

Supplementary Information

On-Surface Growth of Transition-Metal Cobalt Nanoclusters Using 2D Crown-Ether Array

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Supplementary Notes

(1) Home-Built Low-Temperature UHV STM Setup.

STM measurements were performed using home-built UHV-STM equipment consisting of STM, preparation, and deposition chambers. The base pressures of each chamber were below 5.0×10^{-8} Pa, 2.0×10^{-8} Pa, and 1.0×10^{-7} Pa, respectively. The Cu(111) was cleaned in the preparation chamber, and BrCR molecules were deposited in the deposition chamber. Samples and STM tips were transferred between chambers using transfer rods without breaking the UHV. Gate valves separated each chamber. A UHV cryostat (CryoVAC) in the STM chamber was used to cool down the STM setup.

(2) UHV ARPES / LEED Setup.

All ARPES measurements were performed at 80 K using an ultralow-background, high-sensitivity ARPES apparatus with a hemispherical electron energy analyzer (MBS A-1) and twin monochromators (MBS TM-1) for two wavelength regions as setup. He-I α ($h\nu = 21.218$ eV) radiation was performed using a high-density plasma lamp (MBS L-1) combined with an Al filter. LEED with a multichannel plate (MCP) equipped in the preparation chamber was used to detect weak electron signals from the monolayer molecular film. To avoid damage to the deposited molecular film, we used 10–50 eV beam energy. The sample current was below 0.1 μ A during LEED measurements.

Figure S1, ^1H NMR spectrum (500 MHz, CDCl_3 , r.t.) of BrCR.

