Supporting Information

Ordering of Small Molecules on Hydrophobic Self-Assembled *n*-Alkanethiols: Delicate Balance of Interfacial and Intermolecular Interactions

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Further details for no electron-beam-induced effects:

To minimize potential beam-induced changes, we carried out the RHEED experiments at an ultralow dose of 0.001–0.01 $e/Å^2$, which is orders-of-magnitude lower than often used in electron microscopy (see, e.g., *Commun. Biol.* **2021**, 4, 2272). The SAM and solvent molecules used in this study were chemically stable without redox sensitivity. To be certain, we also compared the diffraction features and intensities between the first image (captured within 1–2 seconds of electron exposure) and those after an overnight exposure (more than the typical data acquisition time). No exposure-dependent results were found. In addition, we can also confidently rule out the effect of charging. In the current study, the supporting solid of a 1-mm-thick Au(111) single crystal on a metal sample plate was highly conductive electrically. Furthermore, conductive metal clamps (1 mm × 15 mm) were placed on the two sides of the single crystal, which effectively removed any charges across the sample surface. We monitored the stability of diffraction patterns especially the shadow-edge region. The lack of visible changes confirmed the absence of charging and also the robustness of our findings.

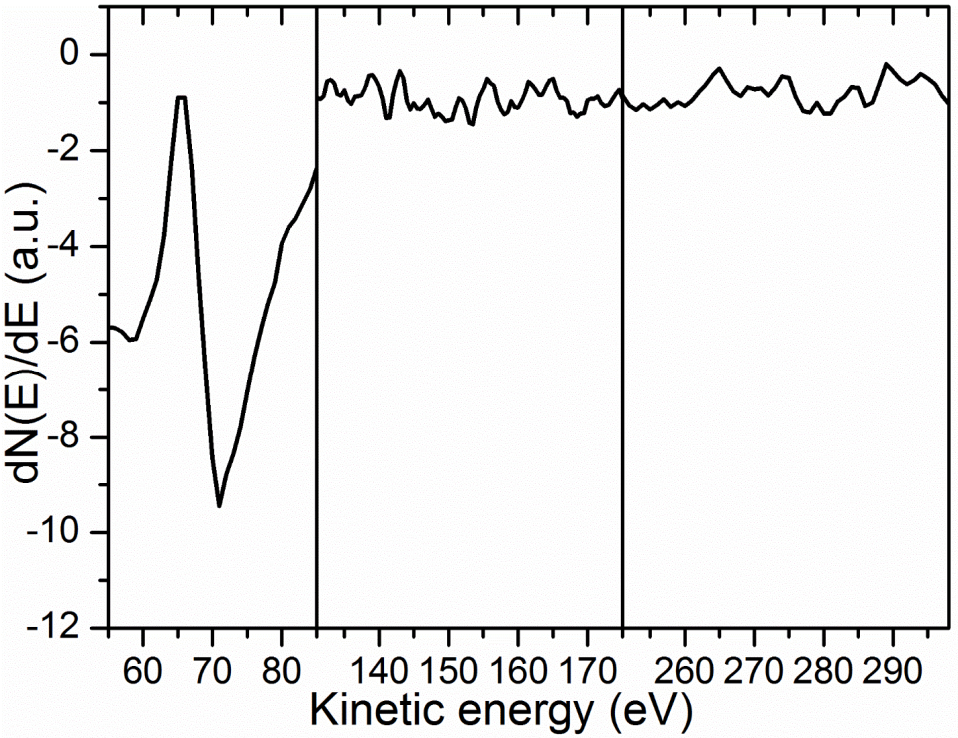

Figure S1. Auger electron spectra of clean Au(111) after multiple rounds of sputtering and annealing. The three spectral windows from left to right correspond to the major peak positions of gold, sulfur, and carbon, respectively.

