Supporting information

Metalated Graphyne-Based Networks as 2D Materials: Crystallization, Topological Defects, Delocalized Electronic States and Site-Specific Doping

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Adatoms source on Au(111) and Ag(111)

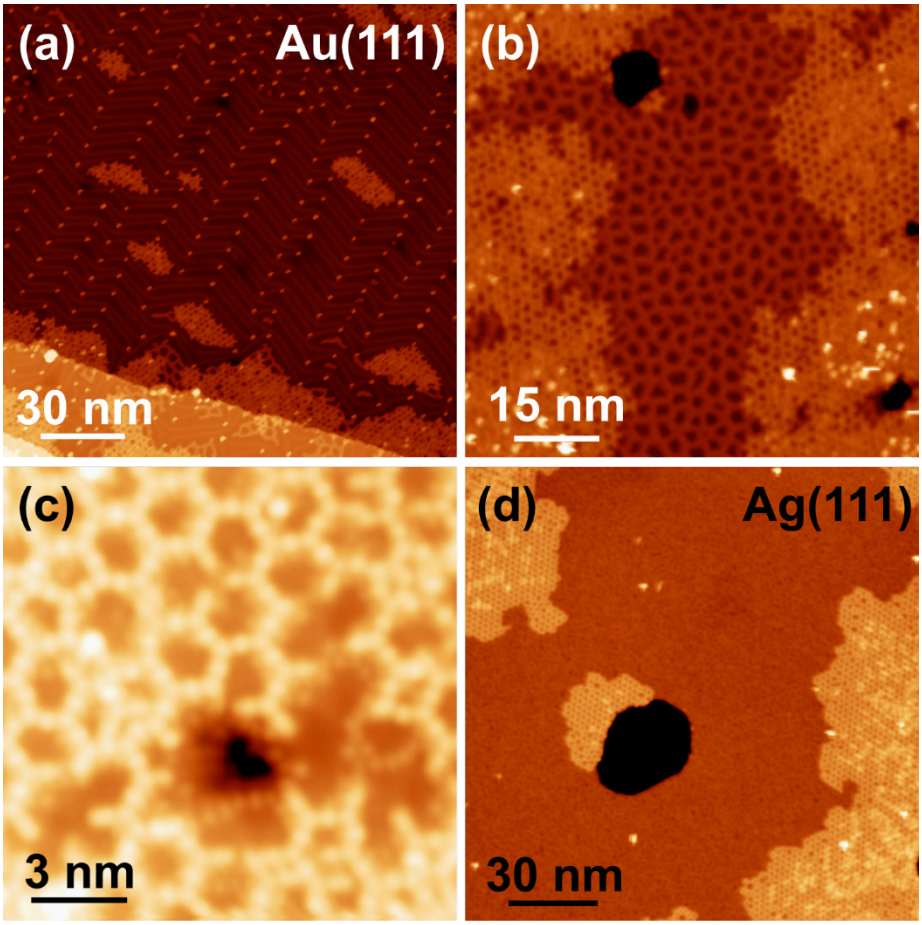

Figure S1. Extraction of metal adatoms from the surfaces. Comparison of Br-TEB on Au(111) at room temperature with (a) low coverage of 0.1 monolayers (ML) and (b) high coverage of 0.8 ML. At high molecular coverage, pits with a depth of 2.4 ± 0.1 Å are observed on the surface terraces, while there are enough natural Au adatoms present at low coverage to saturate the alkynyl radicals. (c) Zoomed-in image of a surface pit surrounded by molecules and Br atoms. (d) Pits with a depth of 2.4 ± 0.1 Å are also observed on Ag(111) with a molecular coverage of 0.4 ML at room temperature. STM parameters: (a, c, d) U = 1.0 V, I = 50 pA and (b) U = 1.0 V, I = 30 pA.

