

## Supplementary Information

### Different observations of CO molecules by using the W-tip and the CO-tip

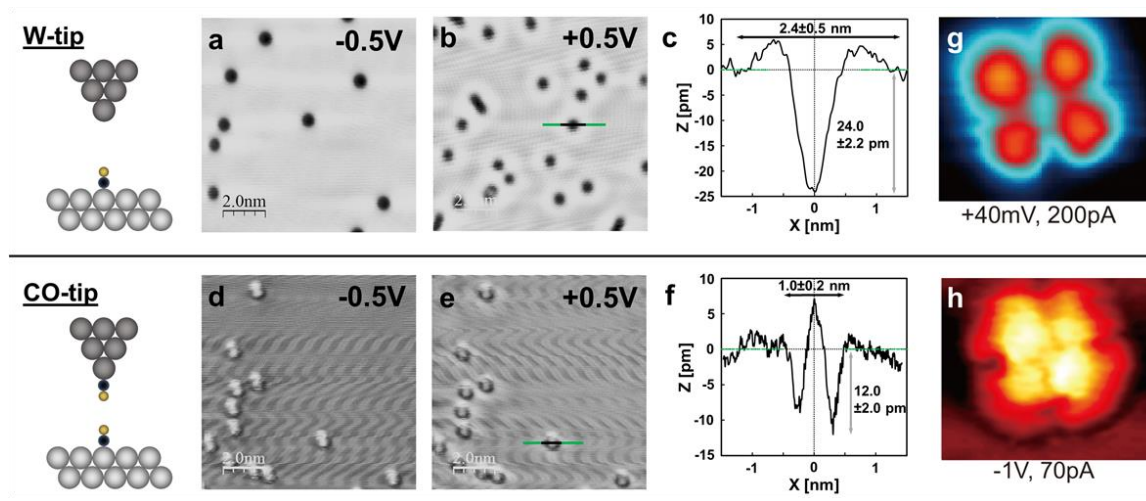


Figure S1. Different STM observations by using a clean W tip and a CO-terminated W tip. (a, b) STM images ( $10 \times 10$  nm<sup>2</sup>) of single CO molecules on Cu(111) observed with a W tip at a sample bias of (a)  $V_s = -0.5$  V and (b)  $V_s = +0.5$  V ( $I = 500$  pA). Single CO molecules were observed as dark spots with halo protrusion. (c) Line profile along the CO molecule in (b) (green line):  $2.4 \pm 0.5$  nm in width and  $1.3 \pm 0.5$  nm in peak-to-peak width. The height of the depression from the Cu substrate surface is  $24.0 \pm 2.2$  pm.  $Z = 0$  pm is set to the Cu substrate surface.  $X = 0$  pm is set to the center of the molecule. (d, e) STM images ( $10 \times 10$  nm<sup>2</sup>) of single CO molecules on Cu(111) observed with a CO-tip, fabricated by vertical manipulation, at a sample bias of (d)  $V_s = -0.5$  V and (e)  $V_s = +0.5$  V ( $I = 500$  pA). Inversely, CO molecules were observed as bright protrusions with halo depression. (f) Line profile of the CO molecule in (e) (green line):  $1.0 \pm 0.2$  nm in width. The depression height is  $12 \pm 2$  pm from the Cu surface.  $Z = 0$  pm is set to the Cu substrate surface.  $X = 0$  pm is set to the center of the molecule. (g, h) STM images of a metal-free phthalocyanine  $H_2Pc$  molecule obtained with a clean W-tip and a CO-tip, respectively. The CO-tip shows a  $C_2$  symmetry of the molecule, while the W tip does not.