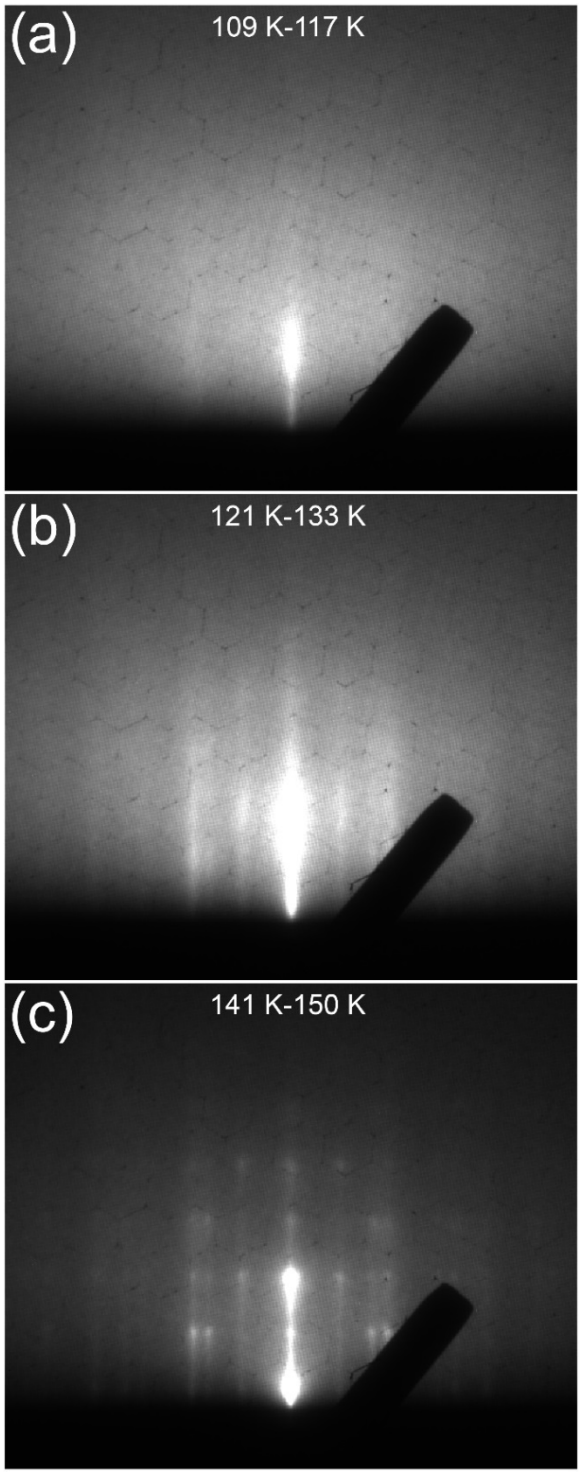

Figure S2. RHEED images of 5-nm ethanol films obtained in the annealing temperature range of (a) 109−117 K, (b) 121−133 K, and (c) 141−150 K.