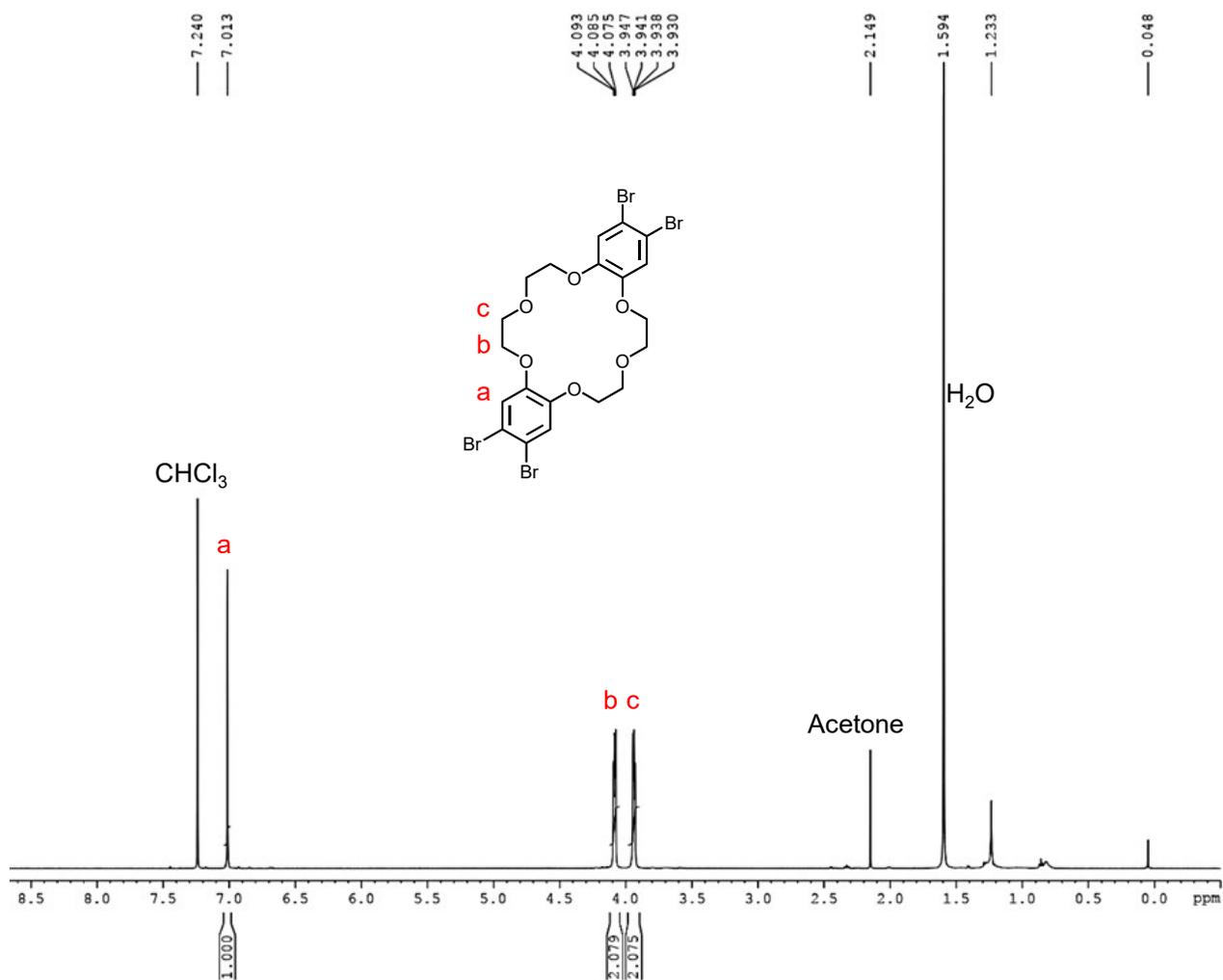


Fig. S1. ^1H NMR spectrum (500 MHz, CDCl_3 , r.t.) of BrCR.

Figure S2, Low- and high-resolution field-desorption mass spectra of BrCR.

