

Electronic Supplementary Information

Multiple Molecular Interactions between Alkyl Groups and Dissociated Bromine Atoms on Ag(111)

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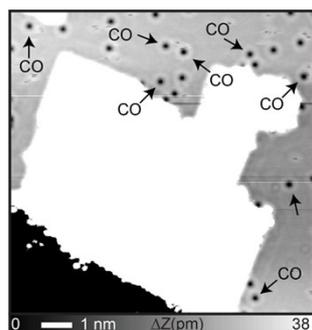


Figure S1. As-deposited molecule **1** on a Ag(111) substrate kept at -163°C . (a) Large-scale STM topography with a narrow contrast. Note that the image is the same as Figure 1a. The adsorbed CO molecules appeared as dips as indicated by arrows.

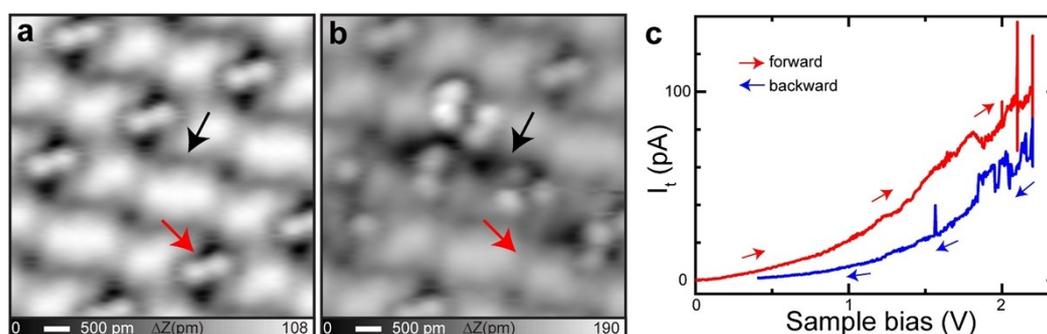


Figure S2. Tip-induced debromination. (a) STM topographies of the self-assemble **1** on Ag(111) before and (b) after the debromination. (c) I/V curve measured during the debromination. The feedback on the tip-sample distance was deactivated at the site indicated by a black arrow, and subsequently the bias voltage was swept to large positive values. When the bias voltage reached 2.2 V, an abrupt change of the tunneling current was detected. Since the radical species was stabilized by bonding to the Ag substrate, the local chemical bonding to the Ag surface induced a complicated contrast. Interestingly, the contact configuration of the alkyl-alkyl groups in the adjacent molecules was also modified as indicated by a red arrow. Measurement parameters: $V = 200$ mV and $I = 10$ pA in (a, b).

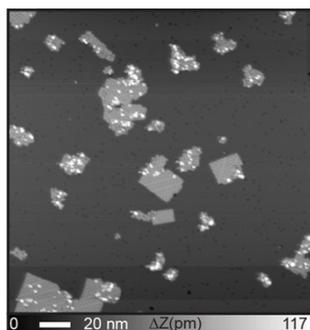


Figure S3. Large-scale STM topography of as-deposited **1** on a Ag(111) substrate kept at -163°C. Several isolated molecular islands are seen. Measurement parameters: $V = 200$ mV and $I = 10$ pA.

