

Supplementary Information

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

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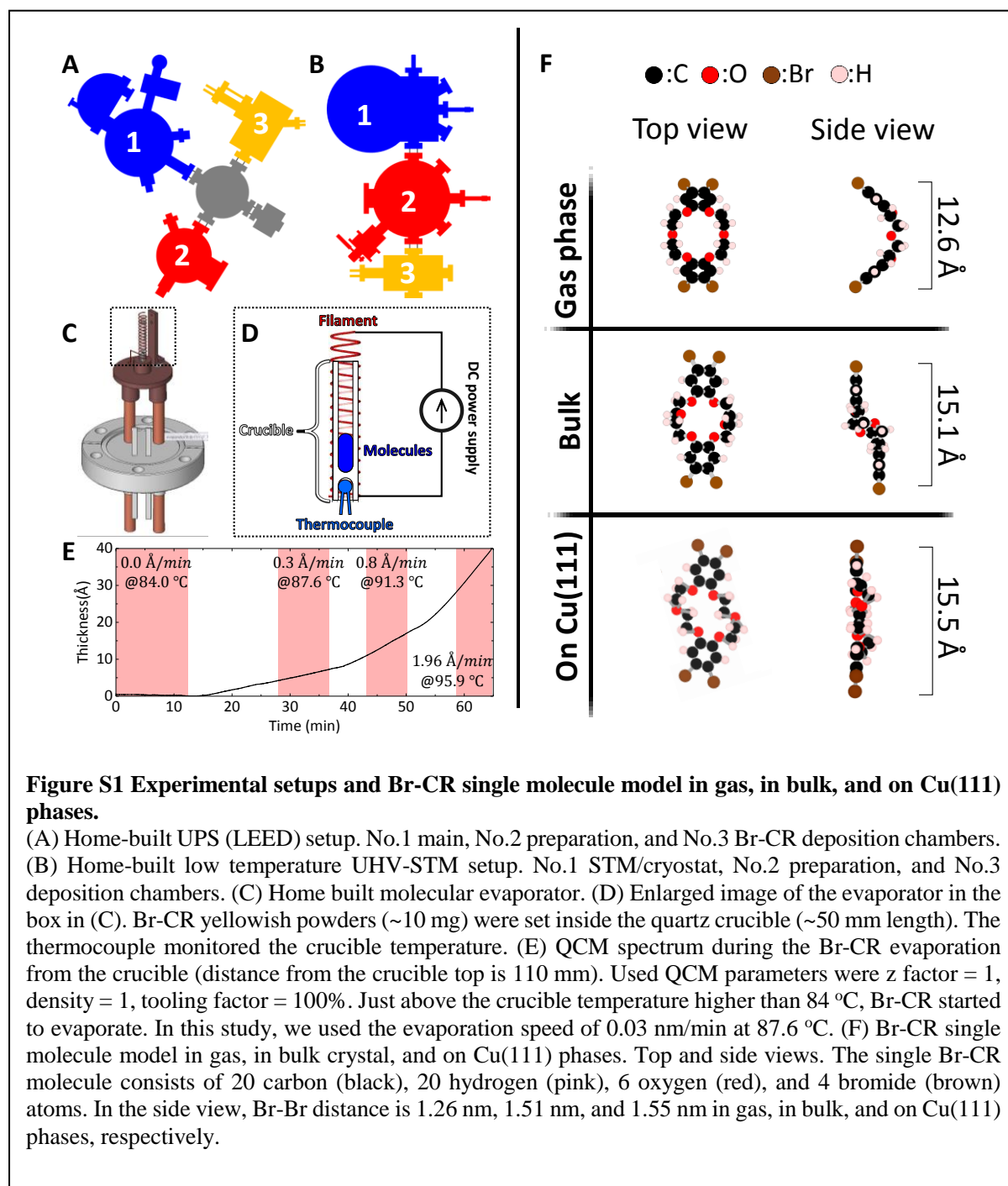