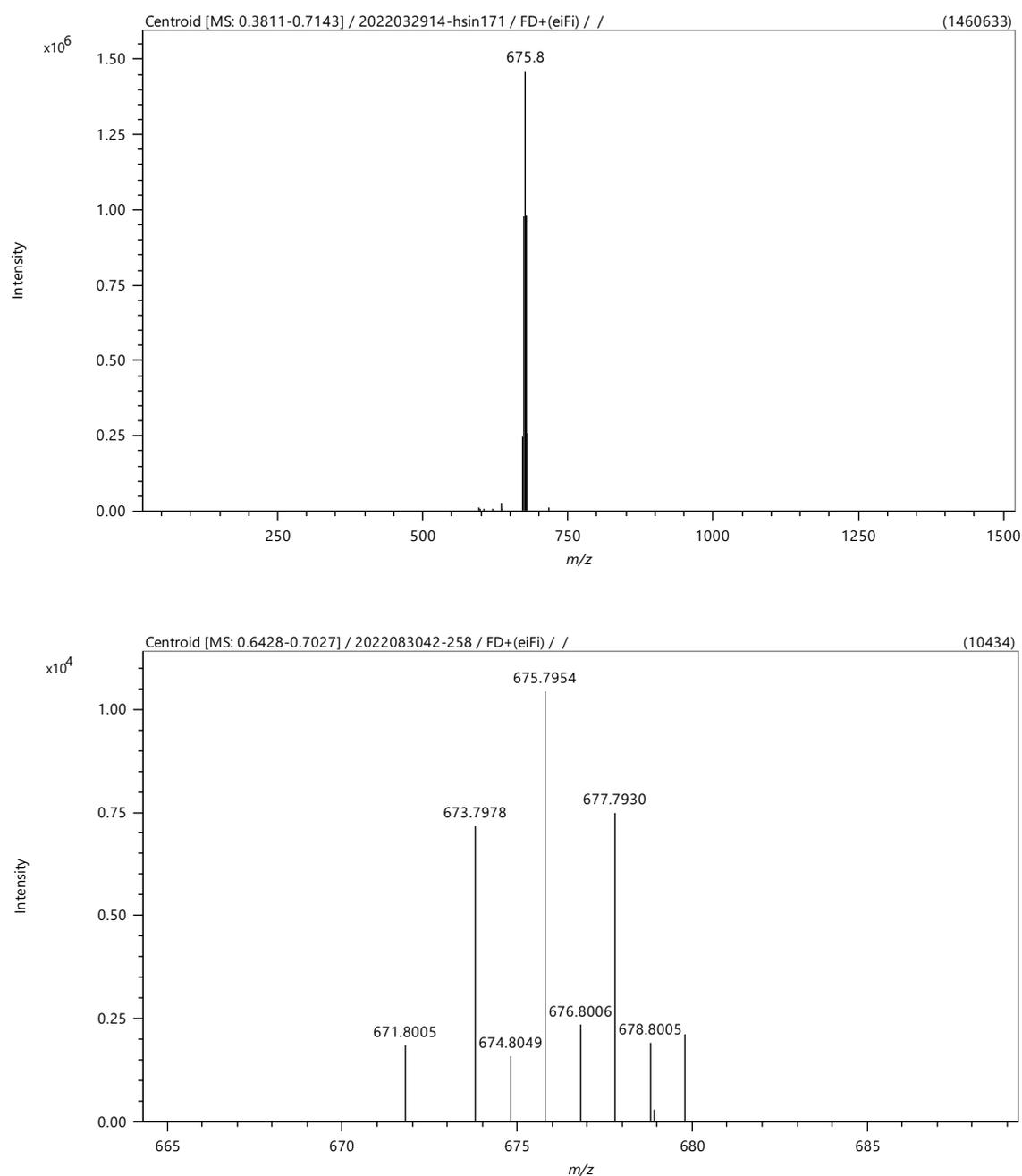


Fig. S2. Low- and high-resolution field-desorption mass spectra of BrCR. The peak at $m/z = 671.8005$ corresponds to $[C_{20}H_{20}Br_4O_6]^+ = 671.79989$ (error = 0.96 ppm).

Figure S3, Single-crystal X-ray crystallographic structure of BrCR.

