Supplementary Information

Well-Ordered Monolayer Growth of Crown-Ether Ring Molecules on Cu(111) in Ultra-High Vacuum: A STM, UPS, and DFT Study

Ryohei Nemoto¹, Peter Krüger^{1,2}, Ayu Novita Putri Hartini¹, Takuya Hosokai³, Masaki Horie⁴, Satoshi Kera^{1,5}, and Toyo Kazu Yamada^{1,2*}

Department of Materials Science, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan.
Molecular Chirality Research Center, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan.

 National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology, Tsukuba Central 2, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan.
Department of Chemical Engineering, National Tsing Hua University, 101, Sec. 2, Kuang-Fu Road, Hsinchu, 30013, Taiwan.

5. Institute for Molecular Science, Myodaiji, Okazaki 444-8585 Japan.

Author Information, Corresponding Author: Toyo Kazu Yamada, *E-mail: toyoyamada@faculty.chiba-u.jp

UHV-STM and UHV-UPS experimental setups and the molecule evaporator with QCM rate check.



Figure S1 Experimental setups and Br-CR single molecule model in gas, in bulk, and on Cu(111) phases.

(A) Home-built UPS (LEED) setup. No.1 main, No.2 preparation, and No.3 Br-CR deposition chambers. (B) Home-built low temperature UHV-STM setup. No.1 STM/cryostat, No.2 preparation, and No.3 deposition chambers. (C) Home built molecular evaporator. (D) Enlarged image of the evaporator in the box in (C). Br-CR yellowish powders (~10 mg) were set inside the quartz crucible (~50 mm length). The thermocouple monitored the crucible temperature. (E) QCM spectrum during the Br-CR evaporation from the crucible (distance from the crucible top is 110 mm). Used QCM parameters were z factor = 1, density = 1, tooling factor = 100%. Just above the crucible temperature higher than 84 °C, Br-CR started to evaporate. In this study, we used the evaporation speed of 0.03 nm/min at 87.6 °C. (F) Br-CR single molecule model in gas, in bulk crystal, and on Cu(111) phases. Top and side views. The single Br-CR molecule consists of 20 carbon (black), 20 hydrogen (pink), 6 oxygen (red), and 4 bromide (brown) atoms. In the side view, Br-Br distance is 1.26 nm, 1.51 nm, and 1.55 nm in gas, in bulk, and on Cu(111) phases, respectively.



UPS, STM atomic image, and STS surface state results obtained on the Cu(111) substrate.

STM images of extra adsorbates on Cu(111).

One might be noted that, in Fig. 3A, most of the Cu substrate surface (see *e.g.* surroundings of the island in Fig. 3F as well as terraces in Fig. S3C) was covered by very many adsorbates (diameter: \sim 1 nm, height: 50-100 pm). These could be isolated single Br-CR molecules which did not contribute to grow the islands or impurities included in the Br-CR powders, while we performed the Br-CR growth in UHV with a long (>1 day) degas process. These adsorbates could be the reason why the Cu(111) surface state is UPS spectrum is strongly suppressed by only the small coverage of Br-CR films (see Fig. 4C).



Figure S3 Extra adsorbates on the surface of 0.05 and 0.25 ML Br-CR on Cu(111). (A) STM topographic image obtained on 0.05 ML Br-CR on Cu(111) ($50 \times 30 \text{ nm}^2$, $V_s = -0.7 \text{ V}$, $I_t = 100 \text{ pA}$). In the island, bright spots together with the stripe patterns are observed frequently between domains (domain boundaries). (B) Line profiles along the black, gray, and purple arrows in (A). (C) STM topographic image obtained on 0.25 ML Br-CR on Cu(111) ($100 \times 60 \text{ nm}^2$, $V_s = -0.7 \text{ V}$, $I_t = 100 \text{ pA}$). Here, on the Cu(111), many chain structures were observed. (D) Line profiles along the black and gray arrows in (A).

Angle-resolved UPS results.



DFT calculations of free Br-CR molecules (see Fig. S5)

In order to better understand the energetics of Br-CR adsorption, we have studied the stiffness of the free Br-CR molecule and the energy barrier between the gas phase ("bent") and the crystal phase ("stepped") conformation. These calculations were done using the Gaussian09 software with 6-31(d) basis and B3LYP potential. In the bent conformation, the calculated angle Θ between the two benzene rings is 112°. Fig.S5A shows the energy as a function of Θ which was controlled by fixing the distance between the Br atoms. The energy cost of bending the molecule by ±35°, is only 0.1 eV, which demonstrates the high flexibility of Br-CR. For making the molecule flat ($\theta = 180^\circ$) a moderate energy of 0.7 eV is required.

We have calculated the energy barrier between the bent and stepped conformation, see Figs. 5C and 5D. In order to find a low energy path, the oxygen crown was first twisted by fixing the dihedral angle of CCOC groups (blue atoms in conformations No.2-4) until the crown ring resembles that of the stepped configuration. Then the whole molecule was bent by controlling a Br-O-Br angle (blue atoms in conformations No.5-10). The calculated energy barrier height is 0.35 eV from the bent conformation and 0.12 eV from the stepped conformation (No.11 in Fig. S5D). These energies are much smaller than the adsorption energy on Cu (2.6 eV) which explains that the crown may become strongly distorted upon adsorption on Cu.





UPS and DFT results of work function variation due to Br-CR adsorption on Cu(111).

SPALEED results of Br-CR film on Cu(111).



This Br-CR film was prepared in a different manner compared to the main manuscript. First, a thick Br-CR film was deposited on Cu(111) at 300 K, and the thicker layers were desorbed by subsequent annealing (~500 K). Then, only the interface monolayer film could remain. (A) SPA-LEED image at 41.0 eV. The (00) spot locates at the center. (B) Simulated LEED spots. Observed spots in (A) were marked as filled circles. Blue, green and red colors are caused by three domains of the Br-CR film. The obtained unit cell: $\vec{a'} = 0.88$ nm, $\vec{b'} = 1.79$ nm, $\theta = 90^{\circ}$.