### Tip-sample distance by varying sample voltage

The influence of the molecular vibration excited via the electron injection from the STM tip may also be considered. From previous studies that used electron energy loss spectroscopy, the vibration of the entire CO molecule against the surface is known to be approximately 50 meV.<sup>1-3</sup>

To rule this factor out, we verified this argument by changing the tip-sample distance by varying the sample voltage. We scanned the adsorbed CO with the CO tip at biases ranging from 50 mV to 10 mV ( $I = 1$  nA). Notably, we did not observe CO hopping in the STM scanning at 50 mV and above. Instead, we observed the hopping after decreasing the bias gradually in steps of 10 mV (see solid line in Fig. S2a). At 50 mV (see Fig. S2b), the hopping probability below 1% was observed. After decreasing the sample bias, the hopping probability increased, e.g. at 30 mV, almost 90% of the adsorbed CO molecules on the surface were pushed

by the CO tip (see Fig. S2c), i.e., the observed CO manipulation was not due to the voltage-induced electron excitation. Upon further lowering the bias voltage to 10 mV, almost all the CO molecules were moved by scanning and therefore, no stationary images of a single CO molecule were captured.

The above behavior is consistent with the hopping induced by dipole–dipole interaction. With STM, owing to the constant current feedback, bias variation also changed the tip–sample separation as  $I \propto \exp[-\kappa(S_0+z)] = \exp[-2(2m(\phi-eV))^{1/2}/\hbar (S_0+z)]$ , where  $\hbar$  is the Planck's constant,  $m$  is the electron mass, and  $\phi$  is the barrier height. The dashed line in Fig. S2a shows the tip–sample separation as a function of the bias voltage estimated from the above formula. As it can be observed, lowering the bias voltage renders the tip–sample gap smaller. The higher hopping probability at low-bias voltage can be explained by the enhanced repulsive interaction owing to a smaller tip–sample gap.

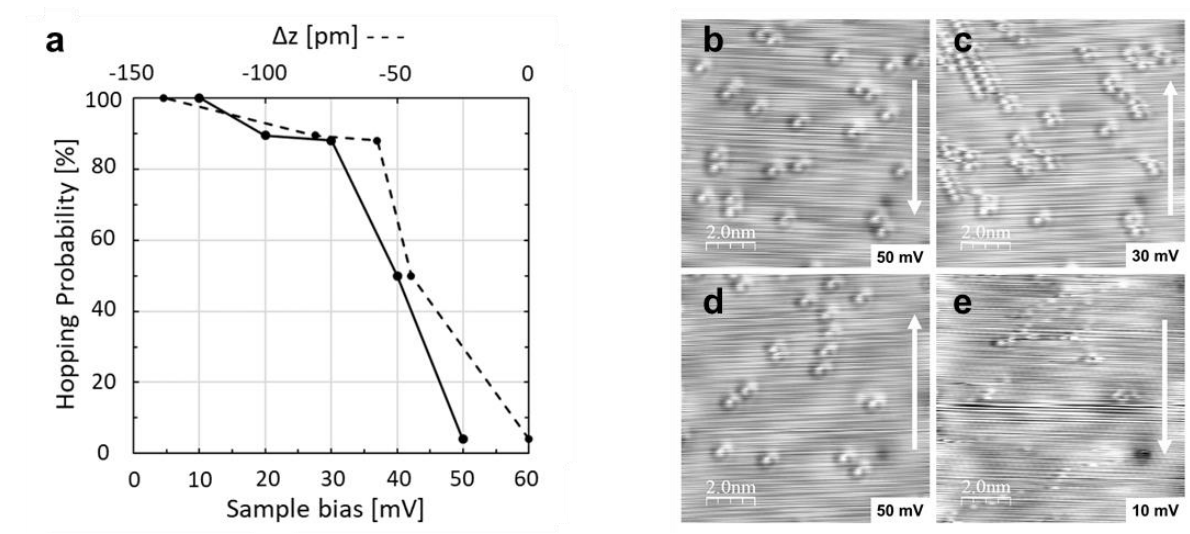


Figure S2. (a) Hopping probability as a function of sample bias (solid line) and tip apex displacement (dashed line) at a constant tunneling current of 1.0 nA. STM images ( $10 \times 10 \text{ nm}^2$ ) of CO single molecules on Cu (111) scanned with the CO-tip in sequence of the bias voltage of (b) 50 mV to (c) 30 mV, and (d) 50 mV to (e) 10 mV, where the tunneling current was fixed:  $I=1 \text{ nA}$ . The white arrows show the CO-tip scanning directions, i.e. from bottom to top or vice versa. CO molecules are observed like multiple chains because together with the scanned CO-tip the CO molecules on the substrate moved. At low biases, the opposing COs from the tip and the sample repel each other making the chain-like contrast as in (c). At 10 mV, no stationary CO could be observed as the tip-sample are very close together as seen in (e).

