Insight into Organometallic Intermediate and its Evolution to Covalent Bonding in Surface-Confined Ullmann Polymerization

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Supporting Information

Supporting Information: Contents

1. Additional experimental results

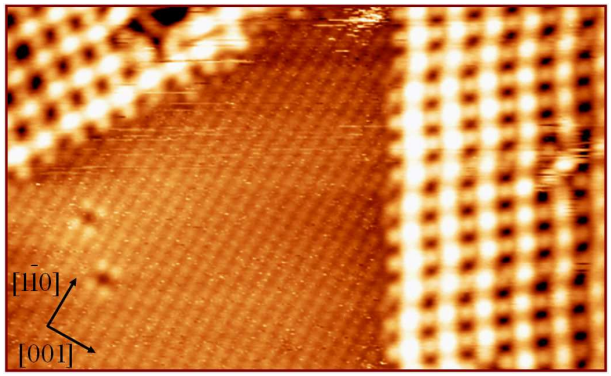

Figure S1. STM image of organometallic submonolayer on Cu(110) at RT (13.0×7.9 nm^2, I_t=0.77 nA, V_s=-0.76 V). Two mirror-symmetric domains of the organometallic structure and the atomically resolved copper substrate are visible.

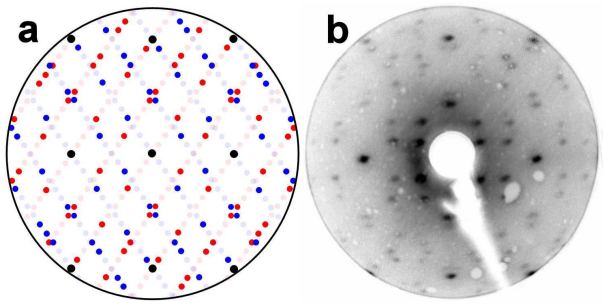

Figure S2. Simulated LEED pattern[1] (a) due to two molecular domains identified by the matrices (2, 2 | -4, 9) (blue) and (2, -2 | 4, 9) (red); black spots are due to copper. Missing spots of the experimental LEED pattern (b) are dimmed in the simulation for comparison purpose.

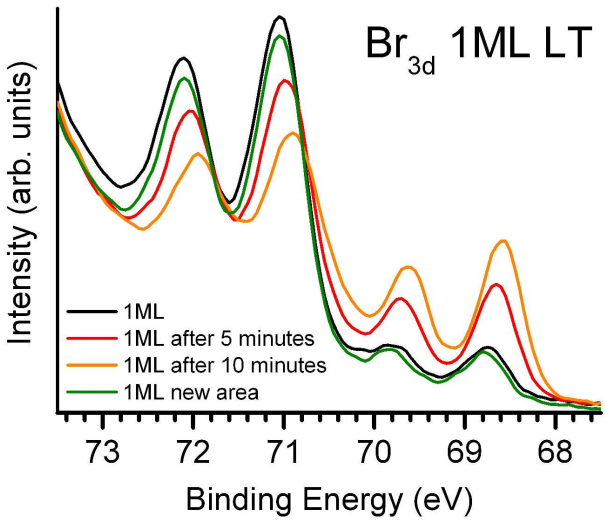

Figure S3. Core level spectra of Br 3d, using an excitation energy of hν=390 eV. The sample is held at 100 K (LT), and repeated spectra are shown as a function of exposure time to synchrotron radiation. The sample is progressively damaged by increasing exposure to the beam.[2] Changing the position at which the beam strikes the surface recovers spectra (green) similar to the first (black).

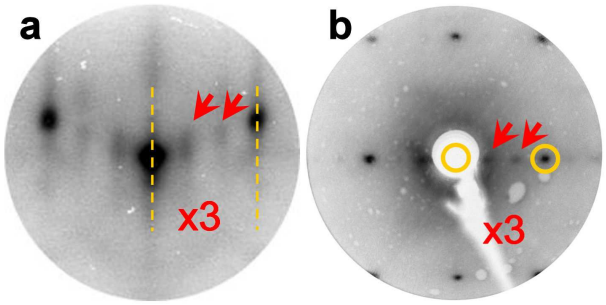

Figure S4. RHEED (a) and LEED (b) experimental patterns of the dBB on Cu(110) after annealing at 500 K (i.e. polymer phase). The x3 periodicity along the [001] direction exists in both cases.

