Supplementary Information

Growth of Transition-Metal Cobalt Nanoclusters on 2D Covalent Organic Frameworks

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Figure S1

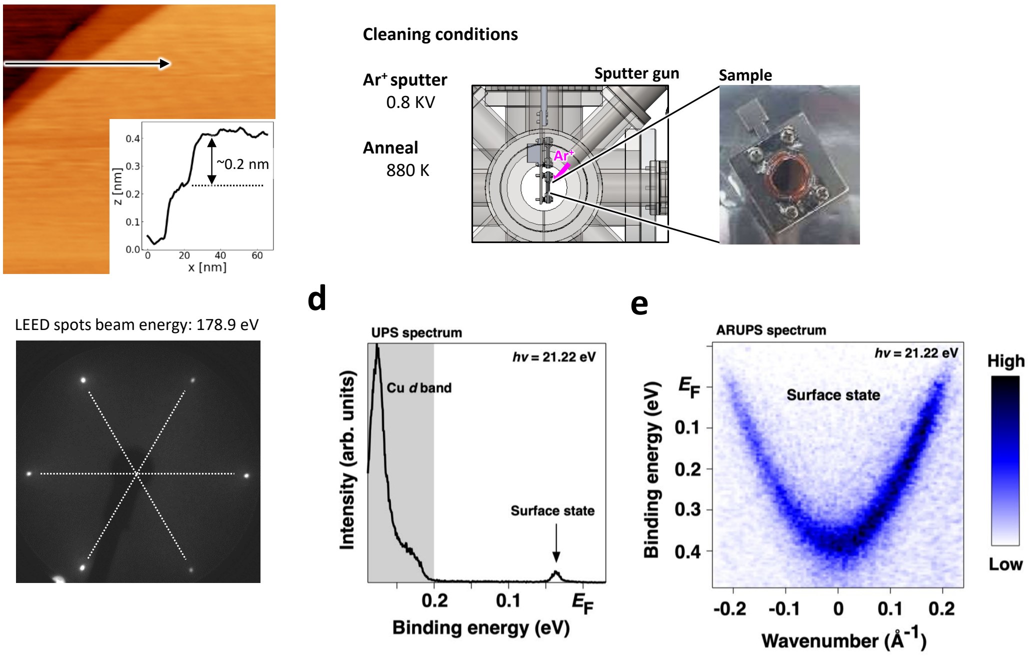

Figure S1. STM/LEED/ARUPS results on a cleaned Cu(111) substrate. (a) STM topographic image (100 × 100 nm^2, V_s = -1 V, I = 100 pA) with a height profile along the arrow. (b) Cleaning setup model inside the UHV preparation chamber. A Cu(111) single crystal fixed onto the Mo sample holder with Ta sheet springs was set into the heating stage inside the preparation chamber. The sputter gun (Ulvac, FIG-5) pointed to the sample surface accelerated Ar ions to the Cu(111) surface and sputtered the surface. After the sputtering, hot electrons accelerated from the filament located behind the sample holder to the Mo sample plate, which temperature was monitored using a pyrometer (Japan sensor, FTZ6-P300-10522, spectral range of 0.8-1.6 μm, emissivity 0.42). (c) LEED spots with a beam energy (BE) of 178.9 eV/ (d) UPS spectrum. (e) ARUPS spectrum.