### DFT calculation model for CO-monomer and CO-pair

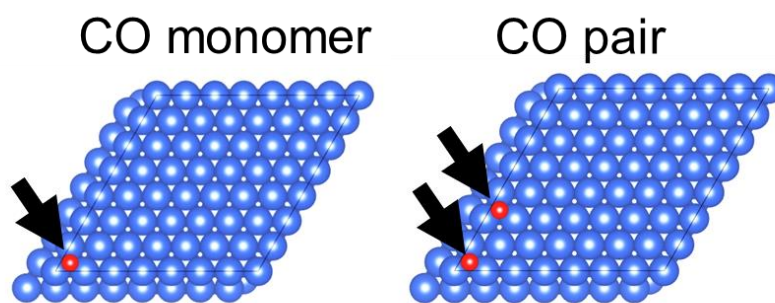


Figure S3. Sphere models for calculation of electrostatic potential in Fig. 3c. Blue spheres denote Cu atoms of the substrate, forming a (7×7) unit cell (Cu five monolayer stacking). Red spheres denote adsorbed CO single molecules.

### Statistical distribution analysis

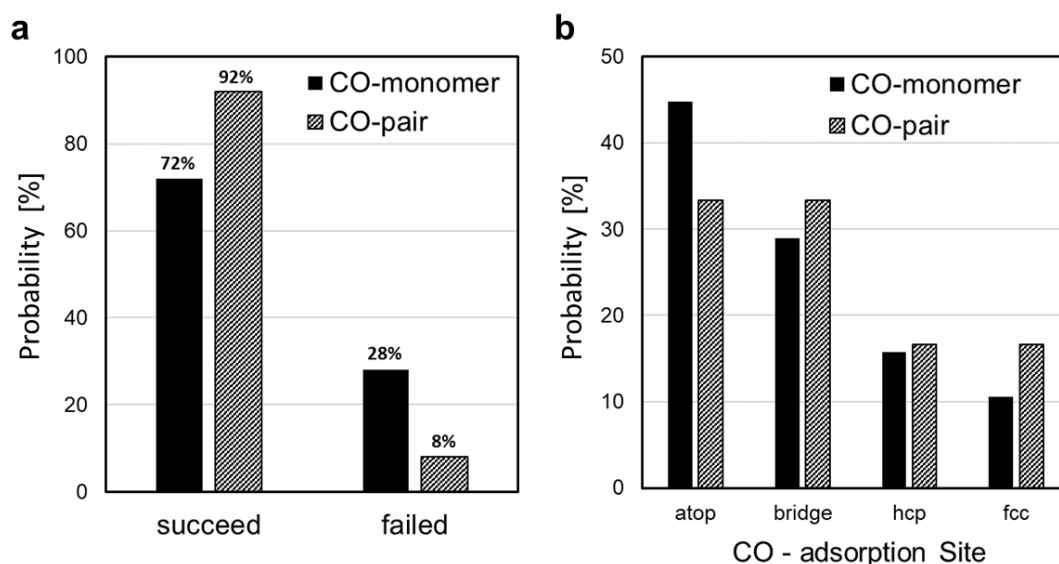


Figure S4: Statistical distribution analysis of CO-monomer and CO-pair. (a) Success/fail manipulation probability. (b) Adsorption site preference after the hopping.

### Cu(111) substrate and CO lateral manipulation

After cleaning the Cu (111), an STM topographic image obtained on Cu(111) shows atomic terraces larger than 100 nm (see Fig. S5a). An enlarged image of the surface shows a hexagonal symmetry of fcc-Cu(111) atomic array (see Fig. S5b). A  $dI/dV$  spectroscopy curve averaged more than 100 single curves lowering signal-to-noise ratio shows a peak at  $-0.35$  eV below the Fermi energy, which energy position corresponds to the Cu(111) surface state (see Fig. S5c). A chemical-identified tip found three kinds of impurities on the surface (Fig. S5d), where after further deposition of CO gas at 0.1 L (Langmuir), one of the three started to increase to about 15 single molecules per  $15 \times 15$  nm<sup>2</sup>, thus we confirmed the dark depression to be the CO

single molecule. From line profiles across the dark spots at +0.5 V, depicting electron tunneling from the tip to the CO molecule's LUMO orbital, where a bright halo-shaped protrusion with a diameter of  $\sim 2.4$  nm (height  $\sim 5$  pm) was observed. The single dark-spot has a depth of  $\sim 24$  pm, which observation is in good agreement with previously done experiments.<sup>4,5</sup>