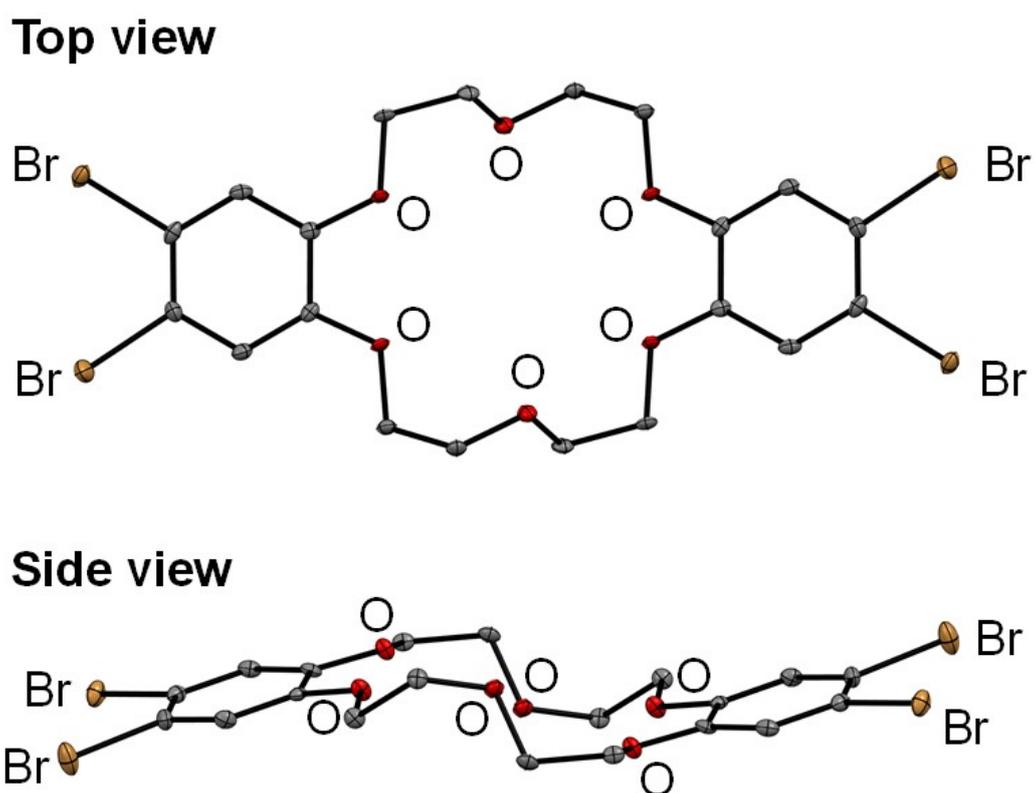


Fig. S3. Single-crystal X-ray crystallographic structure of BrCR with ellipsoid plot with 50% probability. Hydrogen atoms are omitted for simplification.

Figure S4, ARPES spectra using He-II light source (40.8 eV).

Figure S1b shows the difference between spectra in Fig. S1a before (blue line) and after (red line) the Co deposition on the Br-CR film on Cu(111).

