Supporting Information

Diastereoselective Ullmann Coupling to Bishelicenes by Surface Topochemistry

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Experimental and Theoretical Details

The STM images were acquired using a variable temperature-STM (Omicron Nanotechnology) with a tip made from tungsten and fabricated by electrochemical etching. The sample could be cooled down to about 50 K by using a liquid He continuous flow cryostat. The microscope stage remained at room temperature during the measurements.

XPS measurements (Specs PHOIBOS 100 electron analyzer) were conducted in normal-emission using non-monochromatic Al Kα X-rays. The binding energy scale was calibrated with the Au 4f7/2 (84.0 eV) peak and the Fermi level (0.0 eV) of the Au crystal. The intensities were normalized with respect to the Au 4f7/2 signal. The background obtained on clean Au(111) was subtracted from the spectra.

Calculations were performed with AMBER-Force fields on a four-layer Au(111) slab using periodic boundary conditions. The gold atoms of the surface were kept fixed, but no constraint was applied to the molecules. For each configuration of Au-bis[7]H intermediates, 21 different initial starting-positions were considered. The calculations were performed for *(M,P)* and *(P,P)*-Au-bis[7]H. As test the enantiomers *(M,M)*-Au-bis[7]H and *(P,P)*-Au-di[7]H were compared, leading to identical values within an error of ± 0.5 kcal/mol.

Table S1. Comparison of structural parameter of the ordered bishelicene phases on Cu(111) and Au(111).

Structure	# of atoms per unit cell	# of molecule per unit cell	a [Å]	matrix notation	area / molecule [Å^2]
diamond Au	54	2	2.88	(6 –2, 3 8)	193.95
diamond Cu	68	2	2.55	(7 –1, 5 9)	191.47
zigzag Au	89	2	2.88	(6 –1, 5 14)	319.65
zigzag Cu	110	2	2.55	(7 –1, 5 15)	309.72
line Au	27	1	2.88	–	193.95

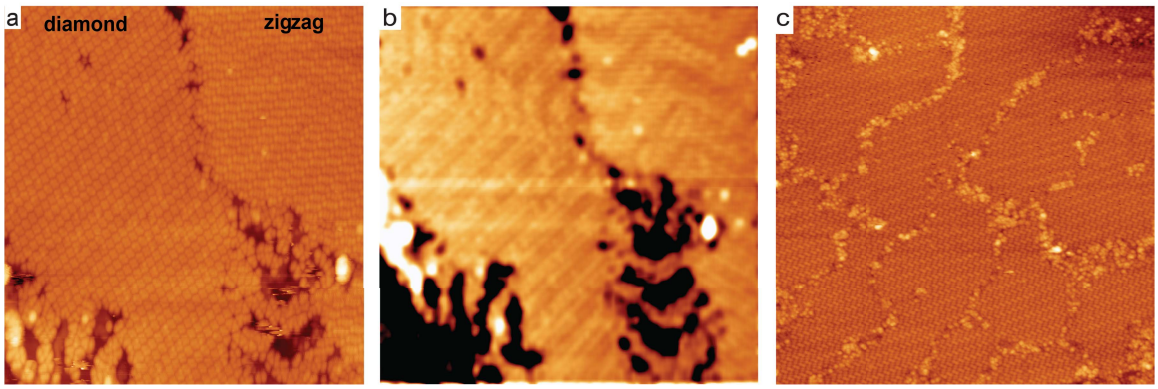

Figure S1. (a) Large scale STM images showing coexistence of the diamond and the zigzag phase at a coverage of 85% of the saturated monolayer (a,b; 65.5 nm × 65.5 nm, 30 pA, –3.55 V) (b) Same as (a), but after Gaussian filtering with a radius 2.9 nm and contrast enhancement. (c) Large area of the zigzag structure with several, identically aligned domains (c; 121 nm × 121 nm, 30 pA, 3.4 V).