Temperature dependence of the Br-TEB-structures on Ag(111) and Au(111)

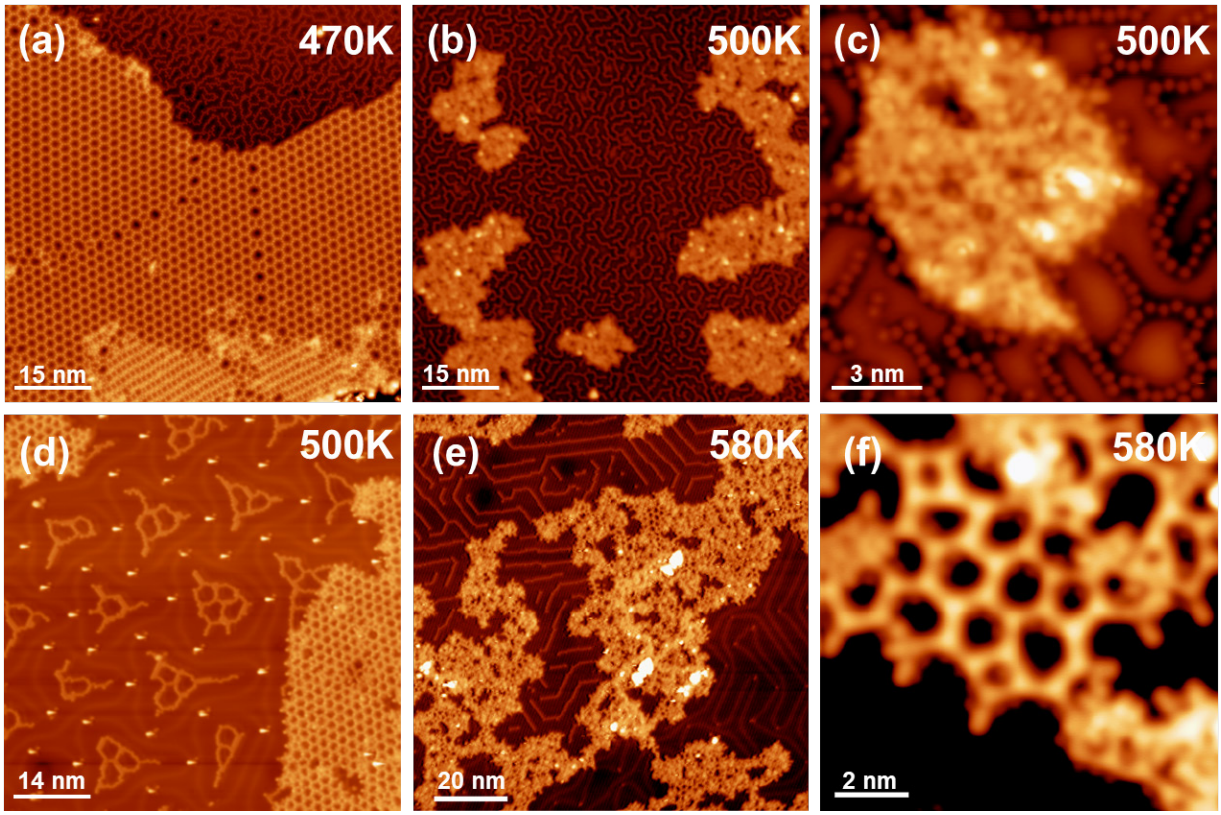

Figure S2. (a-c) Structures after subsequent annealing of the Ag-*bis*-acetylide networks on Ag(111) to (a) 470 K, (b-c) 500 K. Most of the molecules desorbed from the surface at 500 K (b), leaving some undefined structures (zoomed-in image in c). (d-f) Structures after subsequent annealing of the Au-*bis*-acetylide networks on Au(111) to (d) 500 K and (e-f) 580 K. The molecules stay on the surface at these high temperatures and form small C-C coupled covalent networks (zoomed-in image in f). STM parameters: (a) $U = 1.8$V, $I = 300$ pA, (b) $U = -1.0$V, $I = 300$ pA, (c) $U = 0.3$ V, $I = 300$ pA, (d) $U = 1.8$V, $I = 300$ pA, (e) $U = 1.0$V, $I = 50$ pA and (f) $U = 0.1$ V, $I = 300$ pA.