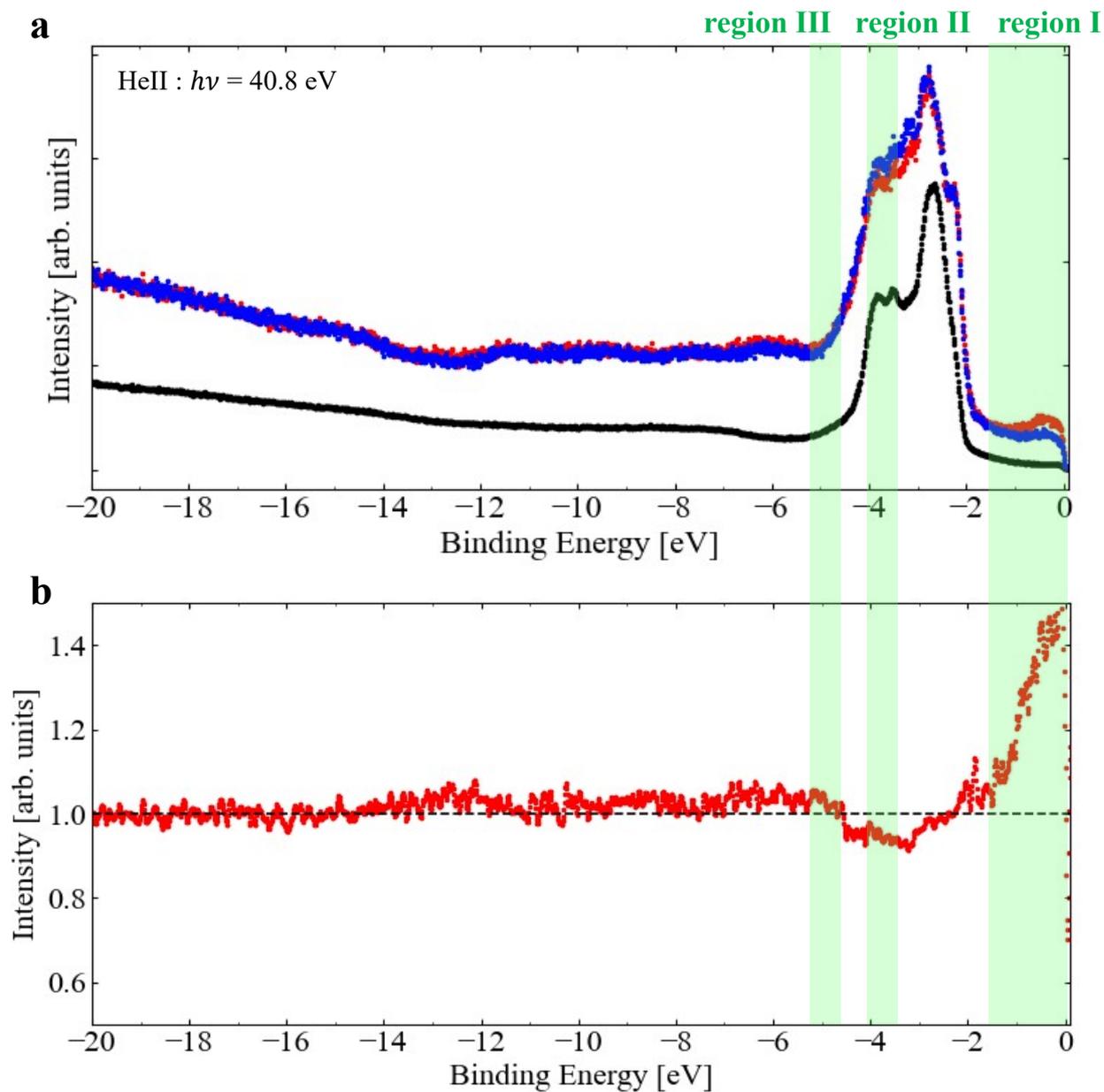


Fig. S4. ARPES spectra using He-II light source. (a) ARPES spectra obtained from the Cu(111) substrate (black line), 1 ML BrCR film on Cu(111) (blue line), and 0.57 ML Co on 1 ML BrCR film (red line). (b) Difference between the blue and red lines in (a).

Figure S5, ARPES, E-k maps.

Figure S5 shows ARPES E-k maps obtained on 0.57 MLs Co / Cu(111), 1 ML Br-CR film / Cu(111), and 0.57 MLs Co / 1 ML Br-CR film / Cu(111). Weak, faint features of parabolic bands caused by forming the Co/crown nanoclusters are found in Fig.S2c. It could be interesting to reveal the origin of the quantum confinement at the complicated interface. However, it is necessary to repeat the ARPES experiments for a well-oriented system to discuss in detail [Matsuda, I.; Tanikawa, T.; Hasegawa, S.; Yeom, H. W.; Tono, K. and Ohta, T. Quantum-Well States in Ultra-Thin Metal Films on Semiconductor Surfaces. *e-J. Surf. Sci. Nanotech.* **2004**, 2, 169-177].