Figure S2

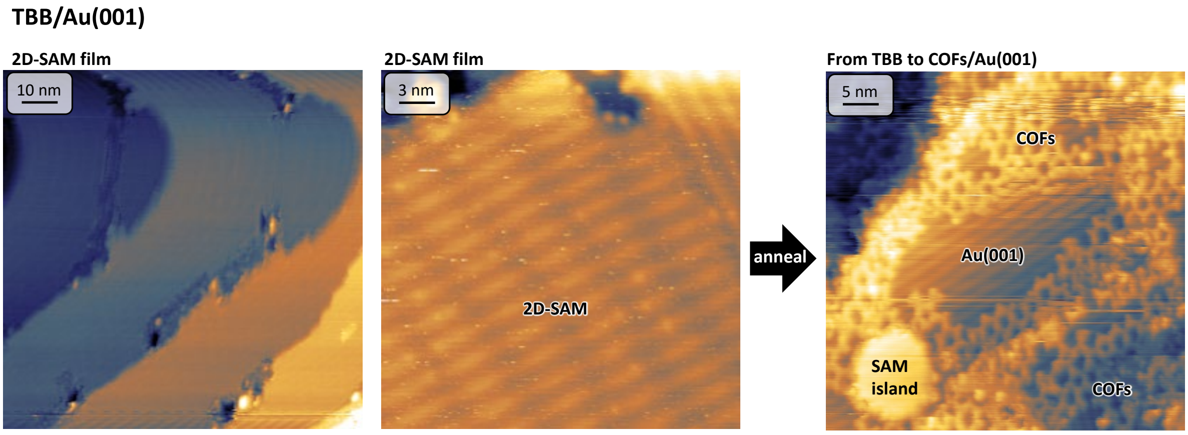

Figure S2. .STM imaging on the TBB SAM film growth on Au(001) before and after the thermal annealing. STM topographic images from left to right: 100 × 100 nm^2, V_s = -1.9 V, I = 10 pA; 30 × 30 nm^2, V_s = -1.4 V, I = 10 pA; 50 × 50 nm^2, V_s = -2 V, I = 10 pA.