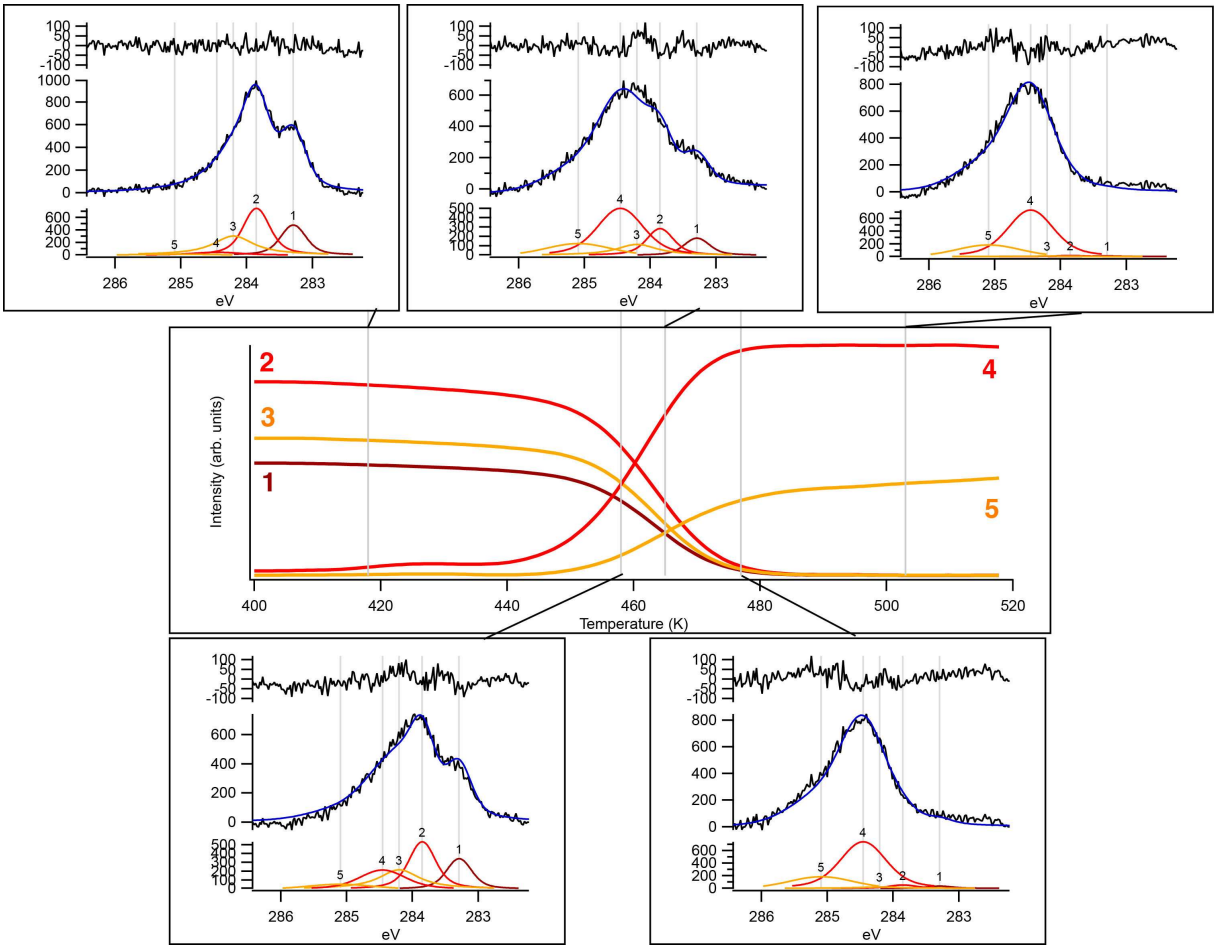

Figure S5. Details of the fast-XPS, including fitting through the polymerization transition region. Peak coloring and labeling are the same as used in the MS Figures 4 and 7b. The positions of the