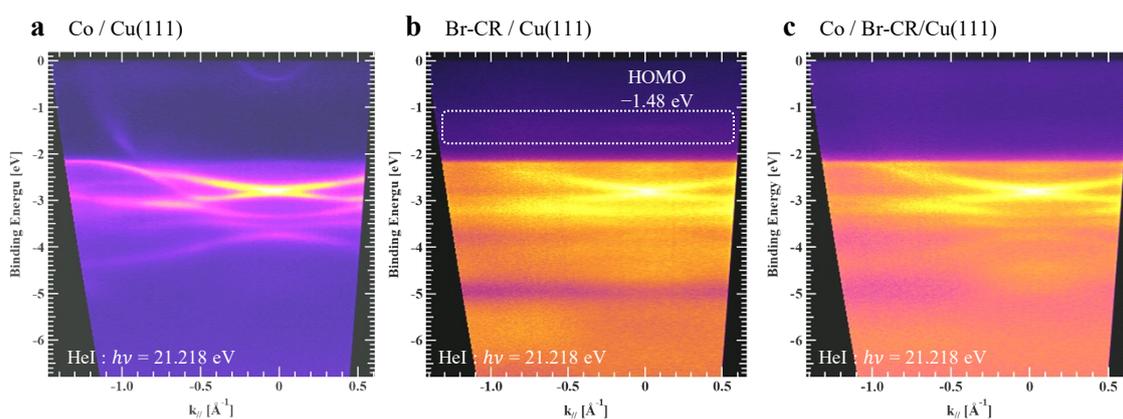


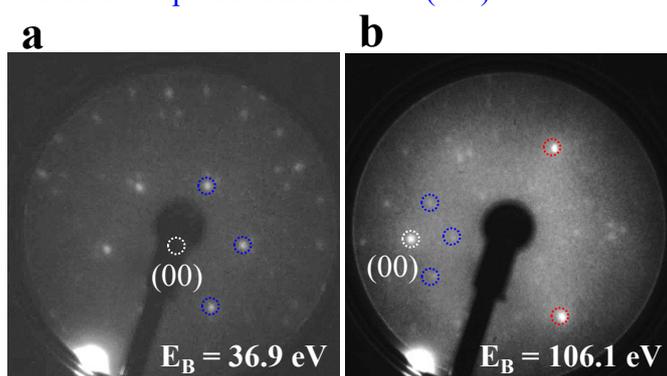
Fig. S5. ARPES maps using the He-I light source obtained on (a) 0.57 MLs Co / Cu(111), (b) 1 ML BrCR film / Cu(111), and (c) 0.57 MLs Co / 1 ML BrCR film / Cu(111).

Figure S6,

Figure S6a shows a LEED image obtained with an incident beam energy of $E_B = 36.9$ eV from the BrCR regular arrangement before Co deposition. LEED with a multichannel plate (MCP) equipped in the preparation chamber was used to detect weak electron signals from the monolayer molecular film. To avoid damage to the deposited molecular film, we used 10–50 eV beam energy. The sample current was below 0.1 μA during LEED measurements. Six-fold symmetric spots (blue circles) with satellite spots indicate three-fold domains of periodic BrCR arrays in agreement with the previous study [Well-Ordered Monolayer Growth of Crown-Ether Ring Molecules on Cu(111) in Ultra-High Vacuum: A STM, UPS, and DFT Study, Nemoto, R.; Krueger, P.; Hartini, A. N. P.; Hosokai, T.; Horie, M.; Kera, S.; Yamada, T. K. The Journal of Physical Chemistry C 2019, 123, 18939-18950.]. The LEED image

LEED & ARPES results

before Co deposition Br-CR / Cu(111)



after Co deposition Br-CR / Cu(111)

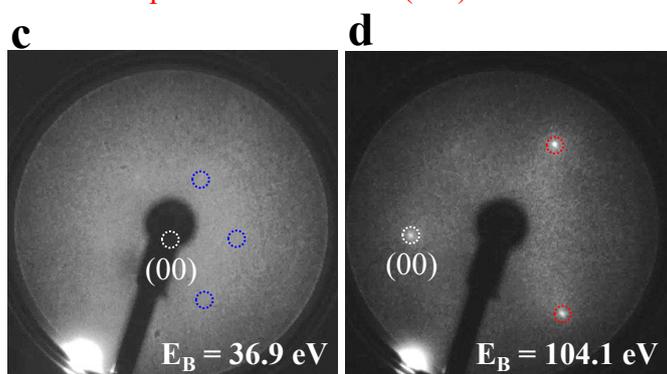


Figure S6. LEED results obtained on the surface before and after the 0.57 MLs Co deposition on the 1 ML BrCR film on Cu(111). (a-d) LEED images measured before (a,b) and after (c,d) the Co deposition. Blue and red dot circles denote LEED spots originated from the (7×4) BrCR array and the fcc-Cu(111) symmetry, respectively. The (00) spot position is marked by the white circle.

in Fig. S6b was obtained from the same surface with $E_B = 106.1$ eV, and the sample surface was gently tilted to see the fcc-Cu(111) spots marked by the red circles. Here, the incident (00) spot is observed on the left-hand side. Fig. S6c and Fig. S6d were obtained after the Co deposition. The LEED patterns derived from the BrCR molecule were about to disappear, but the substrate fcc-Cu(111) spots were confirmed. These LEED results indicate enhancement of the BrCR array disordering due to the Co-BrCR nanocluster formation, which is in good agreement with the nanocluster formation observed in the STM results in Fig.1. Here, we deposited 57 times more Co atoms on the BrCR film. Then, the complete BrCR film could change to metal-organic nanoclusters (see also Fig. S7).