DFT optimized organometallic TEB networks

	TEB-Ag	**TEB-Au**
E_B **per M-C bond relative to TEB-Ag in eV**	-	-0.38
***d* (TEB-M-TEB)** in Å	12.12	12.03

Table S1. Binding energies E_B and molecule-molecule distance d calculated by PBE+D3 in gas phase.

C-C coupling close to topological defects on Ag(111)

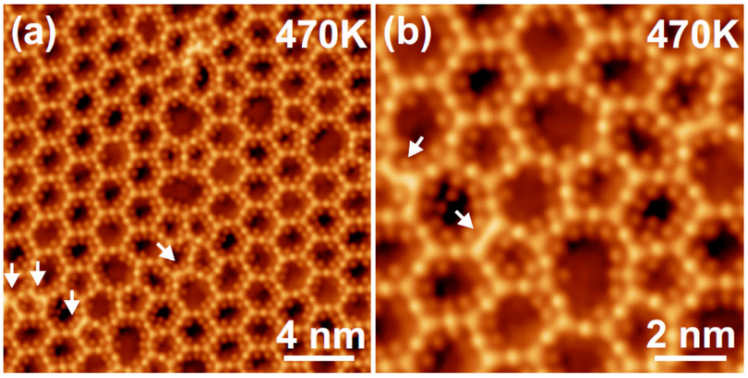

Figure S3. (a) Overview STM image of an area with C-C coupled TEB (white arrows) close to topological defects. (b) Zoomed-in STM image, where C-C bonds can be identified by their increased contrast (white arrows). STM parameter: (a) U = 0.5 V, I = 300 pA; (b) U = 0.5 V, I = 300 pA.

The orientation of the networks

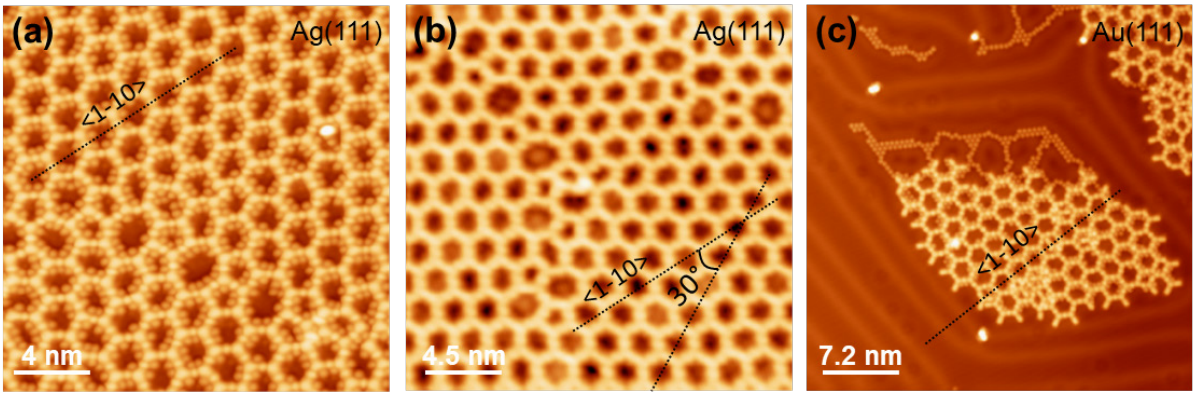

Figure S4. STM images of the metal-*bis*-acetylide networks (a-b) on Ag(111) and (c) on Au(111). On the Ag(111) surface, several rotational domains are observed. The orientation along the <1-10> directions (a) is most frequently observed, however also domains 30° to that exist (b). In contrast, on Au(111) only orientations along the <1-10> directions are found (c). This might suggest a weaker interaction of TEB with the Ag surface compared to the Au substrate. STM parameters: (a) U = 0.47 V, I = 50 pA, 420 K annealing; (b) U = 0.5 V, I = 200 pA, 420 K annealing; (c) U = 0.5 V, I = 30 pA, 470 K annealing.