Figure S3

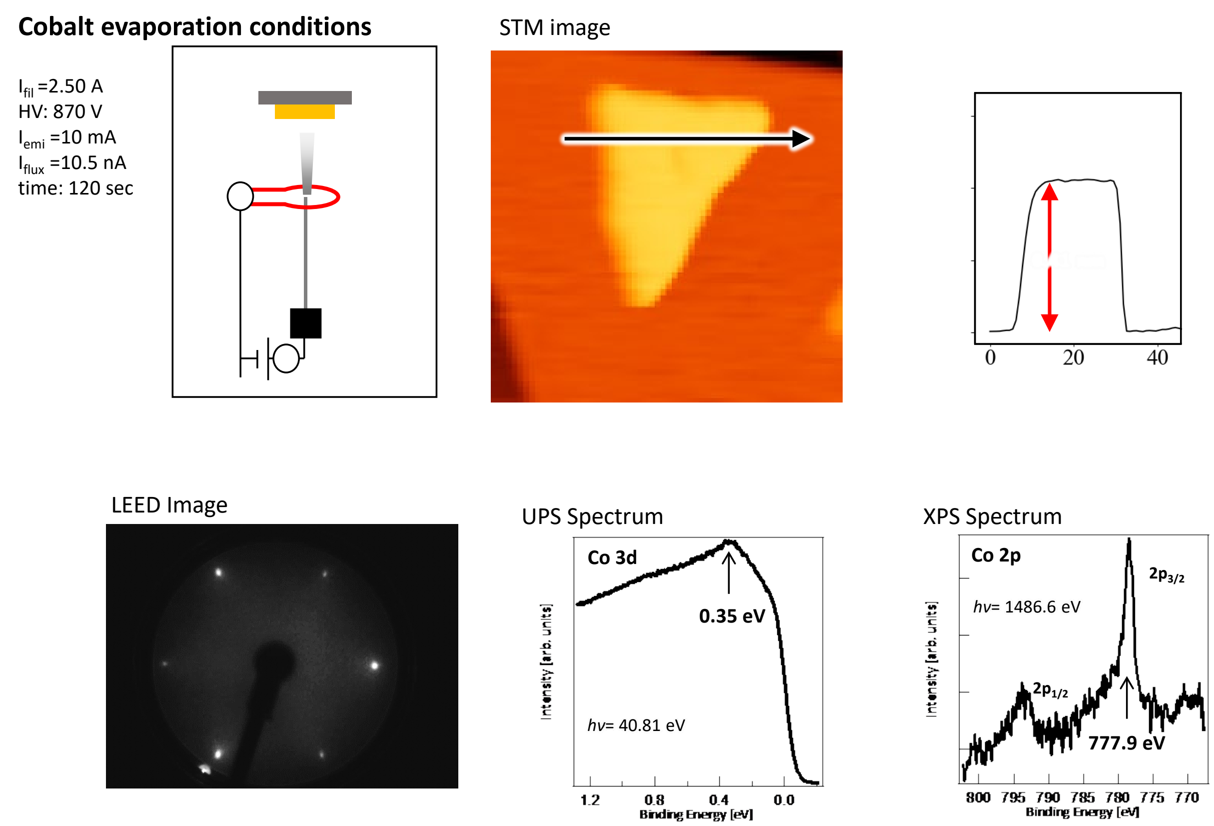

Figure S3. Cobalt (Co) deposition process in UHV preparation chamber. (a) sketch of the electron-bombardment type Co evaporator. (b) STM topographic image (50 × 50 nm^2, V_s = -1 V, I = 1 nA.) of triangular-shaped Co bilayer islands grown Cu(111). (c) Height profile along the arrow in (b). (d) LEED spots obtained on the Co deposition on Cu(111). (e) UPS and (f) XPS spectra obtained on the Co deposition on Cu(111).

Figure S4

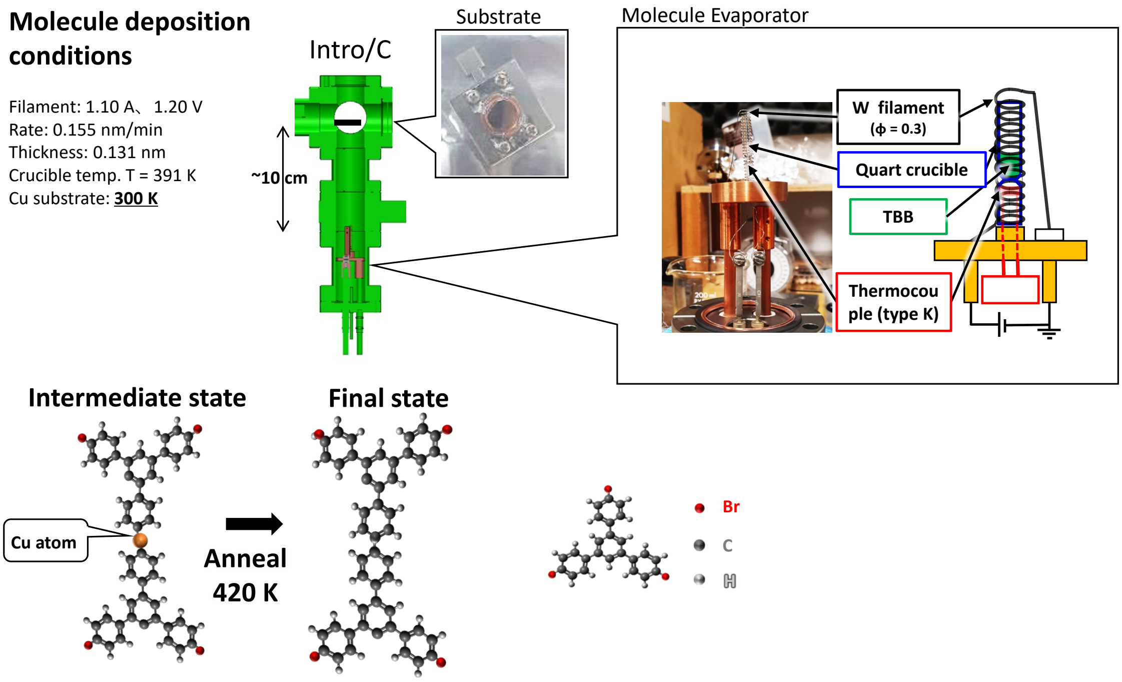

Figure S4. TBB precursor deposition on Cu(111). Molecules were deposited in the UHV introduction chamber. We used a home-built molecular evaporator using a W wire and a quartz tube. Lower panels denote Ullmann reaction models of the TBB precursors from the intermediate to the final state.