Further, we succeeded to manipulate these dark spots by using a W tip. Series of STM images are shown in Fig. S5e, from (1) to (8), where between each image the W tip was approached ( $V_s = -50$  mV,  $I = 30-35$  nA) and moved lateral direction that we wanted to move the CO molecule, and then the tip was retracted as the original position ( $V_s = -50$  mV,  $I = 1$  nA). At the step (8) we made a “smiley” face on the Cu(111) with 11 single CO molecules. Such manipulation process also confirmed that the dark spots are indeed CO.

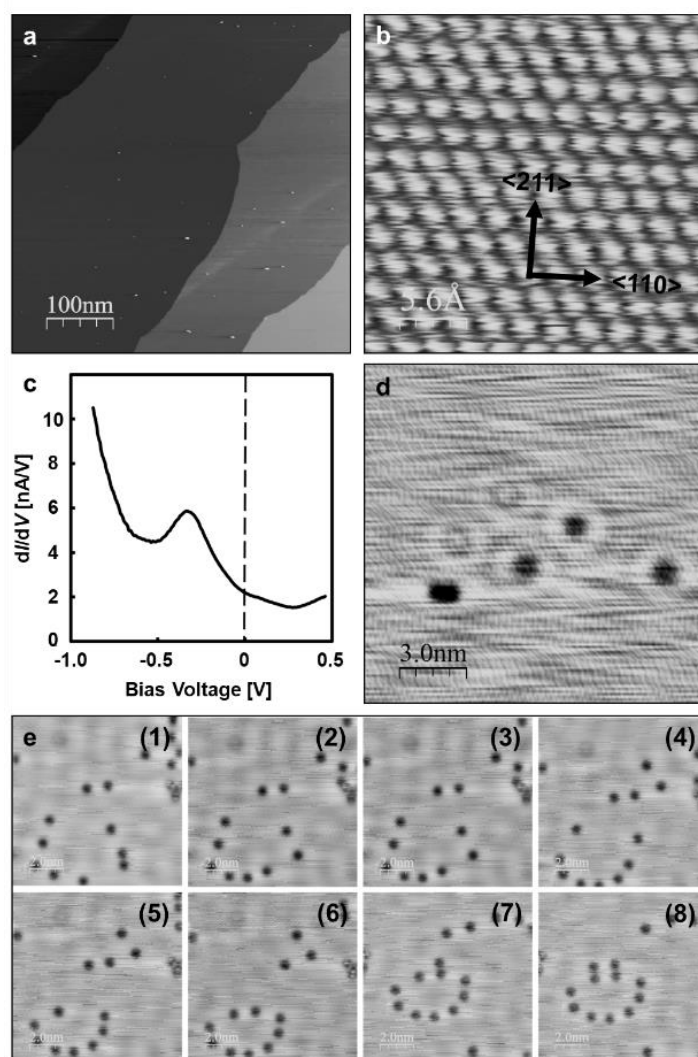


Figure S5. Cu(111) substrate and CO lateral manipulations. (a) An STM image obtained on the Cu (111) substrate after the cleaning process. (b) Atomically-resolved STM image obtained on the Cu(111). Bright spots correspond to single Cu atoms. (c)  $dI/dV$  curve obtained on the Cu(111). (d) Three kinds of dark spots were found on the cleaned Cu(111) surface. One of these increase by introducing CO gas. (e) STM images at the same area, where dark spots are adsorbed CO single molecules. Here, we performed lateral manipulation of the molecule. From (1) to (8), one by one single CO molecules were manipulated and finally

in (8) 'smiley' face was fabricated. STM images were obtained at (a)  $V_s=+0.8$  V,  $I=0.35$  nA, (b)  $V_s=-0.17$  V,  $I=0.73$  nA, (d)  $V_s=-0.5$  V,  $I=1.0$  nA, (e)  $V_s=-0.05$  V,  $I=1.0$  nA.