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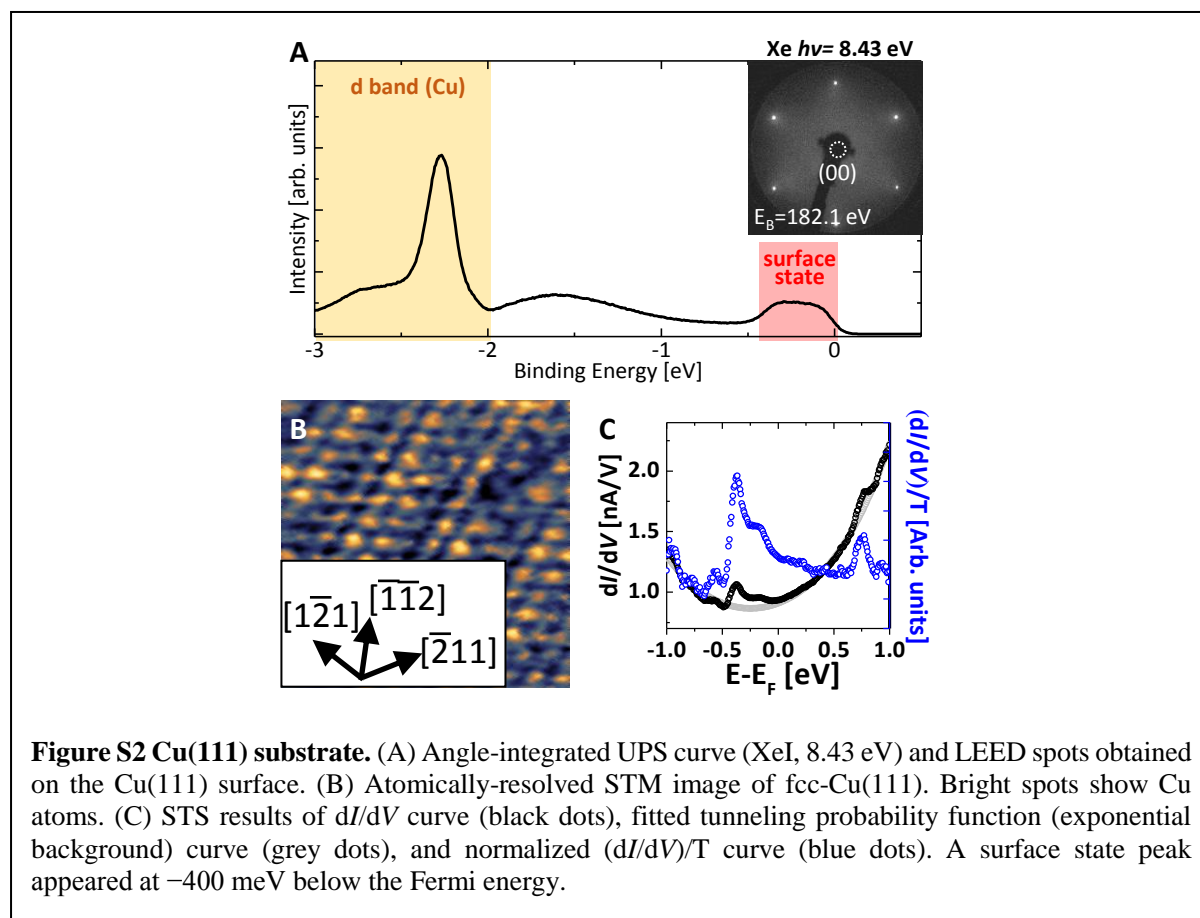
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UHV-STM and UHV-UPS experimental setups and the molecule evaporator with QCM rate check.

