Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supporting Information

Surface-confined [2+2] Cycloaddition Towards One-dimensional Polymers Featuring Cyclobutadiene Units

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1. Overview of phase A and B of 1 on Au(111)

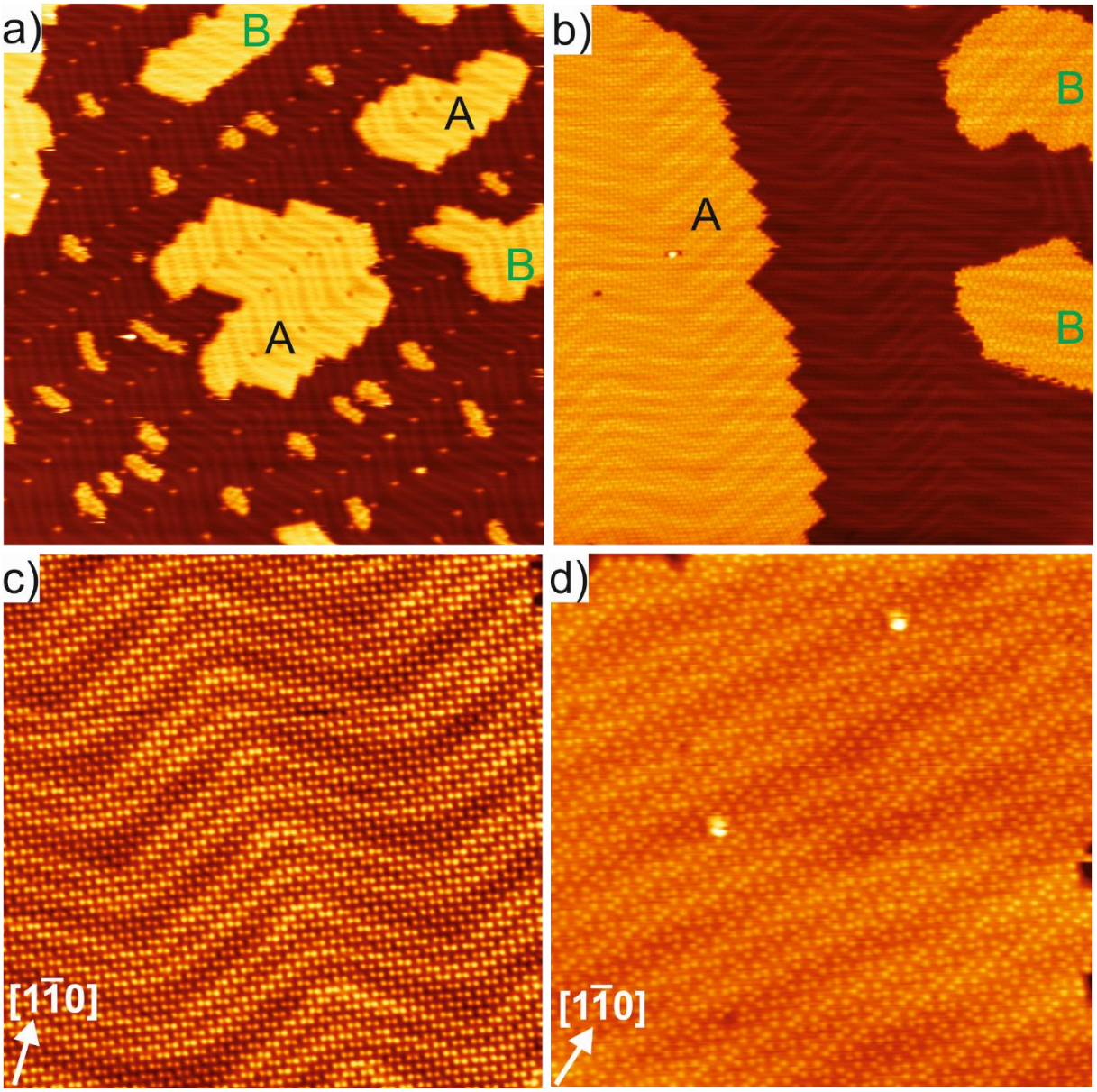


Fig. S1. **Over view STM images of phase A and B of 1 on Au(111)**. **a)**, **b)** (30 pA, -1.6 V) The molecular islands of phase A and B are present with the Au herringbone reconstruction easily visible underneath. **c)** (50 x 50 nm^2; 20 pA, -1.5 V) and **d)** (40 x 40 nm^2; 20 pA, -1.5 V) Zoom-in STM images of phase A and B, respectively.