### Home-built low-temperature UHV-STM setups

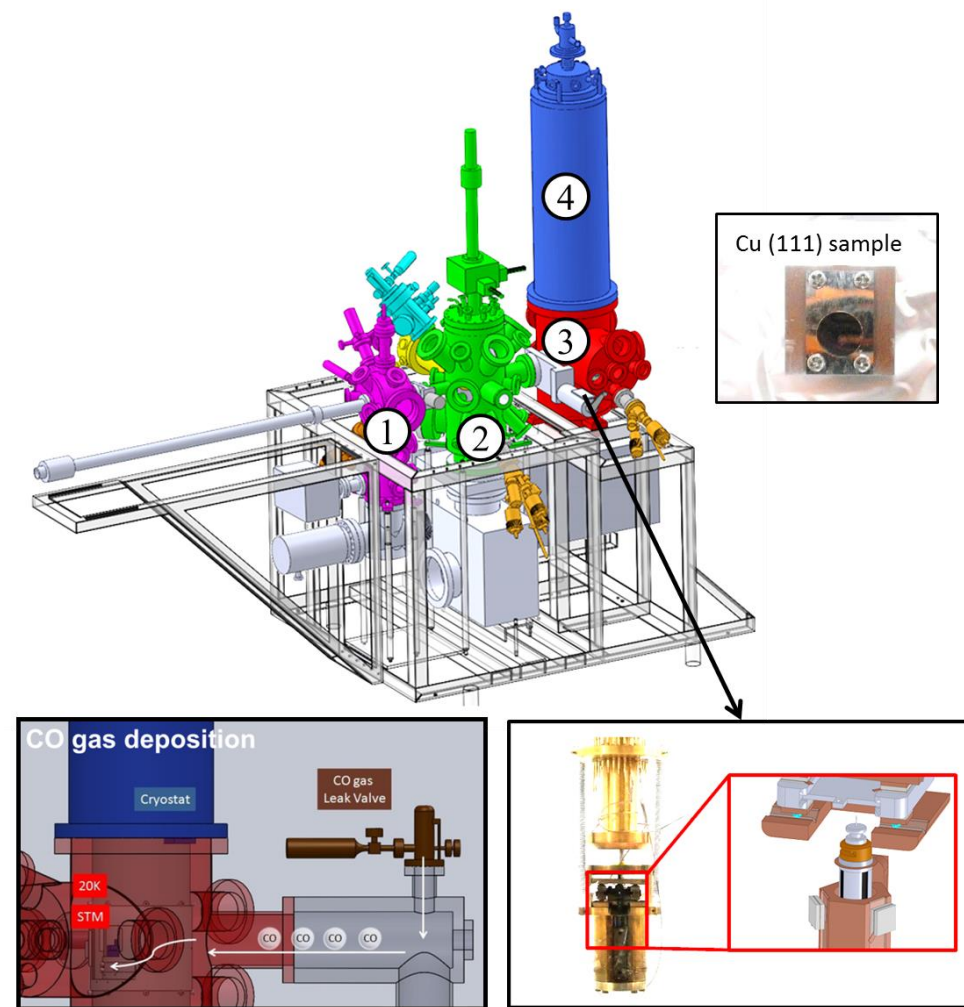


Figure S6. CAD image of our home-built UHV low-temperature STM setup, which consists of introduction, preparation, and STM chambers. Normal STM measurements were performed at 4.6 K with liquid He. All chambers are in UHV condition ( $<5 \times 10^{-8}$  Pa). Bottom right inset shows STM body and zoomed in CAD image of sample stage and piezo tube holding the tip. Right inset is the image of Cu(111) single crystal pinned to a molybdenum sample plate. Bottom left inset shows the CO gas exposure process. CO gas was leaked inside the STM chamber and the cooling shield was opened to expose Cu(111) for deposition. The temperature of substrate recorded was around 10 K.

### **References in Supplementary Information**

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