Figure S5

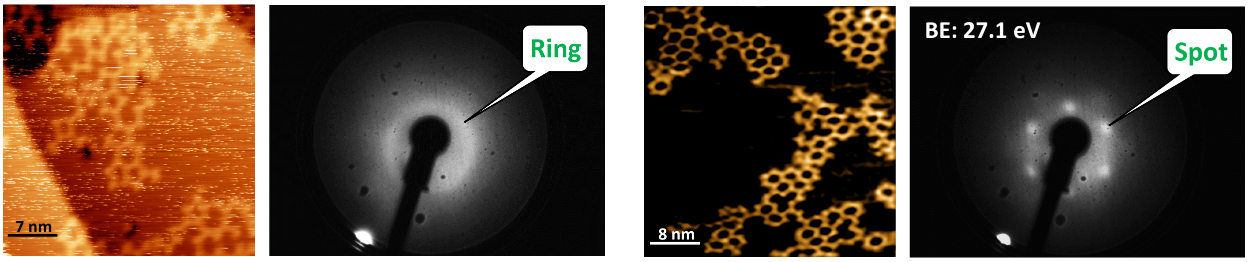

Figure S5. STM topographic images and LEED spots on COFs / Cu(111) before and after the post-annealing to 430 K. Left side: STM image: 35 × 35 nm^2, V_s = 2 V, I = 10 pA. Right side: STM image: 40 × 40 nm^2, V_s = 2 V, I = 10 pA.

Figure S6

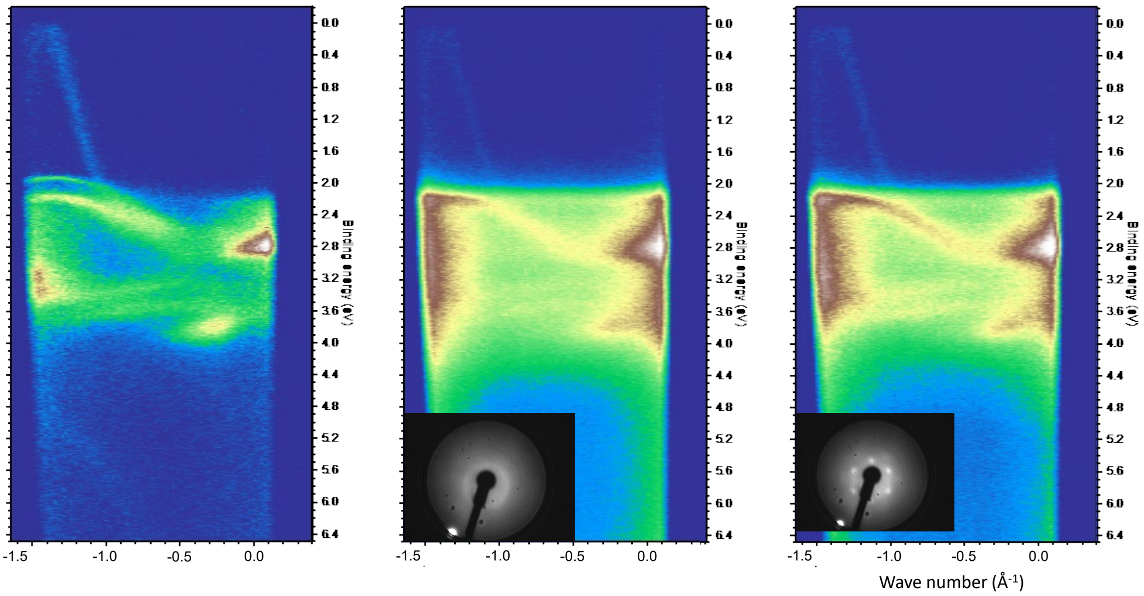

Figure S6. Angle-resolved UPS maps, from left to right, obtained on the bare Cu(111), COFs / Cu(111) before and after the post-annealing. Insets denote LEED spots.