2. Phase B of 1 on Au(111)

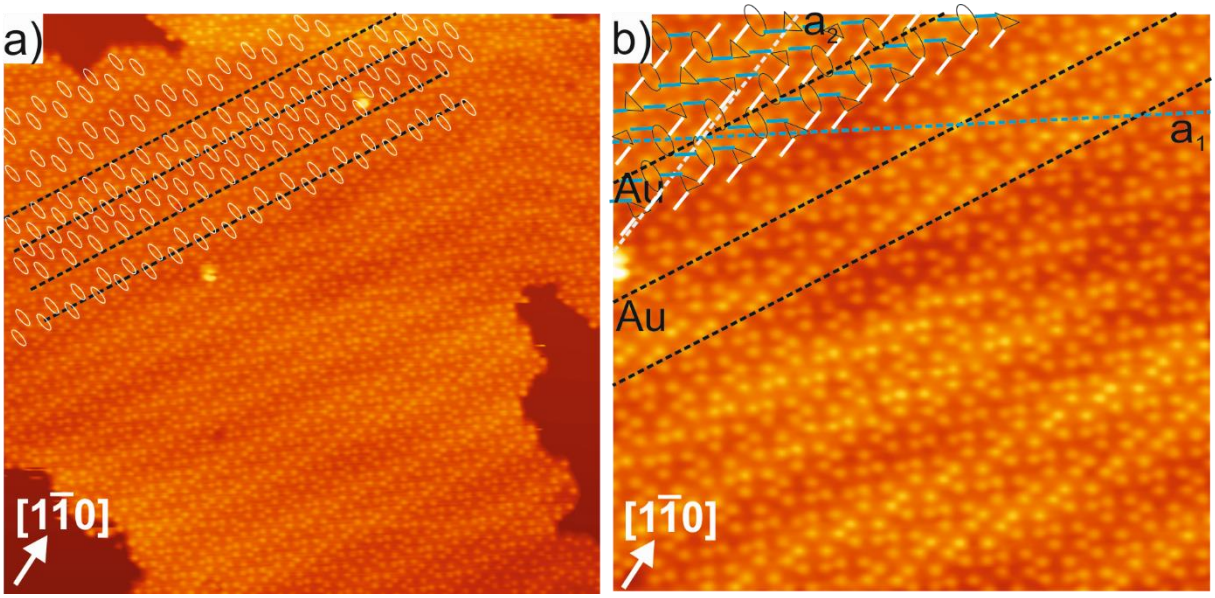
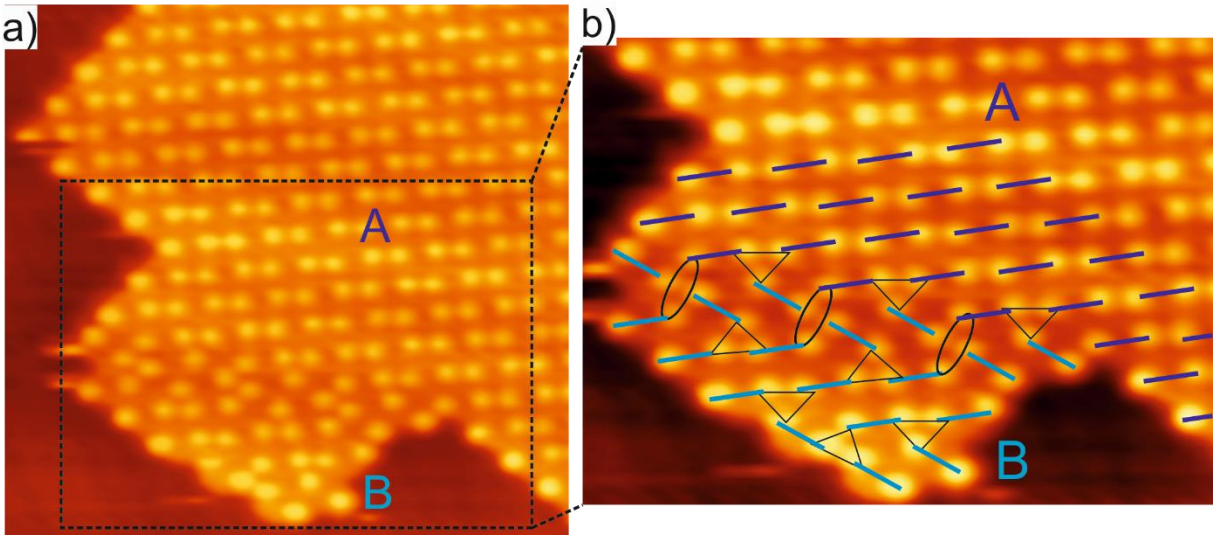