peaks are taken from the high resolution (HR) fits in Figure 4, and their widths and lineshapes were fixed to values that gave good fits for the initial (RT) and final (annealed) portions of the fast-XPS dataset. These parameters must be readjusted owing to the larger pass energy for the electron analyzer used during fast-XPS measurements, which is necessary for achieving a reasonable signal to noise ratio, in order to increase sensitivity at the expense of resolution. During the fit the intensity ratio between peaks 2 and 3 is locked to the fixed value observed in the HR spectra, in order to achieve a first-order approximation of the system as comprising only two chemical states. It is clear that there is a deviation of the fit from the data in the vicinity of the transition. This is likely due to the formation of intermediate states, which are predicted theoretically (ref. 57 in the MS). However, we do not presently have the corresponding HR spectra to investigate this behavior in detail. Further measurements are needed to elucidate this behavior.

2. NEXAFS experimental geometry

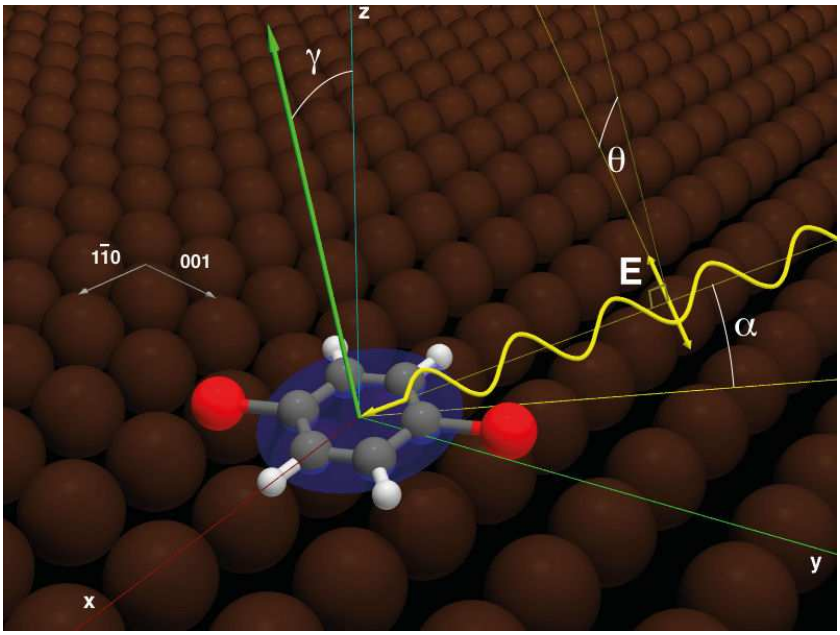

Figure S6. NEXAFS experimental geometry. Linearly polarized radiation falls upon the sample with grazing incidence at fixed angle **α**. The sample can be rotated about the beam axis to change the angle (**θ**) between the polarization vector and the sample surface. The angle **γ** represents the polar angle formed by the **π*** orbital with respect to the sample normal.

3. Phenylene ring orientation by NEXAFS

The π_1* resonances in Figure 6 can be used to extract the geometrical arrangement of phenyl rings, by examining the variation of the NEXAFS intensity as a function of the polarization and incidence angles. The intensity of π_1* resonances decreases strongly at $\theta = 0°$. Cursory inspection of the π_1* intensity suggests that the aromatic ring is almost flat on the surface in both systems, by virtue of this vanishing intensity at $\theta = 0°$. The nonzero intensity around the position of the dominant resonance (~ 285 eV) for $\theta = 0°$ can be attributed to a rehybridization of the molecules

rather than to a tilt of the molecular plane: it has been found in case of aromatic molecules that NEXAFS spectra give such a nonzero intensity also for planar geometries.[3]

REFERENCES

(1) *LEEDsim - LEED Simulation Software*.

(2) Baumgärtner, K.M.; Volmer-Uebing, M.; Taborski, J.; Bäuerle, P.; Umbach, E.; Adsorption and Polymerization of Thiophene on a Ag(111) Surface. *Ber. Bunsen. Phys. Chem.* **1991**, *95*, 1488-1495.

(3) Mainka, C.; Bagus, P.S.; Schertel, A.; Strunskus, T.; Grunze, M.; Wöll, C.; Linear Dichroism in X-Ray Absorption Spectroscopy of Strongly Chemisorbed Planar Molecules: Role of Adsorption Induced Rehybridisations. *Surf. Sci.* **1995**, *341*, L1055-L1060.