Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


Electronic Supplementary Information

# Self-Assembly of Heterogeneous Bilayers Stratified by Au-S and Hydrogen Bonds on Au(111)

*Riku Muneyasu, Takashi Yamada, Megumi Akai-Kasaya, and Hiroyuki S. Kato*[*]

Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

**Contents**



* E-mail: hirokato@chem.sci.osaka-u.ac.jp

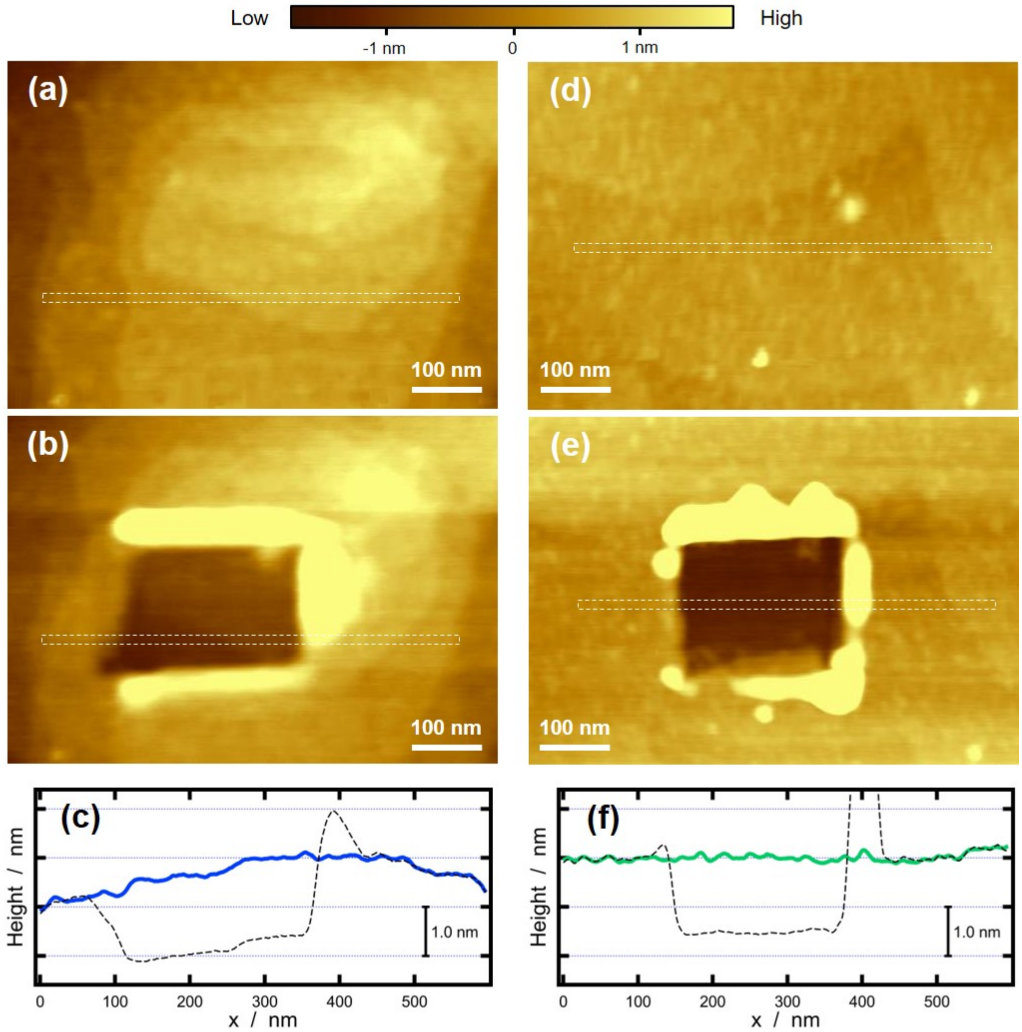


**Fig. S1** Set of topographic AFM images (a) before and (b) after a rubbing and (c) their height profiles for DHN/Im-SAM adlayer formed by the 2-step procedure. The same set of AFM images and height profiles for DHN/Im-SAM adlayer formed by the 1-step procedure are indicated to (d), (e) and (f), respectively. In each set, the images ($800 \times 500$ nm$^2$) were observed at the same area using tapping mode. The adlayer was rubbed in contact mode of AFM (typically $200 \times 200$ nm$^2$). The height profiles along horizontal direction were obtained by averaging vertical height data in the white rectangle area in each image. The bold solid and thin black dashed lines indicate the profiles before and after the rubbing treatment, respectively, in (c) and (f). From the height profile difference, the thickness of the 2-step and 1-step DHN/Im-SAM adlayers are $1.6 \pm 0.1$ nm and $1.5 \pm 0.1$ nm, respectively.