Figure S7

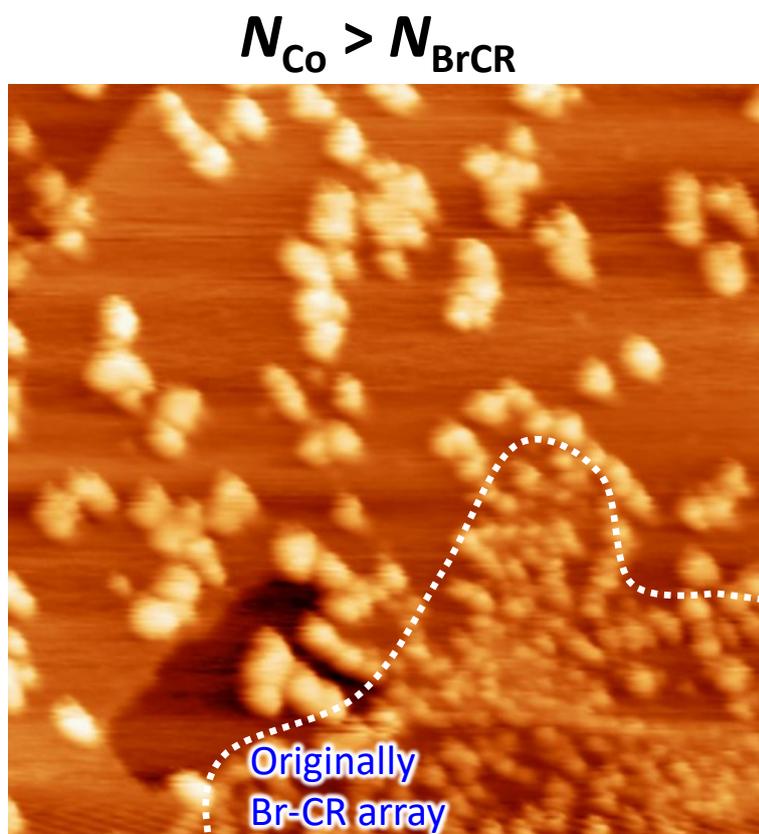


Figure S7. STM topographic image of a complete Co-BrCR nanocluster formation on Cu(111).

Figure S8

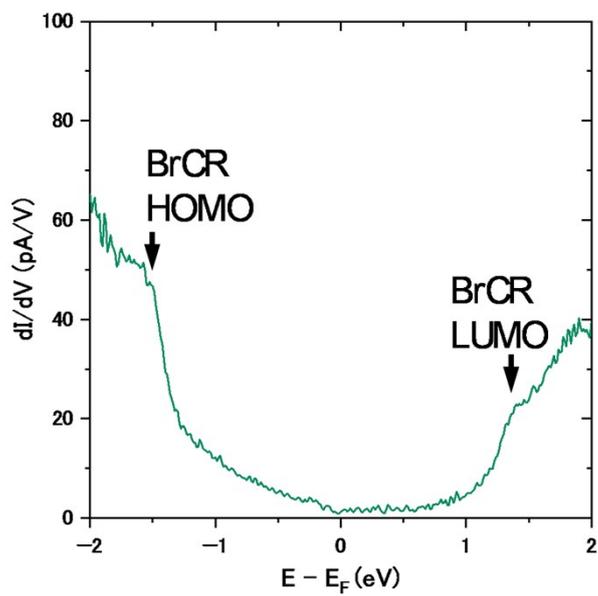


Figure S8. Differential conductance dI/dV curve obtained on the ordered pristine BrCR film on Cu(111): $V_s = -2.5$ V, $I = 1$ nA. Two peak shoulders indicate HOMO and LUMO energy positions.