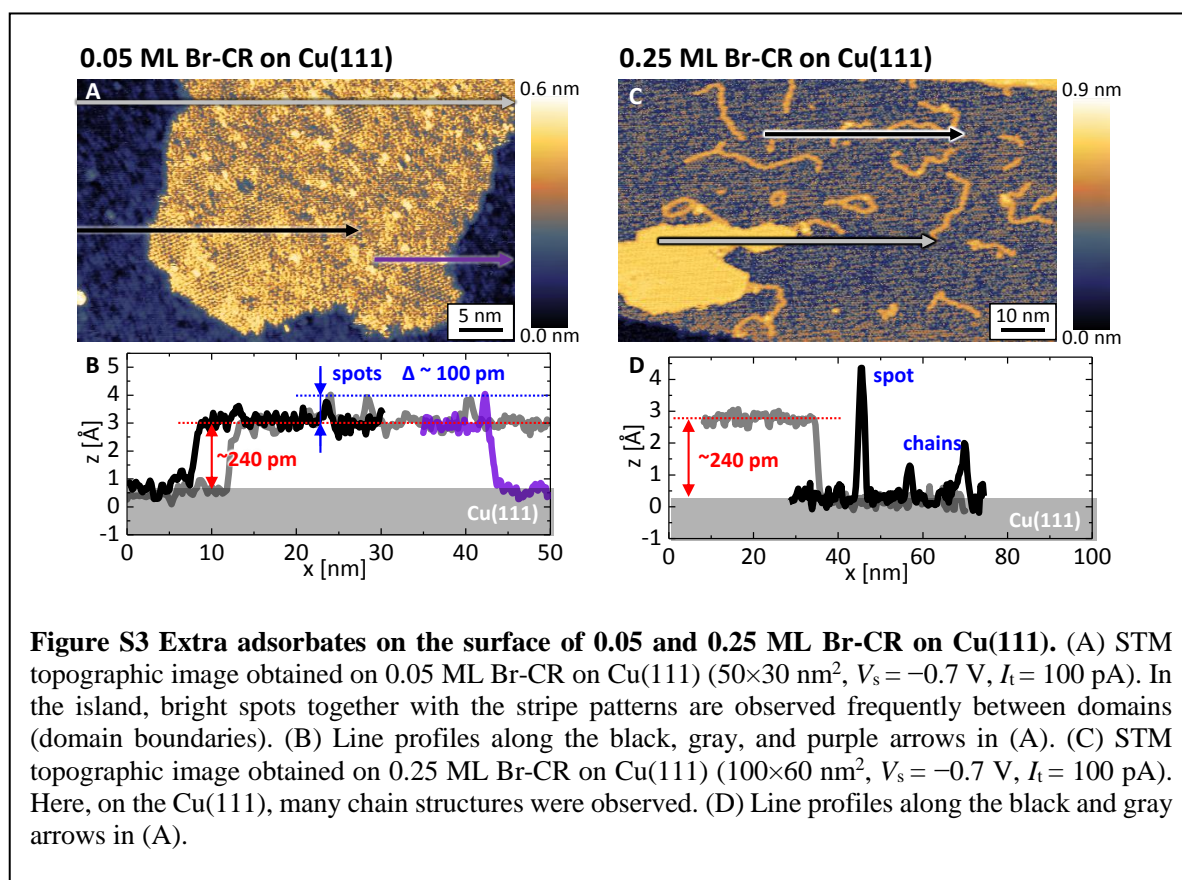


UPS, STM atomic image, and STS surface state results obtained on the Cu(111) substrate.