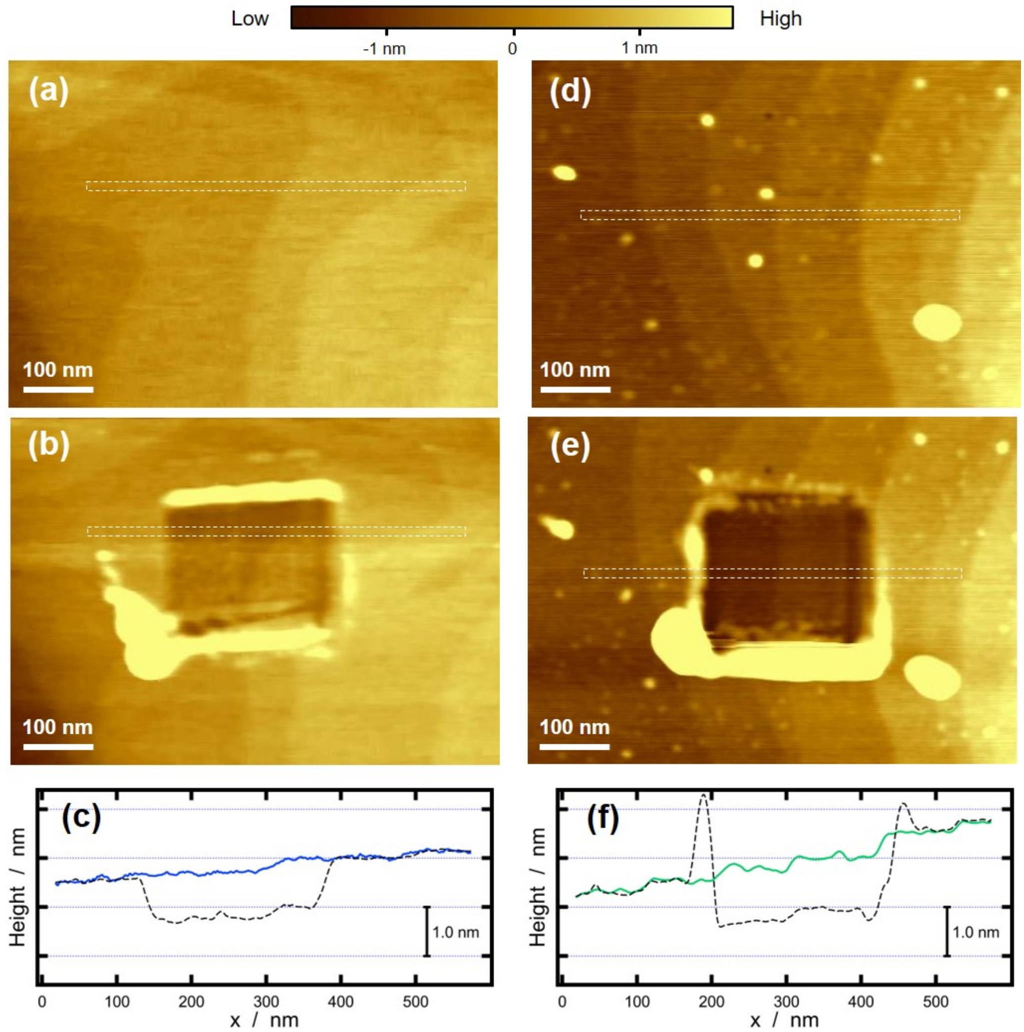


**Fig. S2** Set of topographic AFM images (a) before and (b) after a scrub and (c) their height profiles for Im-SAM adlayer on Au/mica formed by immersion in EtOH solution. The similar set of AFM images and height profiles for Im-SAM adlayer formed in $CHCl_3$ solution are indicated to (d), (e) and (f), respectively. The images (800 × 500 nm$^2$ nm) were observed at the same area using tapping mode. The adlayer was scrubbed in contact mode of AFM (typically 200 × 200 nm$^2$). The height profiles along horizontal direction were obtained by averaging vertical height data in the white rectangle area in each image. The thin solid and black dashed lines indicate the profiles of the adlayers before and after the scrub, respectively, in (c) and (f). For both samples, the thickness of Im-SAM is equally expected as 1.0 ± 0.1 nm. While the images (d) and (e) show some high protrusions, the most of which would be falling objects from unstable cantilevers after repeated scrubbing operations.

