

# Strong Hydrogen Bonds at the Interface between Proton-Donating and -Accepting Self-Assembled Monolayers on Au(111)

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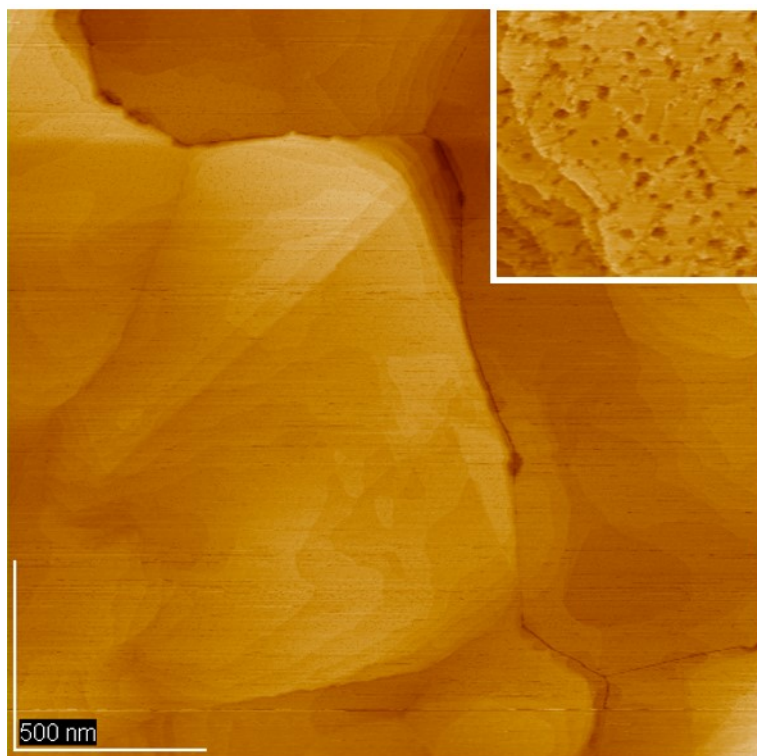


Figure S1. STM images for *n*-decanethiolate-SAM ( $C_{10}S$ -SAM) on the Au thin film deposited on mica (Au/Mica); a wide area image ( $2000 \times 2000 \text{ nm}^2$ ,  $V_s = +1.9 \text{ V}$ ,  $I_t = 0.02 \text{ nA}$ ) and the inset of a narrow area image ( $100 \times 100 \text{ nm}^2$ ,  $V_s = +2.0 \text{ V}$ ,  $I_t = 0.20 \text{ nA}$ ). The images were measured using a PtIr tip at room temperature in air. The wide area image clearly shows that the Au thin film consists of large grains and top of the grains are widely flat, in which the atomically flat terraces and steps reflecting the morphology of the Au substrate beneath  $C_{10}S$ -SAM are recognized. In the narrow area image, in addition, patched  $C_{10}S$ -SAM and small dimples, so-called etch pit, on the terrace are confirmed. These features are common characteristics of the well-ordered and densely-packed  $C_{10}S$ -SAMs on the Au(111) surfaces.

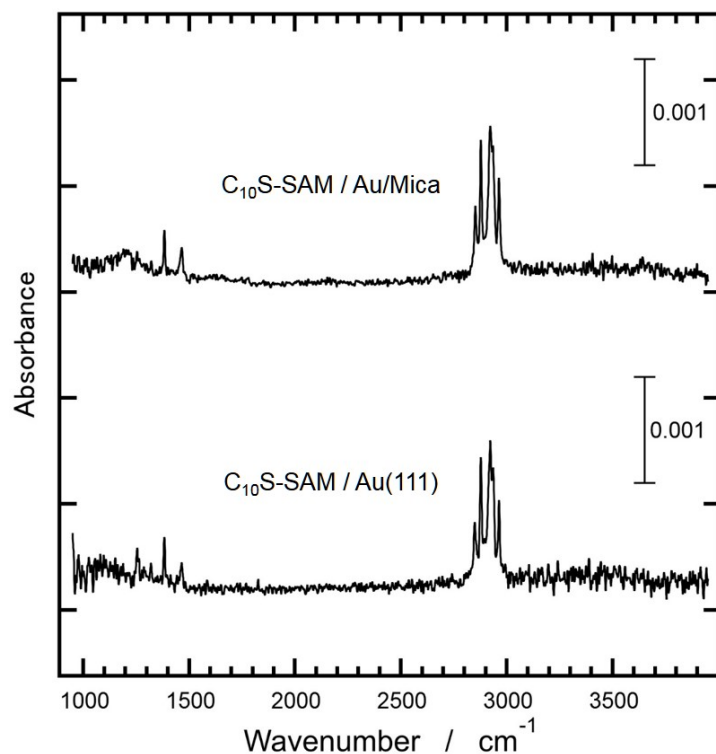


Figure S2: IRAS results for *n*-decanethiolate-SAM (C<sub>10</sub>S-SAM) on the single crystal Au(111) (bottom) and Au/Mica (top). The bending modes and stretching modes of the CH<sub>2</sub> unit and CH<sub>3</sub> group were detected at about 1400 and 2900 cm<sup>-1</sup>, respectively. Although there is a fluctuation of baselines mainly due to instability of our experimental setup, the substrate dependence of the IRAS results for C<sub>10</sub>S-SAM is small. These results indicate that the prepared Au/Mica substrates have enough cleanness and hence similar chemical activity for self-assembly of thiolate in comparison with the single crystal Au(111).

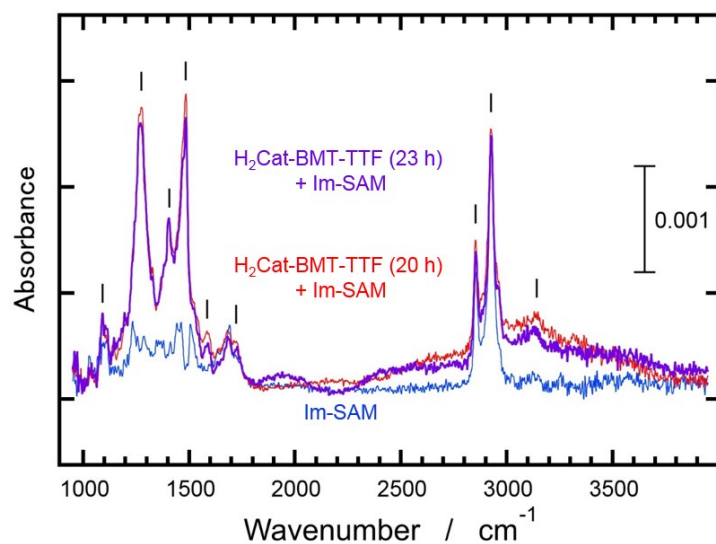


Figure S3 Immersion time dependence of IRAS results for the H<sub>2</sub>Cat-BMT-TTF adlayer on Im-SAM: 20 h (red line) and 23 h (violet line), with that for Im-SAM (blue line). At the sample for 23 h immersion, while a fluctuation of the recorded background is larger than the other, it is confirmed that the frequency and intensity of vibrational peaks for the H<sub>2</sub>Cat-BMT-TTF adlayer are very closed to those at the sample for 20 h immersion.