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

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Figure S1. Series STM images of DDBDT rhombus structures on Au(111) surface at different potentials. Image conditions: (a) Scan area = 43×43 nm², $E_{bias} = -200$ mV, $I_t = 1.000$ nA; (b - c) Scan area = 43×43 nm², $E_{bias} = -1030$ mV, $I_t = 1.000$ nA; (d) Scan area = 42×42 nm², $E_{bias} = -200$ mV, $I_t = 1.000$ nA; (e - f) Scan area = 42×42 nm², $E_{bias} = -529$ 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 nm², $E_{bias} = -200$ mV, $I_t = 1.000$ nA; (b - c) Scan area = 32×32 nm², $E_{bias} = -771$ mV, $I_t = 1.000$ nA; (d) Scan area = 42×42 nm², $E_{bias} = -200$ mV, $I_t = 1.000$ nA; (e - f) Scan area = 42×42 nm², $E_{bias} = -404$ 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, $E_{bias} = -200$ mV, $I_t = 1.000$ nA; (b - c) Scan area = 46×46 nm², $E_{bias} = -422$ mV, $I_t = 1.000$ nA; (d) Scan area = 42×42 nm², $E_{bias} = -200$ mV, I_t = 1.000 nA; (e - f) Scan area = 42×42 nm², $E_{bias} = -525$ 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, $E_{bias} = -200$ mV, $I_t = 1.000$ nA; (b) Scan area = 78×78 nm², $E_{bias} = -240$ mV, $I_t = 1.000$ nA; (c) Scan area = 56×56 nm², $E_{bias} = -200$ mV, $I_t = 1.000$ nA; (d) Scan area = 56×56 nm², $E_{bias} = -1050$ 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 reports^{1, 2}. A pair of redox peak around 0.30 V can be observed, which is referred to the lift of the $(22 \times \sqrt{3})$ 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

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