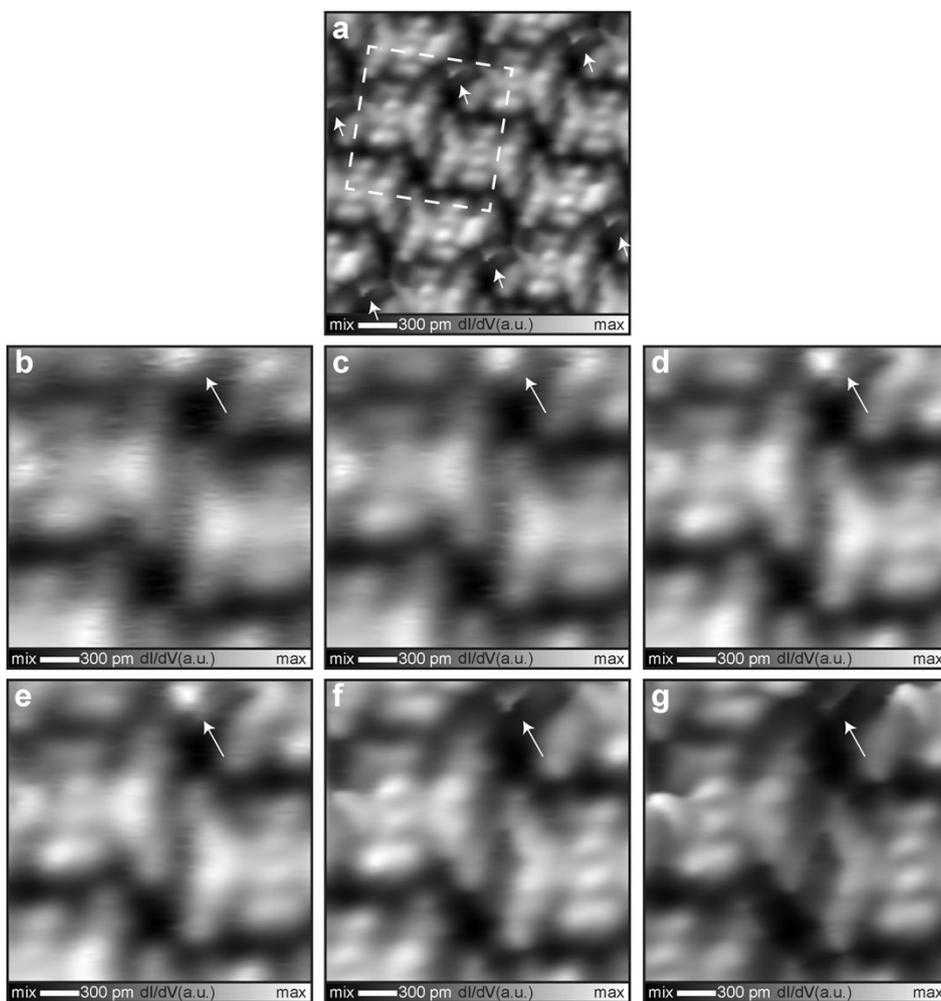


Figure S4. Tilting effect of the CO tip in the dI/dV maps. (a) High-resolution dI/dV map of as-deposited **1** on a Ag(111) substrate kept at -163°C . The arrows indicate the corrugated alkyl-alkyl contacts. (b-g) A series of constant-height dI/dV maps taken by reducing the tip-sample separations (20 pm step per image) in the area indicated by a square in (a). Due to an excessive tilting effect of the CO molecule at the tip, the corrugated part became a polytonally shaped structure for the smallest tip-sample separation in (g). Measurement parameters: $V = 1$ mV.

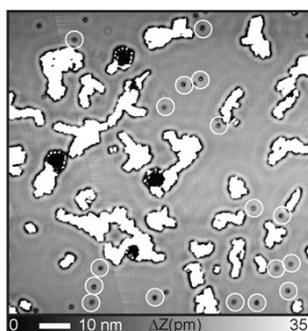


Figure S5. STM topography of the randomly adsorbed **1** formed by warming up the substrate to room temperature. The image is the same as Figure 2a, but with a narrow contrast to enhance the visibility of the Br atoms, enclosed by circles.

