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Organometallic ring vs. chain formation beyond kinetic control: steering their equilibrium in two-dimensional confinement

Claudio K. Krug‡, Qitang Fan‡, Florian Fillsack, Johannes Glowatzki, Nicole Trebel, Lukas J. Heuplick,
Tabea Koehler and J. Michael Gottfried*

Philipps-Universität Marburg, Fachbereich Chemie, Hans-Meerwein-Str. 4, 35032 Marburg, Germany

**michael.gottfried@chemie.uni-marburg.de*

‡ These authors contributed equally to this study and share first authorship.

1. Experimental details

The experiments were carried out in a UHV system consisting of three chambers, allowing complete microscopic and spectroscopic characterization of each individual sample. Deposition of DBAz was performed in a custom-built preparation chamber operated at a base pressure below 10^{-9} mbar**.** The DBAz molecules were deposited from a home-built line-of-sight evaporator consisting of a glass tube as a reservoir for the molecules, a CF16 gate valve and a glass tube, which can be positioned *via* a linear motion, guiding the molecules directly to the single crystal surface. Prior to deposition, the reservoir was cooled to 195 K with a mixture of acetone and dry ice and the gate valve was opened until the pressure in the chamber did not decrease any more to degas the reservoir. Afterwards the Cu(111) single crystal was positioned directly in front of the opening of the glass tube and the gate valve was opened until the desired coverage was reached. The monolayer phase (1.00 ML) is defined as the saturation coverage achieved at room temperature.

Prior to deposition of DBAz the Cu(111) single crystal (purity 99.9999%, roughness <0.01 µm, orientation accuracy <0.1°, from MaTecK/Germany) was prepared by iterated sputtering with Ar^+ ions (1 keV, 12 µA, 30 min) and annealing (800 to 820 K, 10 min) in the STM chamber. The temperatures were measured with a thermocouple directly mounted to the Cu(111) single crystal. Surface cleanliness was confirmed either by XPS or STM. The STM chamber is operated at a base pressure below 2×10^{-10} mbar and houses a SPECS Aarhus 150 STM, which was used for variable temperature STM (VT-STM). VT-STM measurements were performed using an electrochemically etched W tip. For the measurements, the STM was cooled to 100 K with liquid nitrogen and gradually warmed up during measuring. STM images were recorded in constant current mode and processed with WSxM 5.0 Develop 8.5.[1]

XPS experiments were carried out in a third chamber operated at a base pressure below 2×10^{-10} mbar with monochromatised Al Kα radiation using a SPECS XR 50 M X-ray anode, a SPECS FOCUS 500 monochromator and a SPECS PHOIBOS 150 electron energy analyzer equipped with an MCD-9 multi channeltron detector.