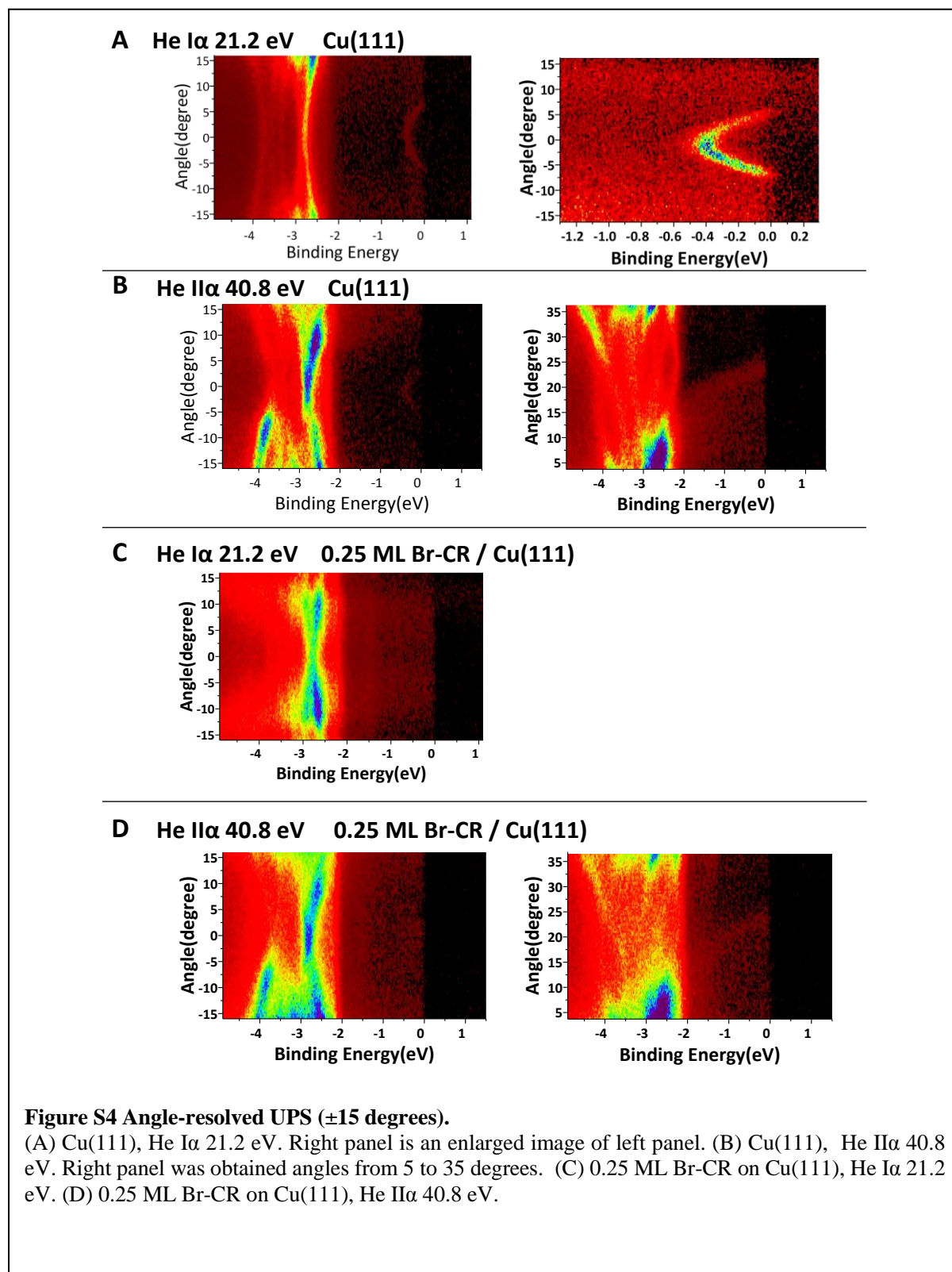


STM images of extra adsorbates on Cu(111).

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: ~ 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).



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 $\pm 35^\circ$, 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.