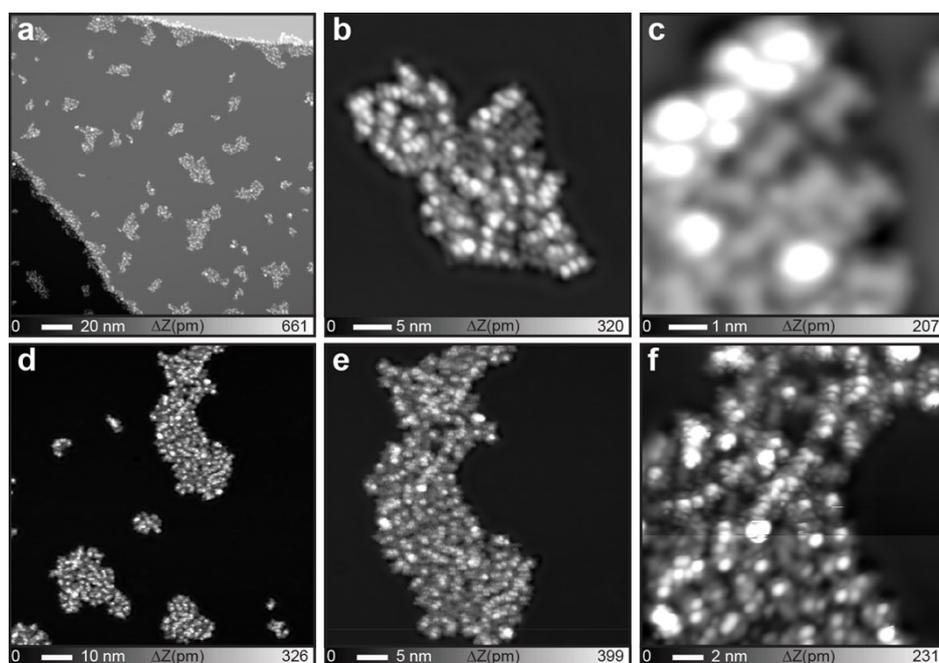


Figure S6. (a-c) STM topographies of **1** after annealing at 100 °C and (d-f) at 130 °C. No ordered structure is seen. Measurement parameters: $V = 200$ mV and $I = 10$ pA in (a,b,d-f), $V = 100$ mV and $I = 10$ pA in (c).

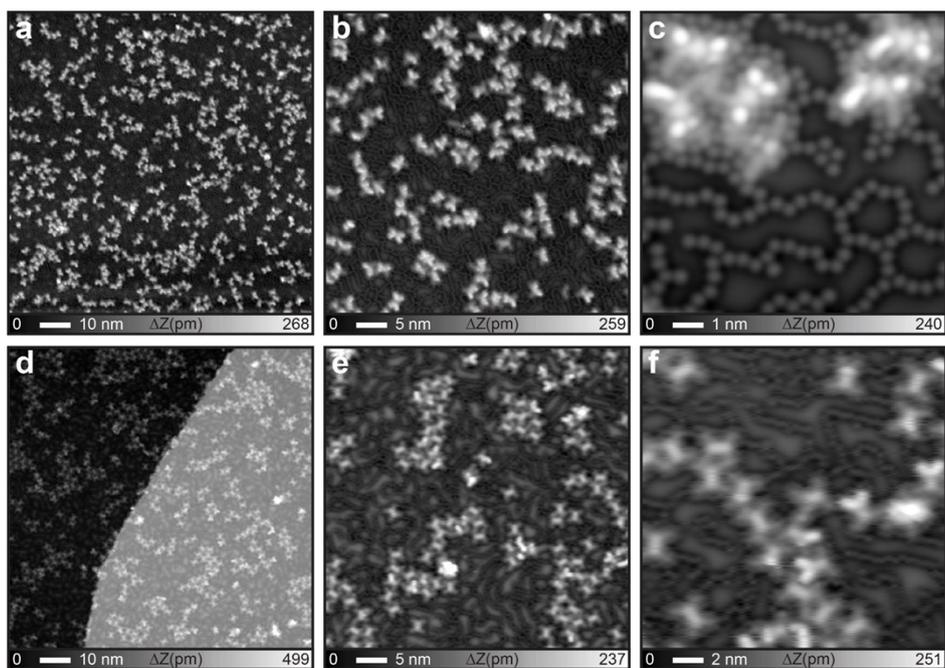


Figure S7. Different annealing temperatures. (a-c) STM topographies of **2** after annealing at 63 °C and (d-f) at 150 °C. Measurement parameters: $V = 200$ mV and $I = 10$ pA in (a, b, d, e), and $V = 100$ mV and $I = 100$ pA in (c, f).