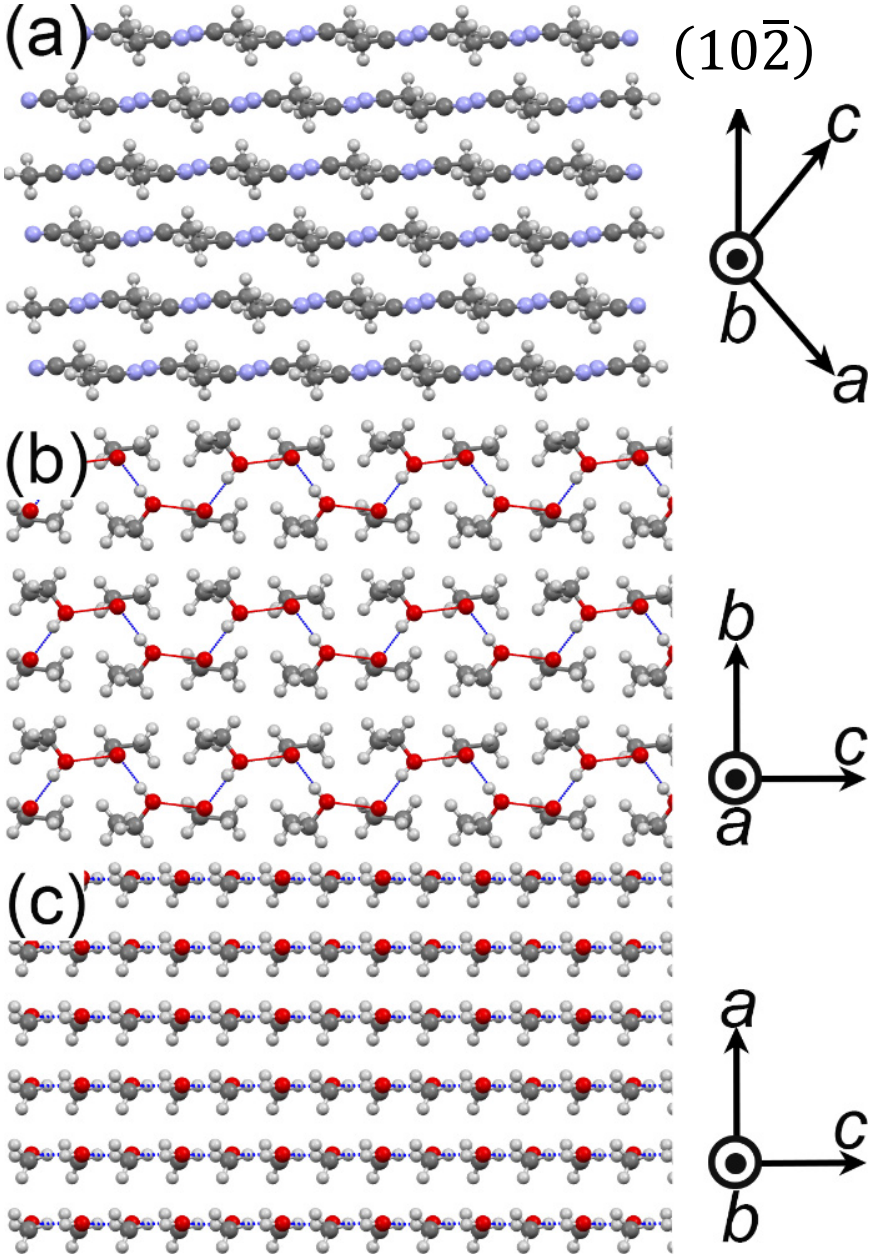

Figure S3. Side view of the molecular crystal structures formed on the hydrophobic SAM surface: (a) Monoclinic α phase of acetonitrile, (b) monoclinic α phase of ethanol, and (c) orthorhombic β phase of methanol. The carbon, nitrogen, oxygen, and hydrogen atoms are in gray, light blue, red, and white, respectively. The blue dashed lines in (b) and (c) indicate the hydrogen bonds.