2. XPS data of 1,3-dibromoazulene on Cu(111)

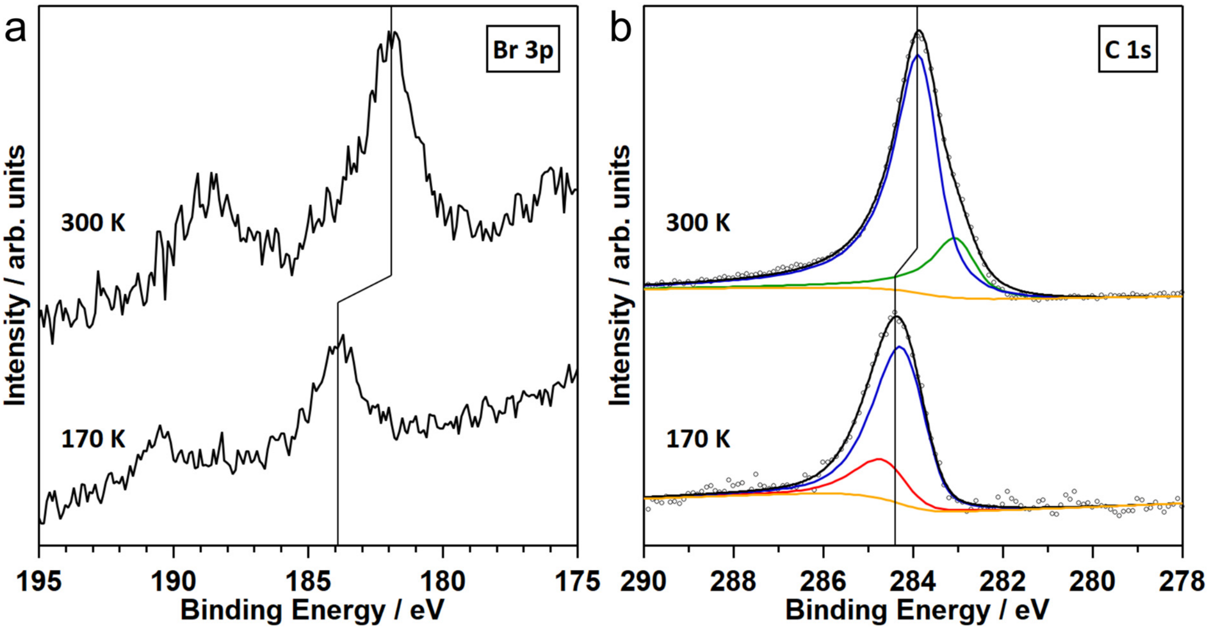

Fig. S1: (a) Br 3p and (b) C 1s XP spectra after deposition of DBAz on Cu(111) at 170 and 300 K, respectively. The shifts indicated by the lines show that the molecule stays intact at 170 K and becomes completely debrominated at 300 K. The C 1s spectra are fitted with two peaks in a 1:4 ratio; black dots: data points, red curve: Br-bonded C atoms, green curve: C-bonded C atoms, blue curves: all other C atoms, black curves: total fits, orange curves: background.

As shown by Fig. S1a, deposition of DBAz on Cu(111) at 170 K results in the Br $3p_{3/2}$ signal located at a binding energy (BE) of 183.9 eV, which is characteristic for the intact C-Br group on the Cu(111) surface.[2,3] The XP spectrum taken after deposition at 300 K exhibits a BE of 181.9 eV for the Br $3p_{3/2}$ peak, which is assigned to Br adatoms chemisorbed on Cu(111).[2,4,5] This shift in BE indicates the dissociation of the C-Br bonds. The formation of C-Cu organometallic bonds is confirmed by the C 1s XP spectra (Fig. S1b). The C 1s XP spectrum obtained at 170 K can be fitted with two species in a 1:4 ratio,[6 7] representing the carbon atoms in C-Br groups at a BE of 284.8 eV and the other carbon atoms at a BE of 284.3 eV, respectively. The C 1s spectrum acquired at 300 K can also be fitted with two components in a 1:4 ratio: the minor peak is located at a BE of 283.1 eV and the major peak at 284.0 eV. The minor peak with lower BE is assigned to carbon bound to copper adatoms, consistent with the formation of an organometallic species.[8] Noteworthy, the major peak of the C 1s spectrum obtained at 300 K is shifted by 0.3 eV towards lower BE relative to that of the C 1s spectrum at 170 K. This shift partly results from the work function increase caused by the chemisorbed Br atoms.[3,9]

3. Chain length distribution at 300 K for two different coverages

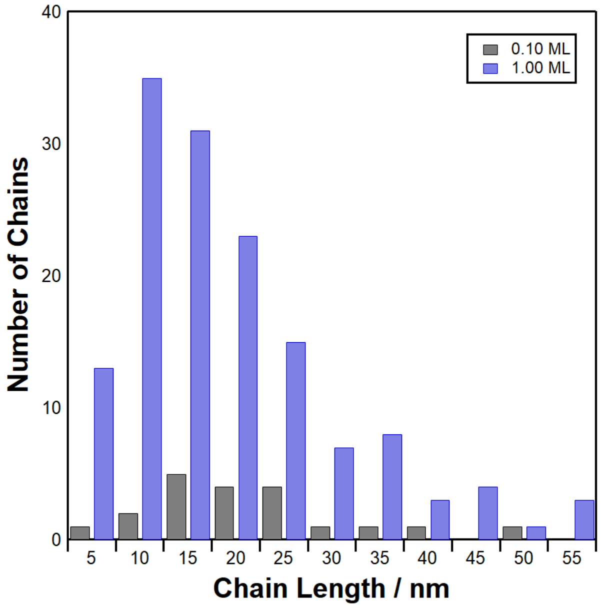

Fig. S2: Chain length distribution for the STM images in Fig. 2. The number on the vertical axis is the absolute number of chains in the image in the respective length interval. The length intervals are 5 nm wide, *i.e.*, the first interval includes all chains up to 5 nm length, while the second interval includes all chains from >5 nm up to 10 nm length.