Fig. S2. **STM topographic images of phase B of 1 on Au(111)**. **a)** (50 x 50 nm^2; 20 pA, -1.5 V) STM image of **1** displays a long-range periodicity of the network. The white ellipses are labelled for the groups of four bright protrusions. Black dotted lines indicate the Au [11$\bar{2}$] direction. **b)** (25 x 25 nm^2) Detailed STM image of the island shown in a) with an overlay of the molecules oriented along directions a_1 and a_2 (blue and white dotted lines, respectively), which both draw an angle of ~22° with the Au [11$\bar{2}$] direction (black dotted lines). The triangles and ellipses indicate for the groups of three and four joint molecules, respectively, which are periodic along the [11$\bar{2}$] direction.

3. Mixture of phase A and B of 1 on Au(111)



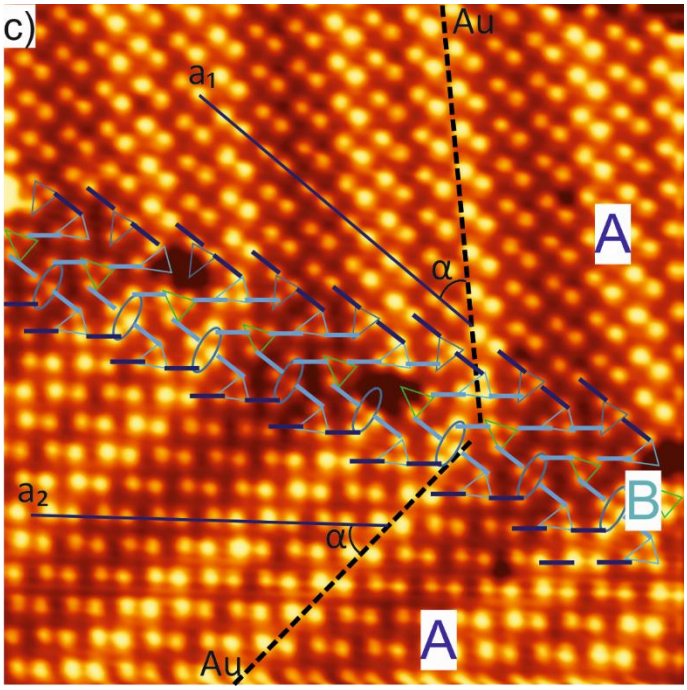
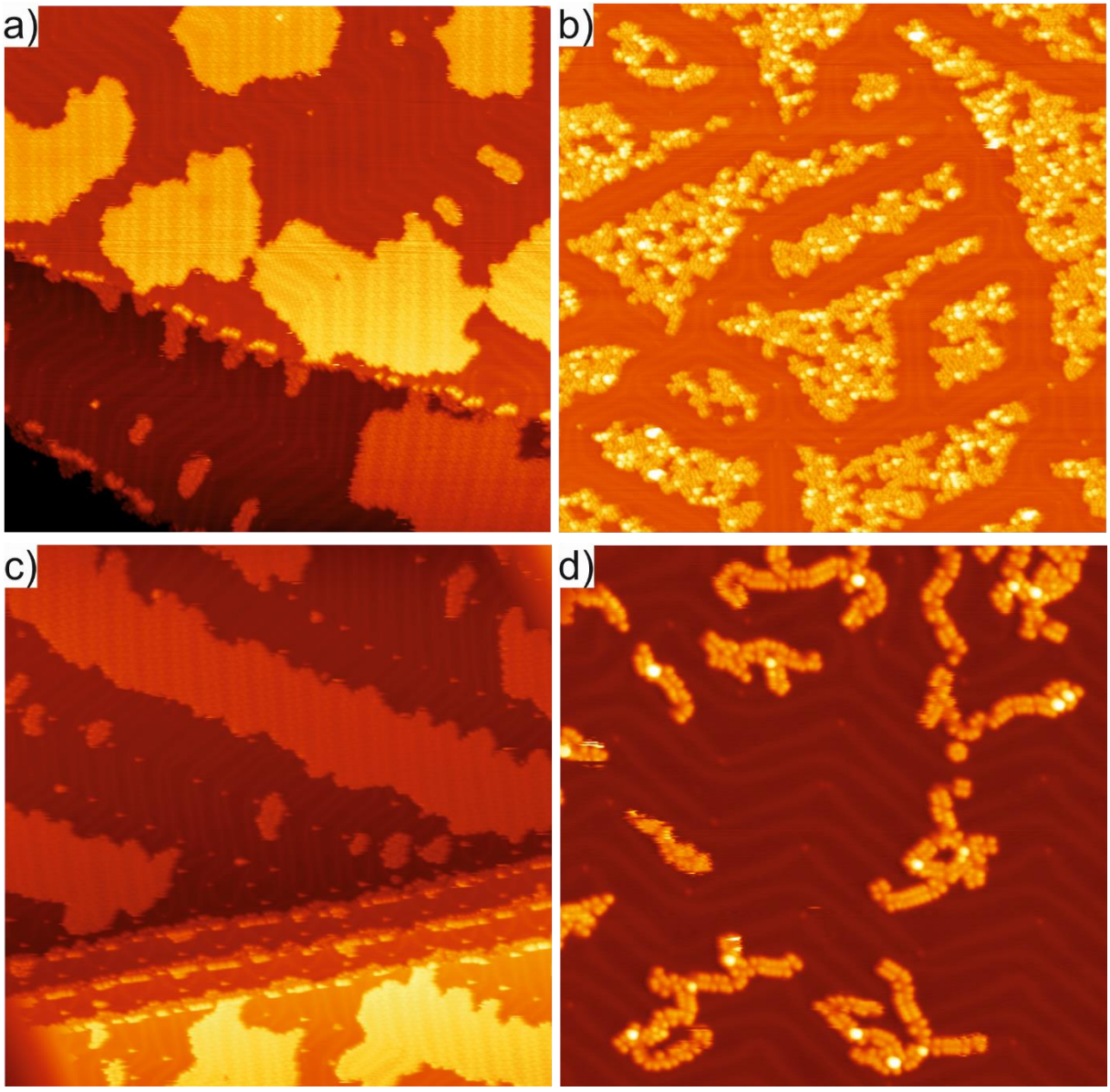