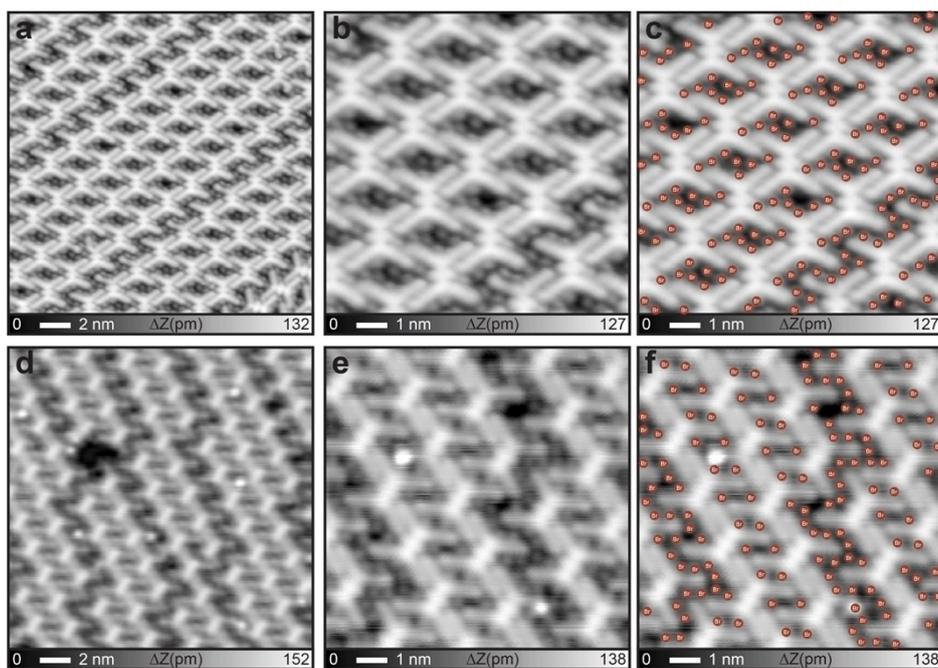


Figure S8. Transition of the self-assembled structures. (a,b) STM topographies after annealing at 210 °C (c) Positions of the Br atoms in the assembly. (d,e) STM topographies after annealing at 220 °C (f) Positions of Br atoms in the assembly. Measurement parameters: $V = 100$ mV and $I = 100$ pA in (a,b,d), and $V = 100$ mV and $I = 1$ nA in (e).

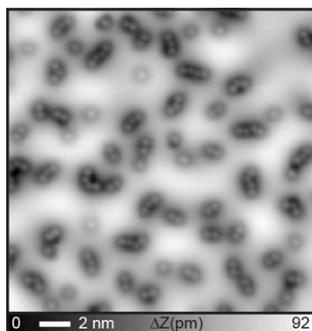


Figure S9. STM topography of the Ag(111) surface after annealing at 270 °C. Since most of the molecules desorbed from the substrate, the surface was decorated only by Br atoms. Measurement parameters: $V = 50$ mV and $I = 100$ pA.

General for Synthesis

All reactions were carried out under an argon atmosphere. All commercially available compounds were used without further purification unless otherwise indicated. Dry toluene was obtained by distillation from CaH_2 prior to use. Column chromatography was performed on Wakogel[®] 60N (neutral) of particle size 38–100 μm . ^1H and ^{13}C NMR spectra were recorded on a BRUKER Ascend[™] 400 ($^1\text{H}/400\text{ MHz}$ and $^{13}\text{C}/100\text{ MHz}$) spectrometer. IR spectra were measured on a Shimadzu IRAffinity-1S spectrophotometer using the attenuated total reflection (ATR) mode. Mass spectra were recorded on a JMS-T100GCV spectrometer in FD mode (GC-MS & NMR Laboratory, Research Faculty of Agriculture, Hokkaido University). Melting points were measured on a Stanford Research Systems OptiMelt MPA100 and are uncorrected.