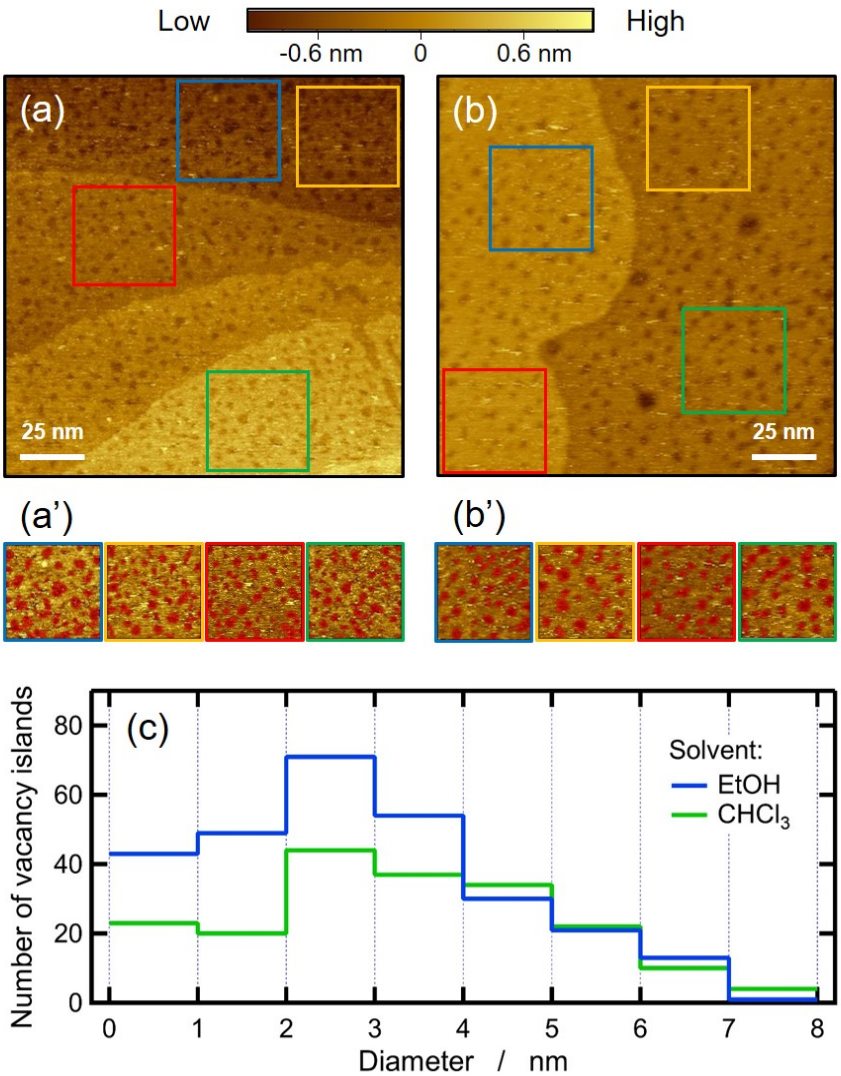


**Fig. S3** STM images for Im-SAMs on Au/mica; (a) Im-SAM formed in EtOH (parameters: 200 × 200 nm$^2$, $V_s$ = +1.5 V, $I_t$ = 0.05 nA) and (b) Im-SAM formed in $CHCl_3$ (parameters: 200 × 200 nm$^2$, $V_s$ = +0.8 V, $I_t$ = 0.10 nA). The images were measured using a PtIr tip at room temperature in air. For both the samples, the atomic steps and the flat terraces including Au vacancy islands reflecting the Au topography under Im-SAM were observed. In comparison of the two samples, we carefully counted the number of the Au vacancy islands in each of the four square areas (50 × 50 nm$^2$) on (a) and (b); the red marked spots shown in (a') and (b') are the vacancy islands objectively identified by an SPM analysis software (Gwyddion). The size distributions of the islands are plotted as a function of their diameter, as shown in (c). The number of the smaller vacancy islands for Im-SAM formed in EtOH is larger than that for Im-SAM formed in $CHCl_3$. As a result, total density of the vacancy islands is 282/100$^2$ nm$^{-2}$ for Im-SAM formed in EtOH and 194/100$^2$ nm$^{-2}$ for Im-SAM formed in $CHCl_3$.