Fig. S3. **Arrangement of phase A and B of 1 on Au(111)**. **a)** (12 x 12 nm^2; 30 pA, -1.8 V) STM image showing an island made up from phase A and B. **b)** (10 x 8 nm^2) STM image of the area indicated by a dashed rectangle presented in a). Based on the size of the **1** molecule and taking into account the domain boundary between phase A and B and the domain edges, one can deduce the molecular arrangement for phase B as depicted by dark and blue lines. Here, we can also recognize the groups of 3 (triangle) or 4 (ellipse) joint molecules. From this particular example, one can generalize the molecular arrangement for phase B as shown in Fig. 2b (main text). **c)** (15 x 15 nm^2; 25 pA, -1.5 V) Boundary between phase A and B. In phase A (top right and bottom left part), the molecules indicated by dark and blue lines arrange along the directions a_1 and a_2, which include an angle α = ~ 45° with the Au herringbone [11$\bar{2}$] direction (dashed lines). In phase B (the narrow slice in the middle), the molecules are oriented parallel to a_1 and a_2 as presented in Fig. S2. The groups of three and four joint molecules are labeled by triangles and ellipses, respectively.

4. On-surface polymerization of 1 on Au(111)



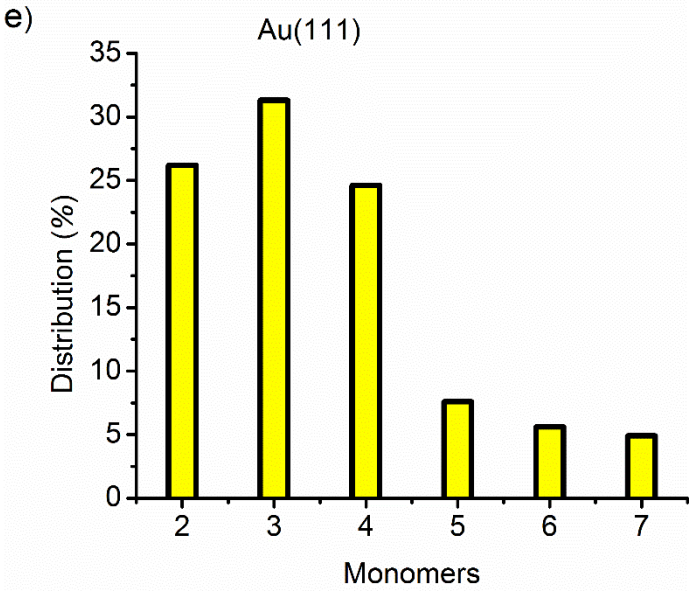
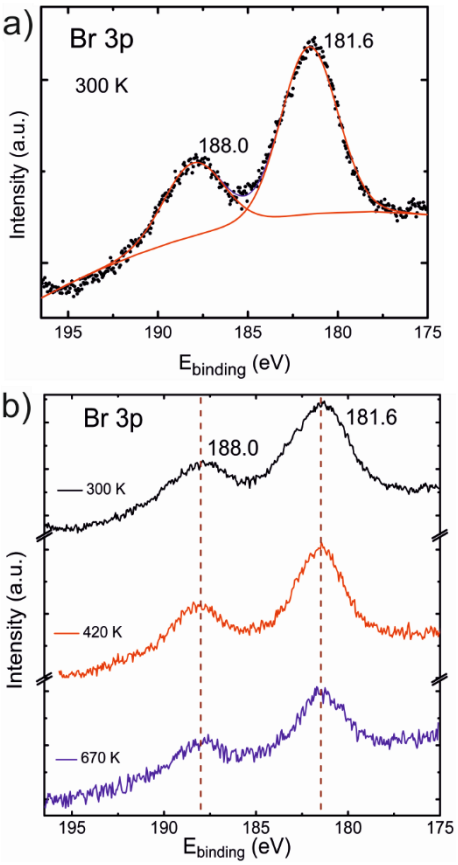


Fig. S4. **Comparison of on-surface polymerization of 1 on Au(111) without and with hydrogen treatment. a)** (100 x 100 nm^2; 20 pA, -1.8 V) The overview STM image shows molecular islands before annealing while the molecular deposition was performed with the substrate held at room temperature. **b)** (100 x 100 nm^2; 20 pA, -1.8 V) STM image of the same sample as shown in a), but after annealing at 550K without hydrogen treatment. Disordered polymer islands can be seen. The herringbone reconstruction is considerably modified. **c)** (100 x 100 nm^2; 20 pA, -1.5 V) Overview STM image showing molecular islands before annealing. **d)** (50 x 50 nm^2; 20 pA, -1.5 V) STM topography showing 1D polymer chains after dosing hydrogen gas for 2h while keeping the substrate at 450 K. In this case, the herringbone reconstruction is unaffected and no sign of split off Br atoms is visible on the surface (discussed in the main text). **e)** Statistical distribution of the number of monomers within the 1D covalently linked polymer chains.

5. XPS measurements of 1 on Cu(111)

***Fig. S5*. XPS measurements of 1 on Cu(111). a)** Br 3p core-level spectrum of DTBTBP deposited at room temperature presents two prominent peaks at 188.0 eV and 181.6 eV after fitting with a single doublet, which correspond to the two binding energies Br $3p_{1/2}$ and $3p_{3/2}$. This is assigned to the split off Br atoms chemisorbed on Cu(111). **b)** Evolution of the spectra with subsequent annealing the substrate from room temperature to 670 K. Note that the intensity of the peaks becomes less pronounced upon increasing the annealing temperature, which indicates that Br atoms gradually desorb from the substrate.



