm², $E_{\text{bias}} = -200$ mV, $I_t = 1.000$ nA; (b – c) Scan area = 46×46 nm², $E_{\text{bias}} = -422$ mV, $I_t = 1.000$ nA; (d) Scan area = 42×42 nm², $E_{\text{bias}} = -200$ mV, $I_t = 1.000$ nA; (e – f) Scan area = 42×42 nm², $E_{\text{bias}} = -525$ mV, $I_t = 1.000$ nA.
**Figure S4.** Series STM images of DDBDT lamellar structures on Au(111) surface at different potentials. Image conditions: (a) Scan area = 78×78 nm², $E_{\text{bias}} = -200$ mV, $I_t = 1.000$ nA; (b) Scan area = 78×78 nm², $E_{\text{bias}} = -240$ mV, $I_t = 1.000$ nA; (c) Scan area = 56×56 nm², $E_{\text{bias}} = -200$ mV, $I_t = 1.000$ nA; (d) Scan area = 56×56 nm², $E_{\text{bias}} = -1050$ mV, $I_t = 1.000$ nA.
Figure S5. (a) Typical cyclic voltammograms of Au(111) electrode in 0.1 M HClO₄ before (black line) and after (red line) the addition of 10⁻⁵ M DDBDT. Scan rate is 50 mV/s.

Figure S5 displays typical cyclic voltammograms (CVs) of bare (black line), DDBDT adlayer (red line) modified Au(111) electrodes in 0.1 M HClO₄ recorded at the scan rate of 50 mV/s. The voltammogram for bare Au(111) electrode in the double-layer potential region is identical to previous reports¹ ². A pair of redox peak around 0.30 V can be observed, which is referred to the lift of the (22 × √3) reconstruction of Au(111) surface. For the DDBDT modified Au(111) electrode, the double-layer charging current decrease obviously, which indicating the adsorption of DDBDT adlayer (red line). The DDBDT adlayer is stable in the featureless double-layer charging region between -0.2 and 0.2 V. Reversible oxidative and reductive peaks can be distinguished at ca. 440 mV, which indicate that redox reactions happened at this substrate potential.
References