Defects in Au-acetylide networks on Au(111)

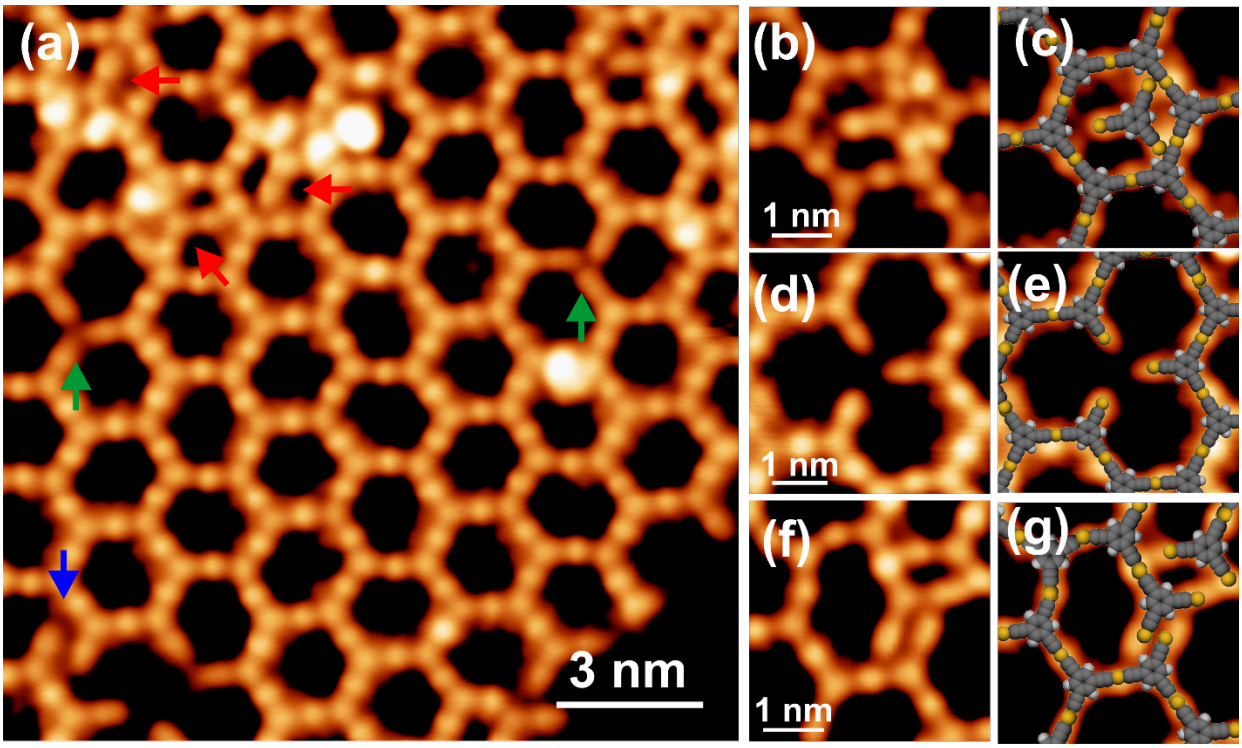

Figure S5. Analysis of defects within the Au-*bis*-acetylide networks at room temperature. (a) Overview STM image of a honeycomb Au-TEB network with different types of defects, marked with arrows in red (TEB in pore), green (TEB vacancy) and blue (parallel Au-C≡C units), respectively. Detailed STM images and corresponding tentative models for (b,c) TEB in pore, (d,e) TEB vacancy and (f,g) parallel Au-C≡C units. STM parameters: (a) U = 1.0 V, I = 50 pA; (b) U = 0.5 V, I = 300 pA; (d) U = 0.3 V, I = 50 pA and (f) U = 0.5 V, I = 180 pA.