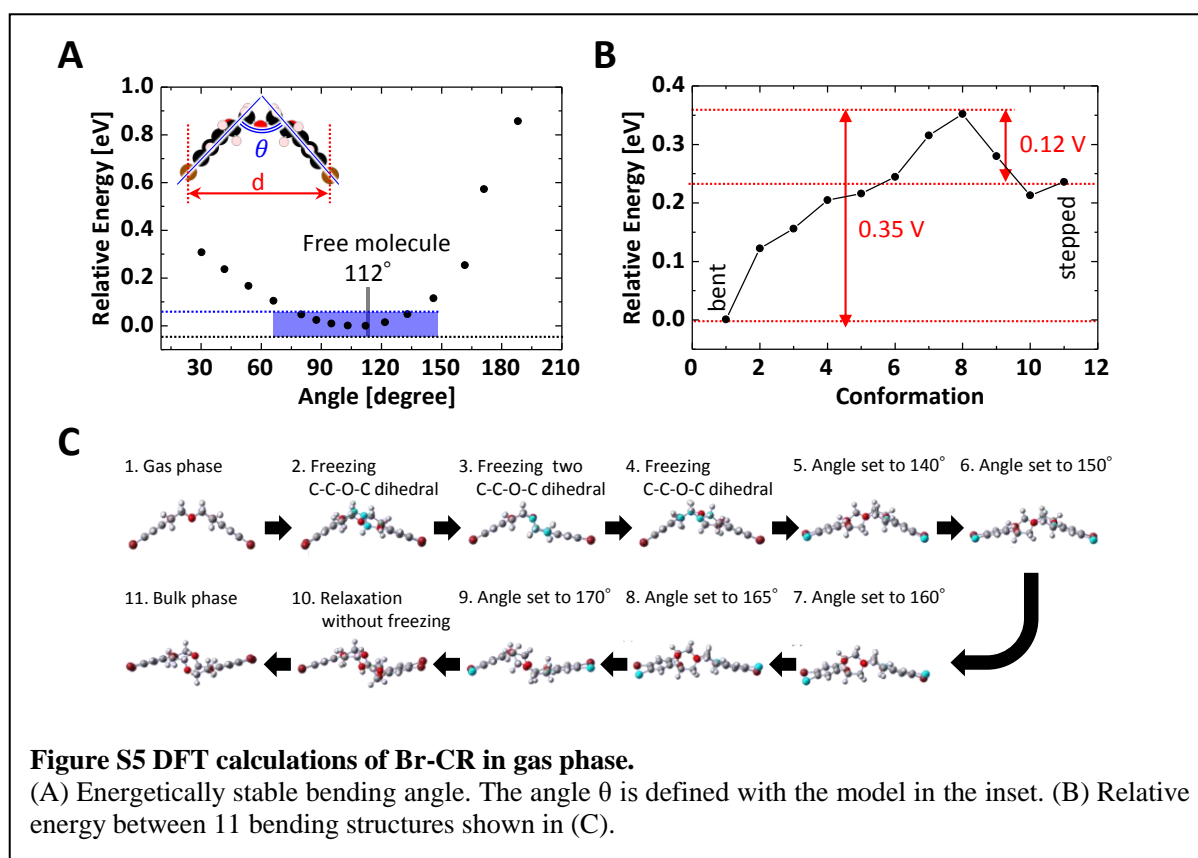
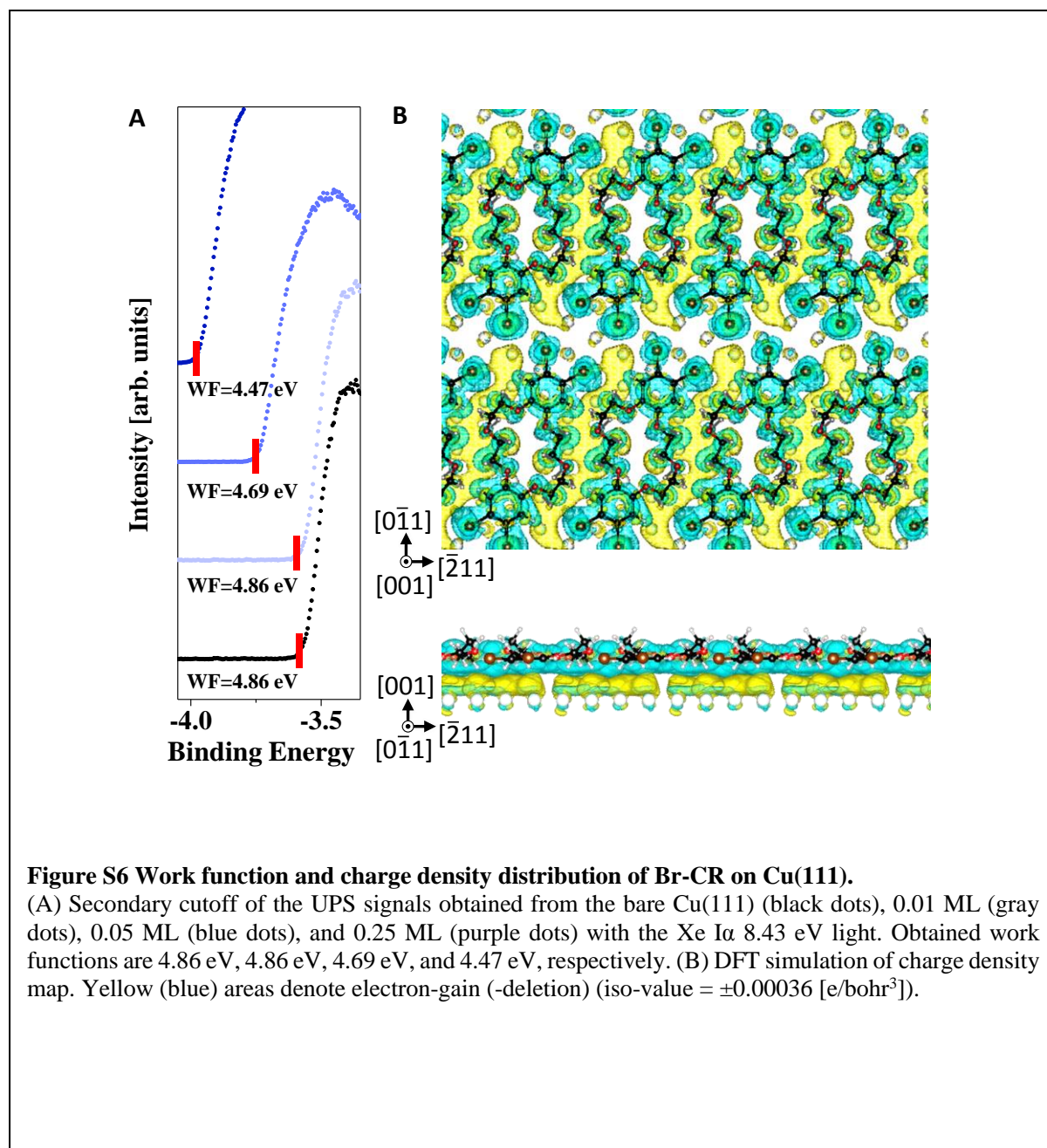


Figure S5 DFT calculations of Br-CR in gas phase.

(A) Energetically stable bending angle. The angle θ is defined with the model in the inset. (B) Relative energy between 11 bending structures shown in (C).

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



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