Figure S7

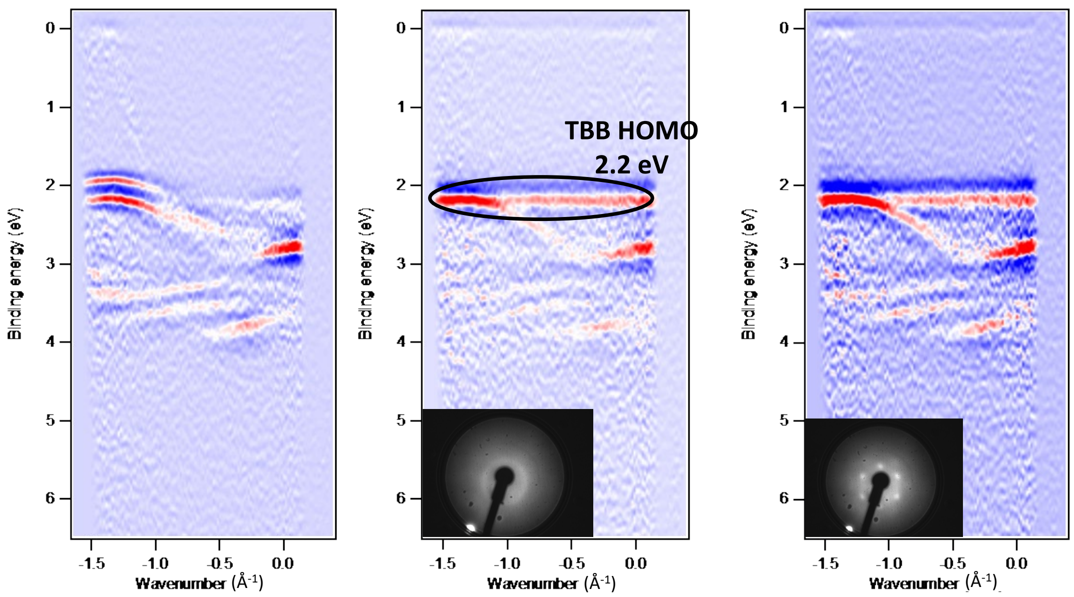

Figure S7. Angle-resolved UPS maps in differential mode, from left to right, obtained on the bare Cu(111), COFs / Cu(111) before and after the post-annealing. Insets denote LEED spots.

Figure S8

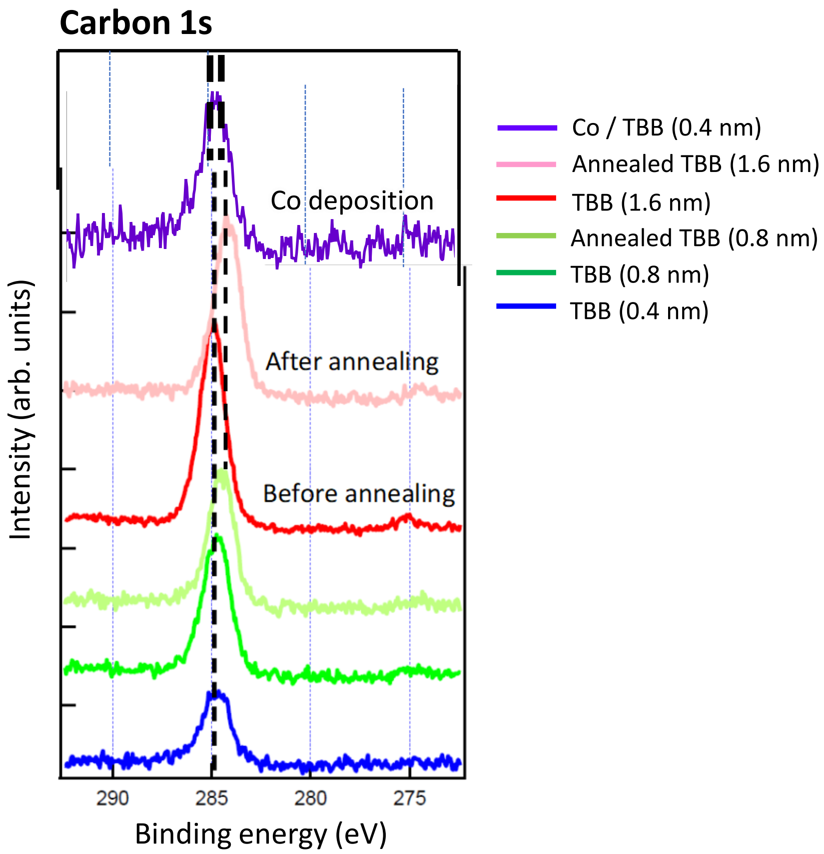

Figure S8. XPS spectra for the C 1s peak obtained at the molecular thicknesses of 0.4 nm (purple and blue lines), 0.8 nm (green and light-green lines), and 1.6 nm (red and pink lines). The spectra for "as grown" (red., blue, green), "annealed" (light-green and pink), and Co deposition on TBB samples are shown. The vertical lines are shown to indicate the approximate positions of each of the peaks. The intermediate state before the annealing includes C-Cu-C bonding, but the final state consists of C-C covalent bonding.