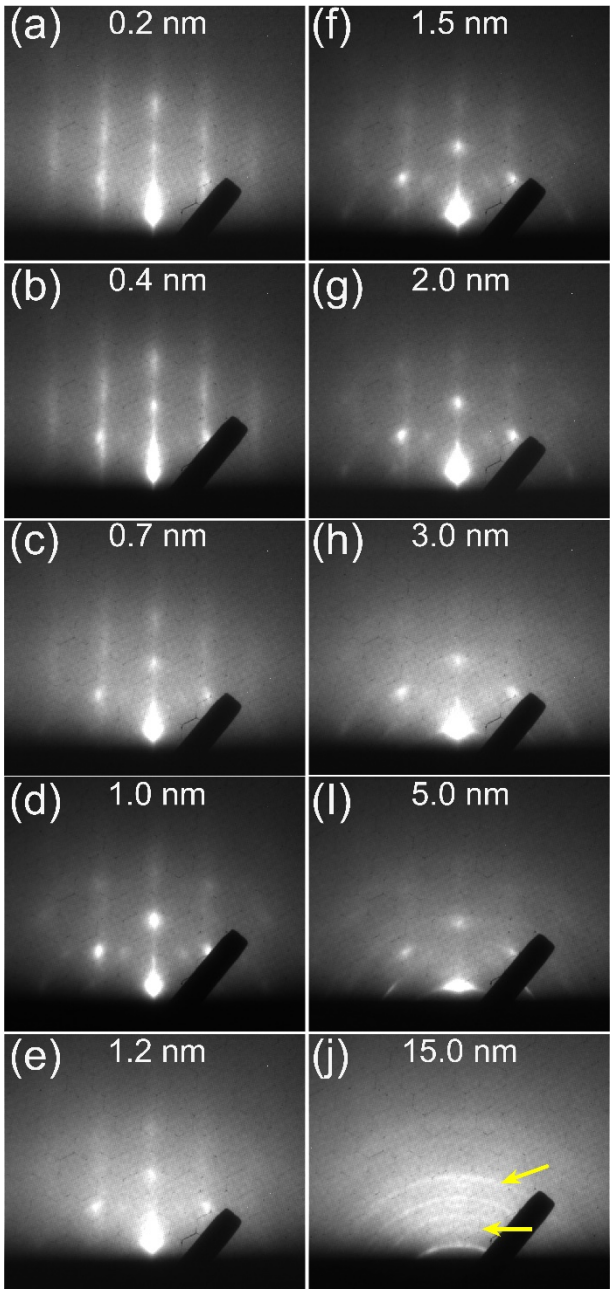

Figure S4. RHEED images of methanol thin films on the hydrophobic SAM surface with different nominal thicknesses. (a-e) Increasing intensities of the Bragg spots from crystalline methanol with decreasing intensities of the SAM diffraction features. The methanol Bragg spots signify the formation of 3D crystalline islands. (f-j) Conversion of the Bragg spots into diffraction rings in a relatively thick film (15 nm), signifying the loss of the epitaxial ordering and the original phase. The two arrows in (j) indicate the diffractions that are present in the orthorhombic α phase but absent in orthorhombic β phase.

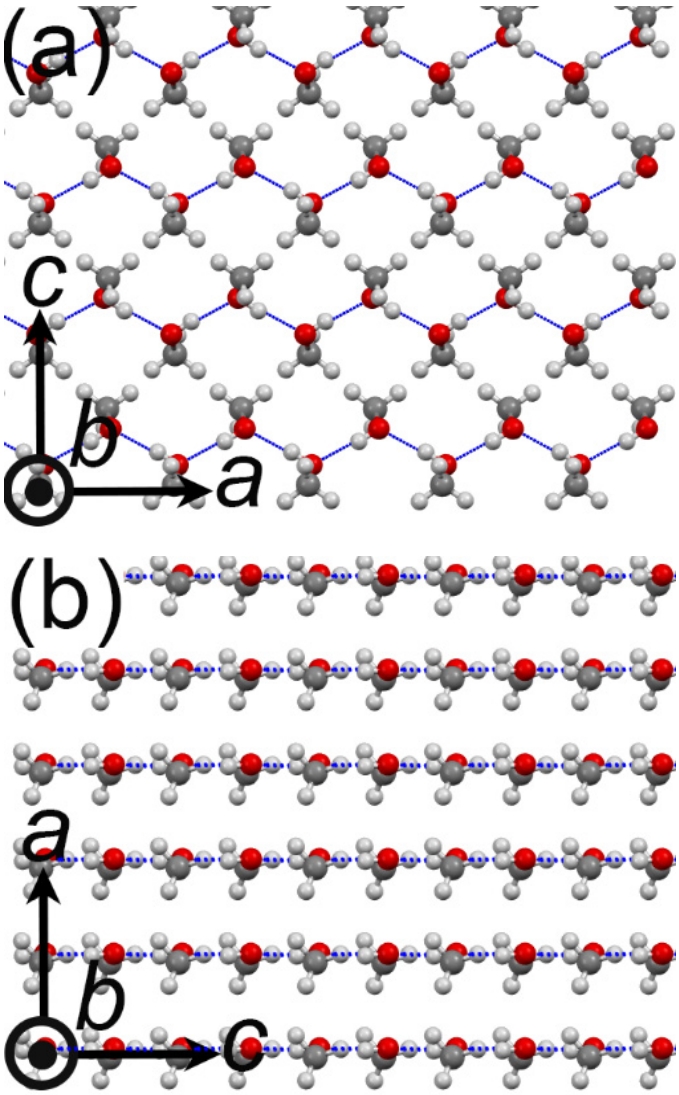

Figure S5. Side view of the two different phases of solid methanol: (a) orthorhombic α phase and (b) orthorhombic β phase. The carbon, oxygen, and hydrogen atoms are in gray, red, and white, respectively. The blue dashed lines indicate the hydrogen bonds.