4. Additional STM images

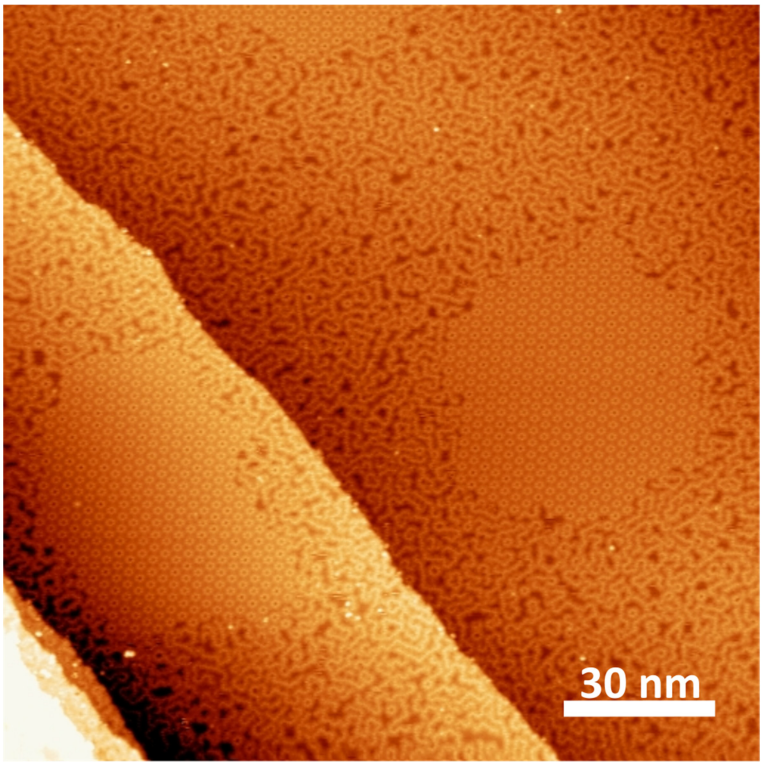

Fig. S3: STM image of the sample in Fig. 3b showing another area with different islands of cyclic hexamers. Tunneling parameters: U = -3.31 V, I = -0.11 nA.

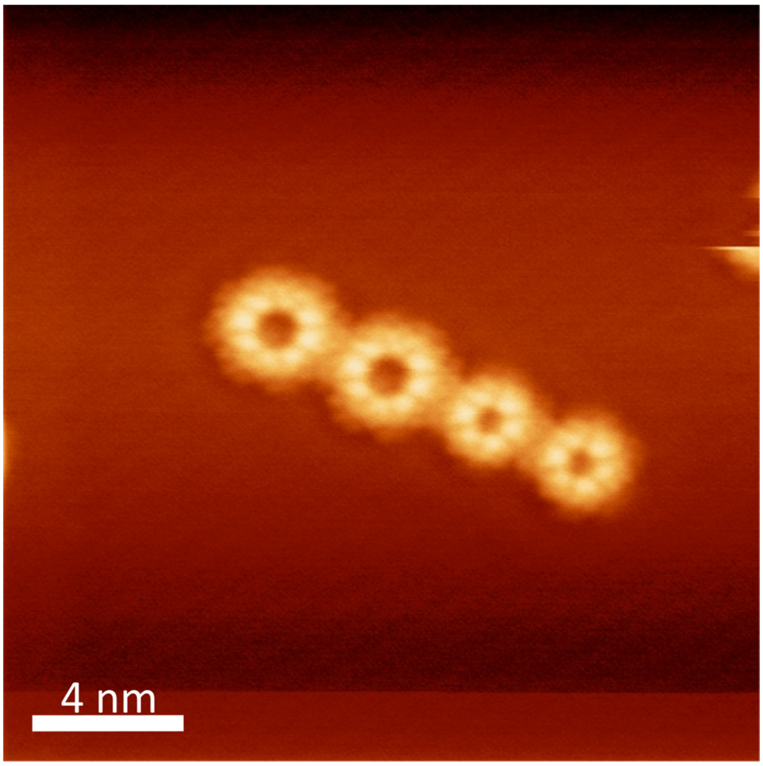

Fig. S4: STM image of the sample in Figure 3a showing two cyclic organometallic octamers (left) next to two hexamers. Tunneling parameters: *U* = -1.40 V, *I* = -0.16 nA.

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