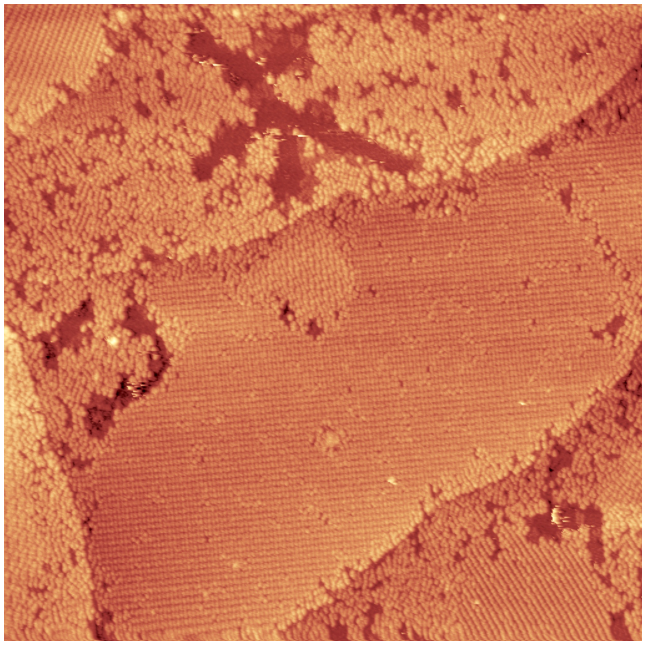

Figure S2. Large scale STM image (150 nm × 150 nm, 26pA, –2.6V) of bis[7]H on Cu(111) close to monolayer coverage after Ullman coupling. The area is dominated by the line structure and only small areas of the zigzag structure are observed. Disordered molecular areas and dark areas contain also smaller objects, which are attributed to Br atoms released due to the C-C coupling reaction.

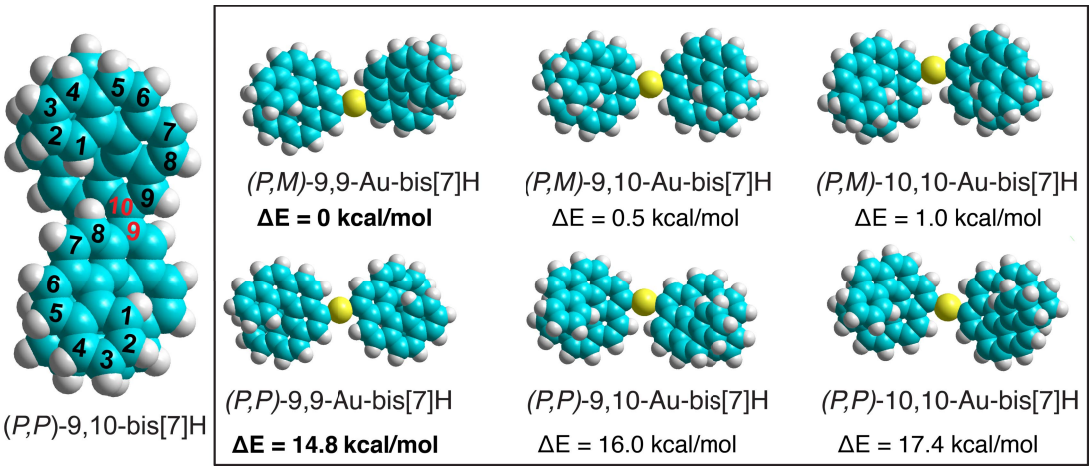

Figure S3. Comparison of organo-metallic heptahelicene Au intermediates of Ullmann coupling on a gold surface by AMBER force field molecular modeling. Results for different intermediate atropisomers, defined by the position of the C-Au-C single bond counted from the *distal* side towards the *proximal* side down at the surface, are presented. The counting of rim carbon atoms for the *(P,P)*-9,10-bis[7]H atropisomer is shown to the left of the box. Heterochiral *meso-(M,P)*-intermediates are generally favored over their homochiral counterparts. The given energy values (ΔE) are the relative energy with respect to the best (minimum) energy configuration, which was obtained for *(P,M)*-9,9-Au-bis[7]H (ΔE = 0.0 kcal/mol).