6. On-surface polymerization of 1 on Cu(111)

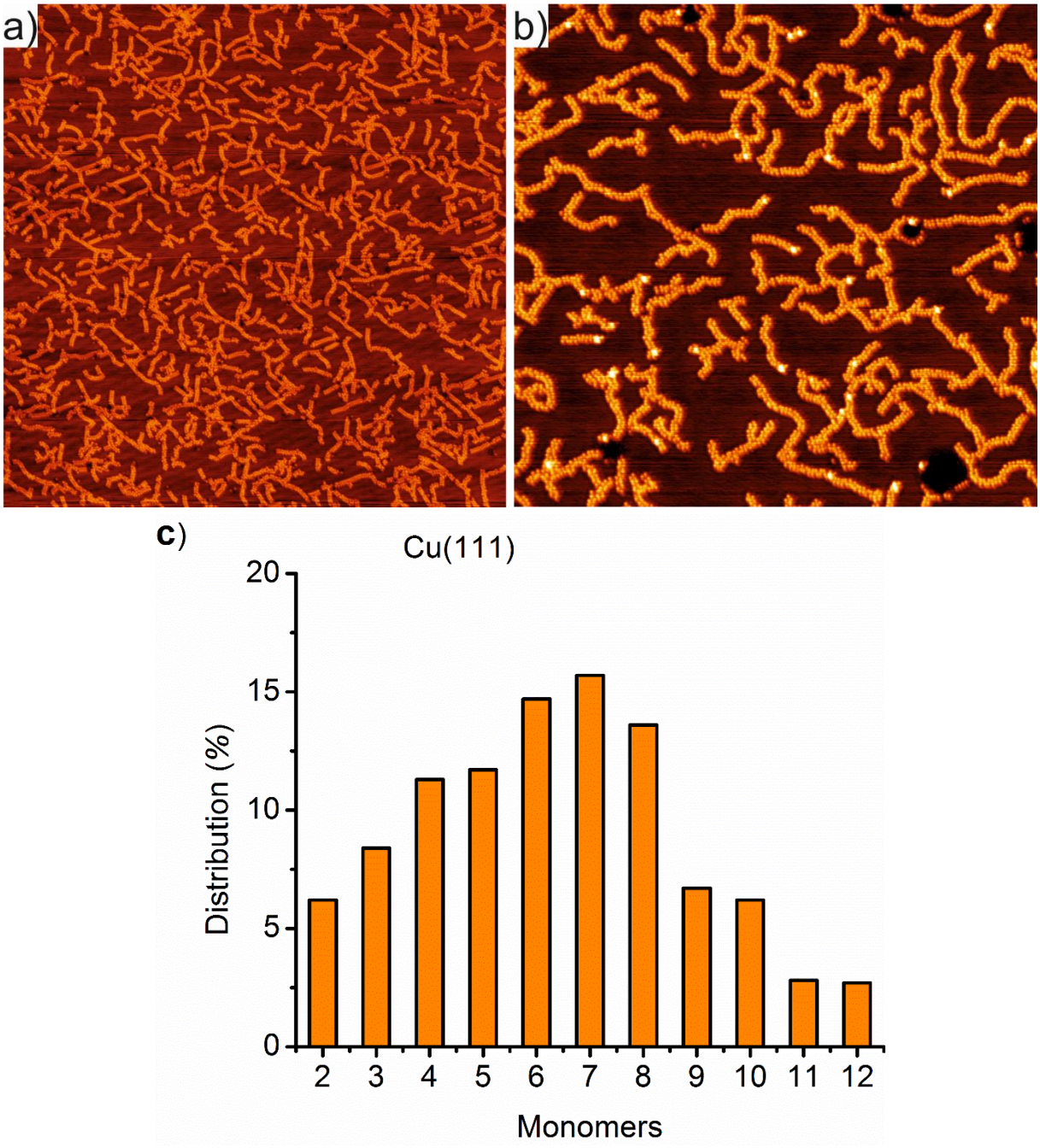


Fig. S6. **On-surface polymerization of 1 on Cu(111) upon thermal activation. a)** (180 x 180 nm^2) Large scale STM image showing 1D polymer chains with the deposition of the molecules onto Cu(111) held at room temperature. **b**) (100 x 100 nm^2) STM image of the same sample after annealing at 480 K. Obviously, the polymer chains remain stable up to high annealing temperature. The stability of the polymeric structure under thermal activation is most likely due to the C-Cu-C bridges. In all images I = 25 pA, V = -1.8 V. **c)** Statistical distribution of the number of monomers within the 1D metal-coordinated polymer chains.