Electronic Supplementary Information

Spontaneous separation of on-surface synthesized tris-helicenes into two-dimensional homochiral domains

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Detailed Methods

The experiments were performed in ultra-high vacuum on Au(111) and Cu(111) single crystals (MaTecK GmbH., 99.999% purity, < 0.1° miscut) prepared by cycles of Ar^+ ion sputtering and annealing. STM images were recorded with a PtIr (90% Pt) tip in constant current mode (Specs Aarhus 150). XP spectra were obtained in normal emission using Al Kα X-rays. The binding energy scale was calibrated using the $Cu2p_{3/2}$ (932.7 eV) and $Au4f_{7/2}$ (84.0 eV) core levels. Background spectra obtained on clean samples were subtracted. The molecules were thermally sublimed from a quartz crucible kept at 100 °C.

The structures were relaxed on Au(111) and Cu(111) slabs (4 layers) using molecular mechanics (Hyperchem 8.0, Amber force field). The frontier orbitals (cutoff 0.001 $e/Å^3$) were calculated using extended Hückel calculations in Hyperchem. To compare with the STM images, the highest 2*n* occupied orbitals were considered. *n* corresponds to the number of [4]helicene units.

Table S1 Imaging parameters. The images were obtained at 120 K because on Au(111) the molecules were highly mobile at room temperature. Also the organometallic complexes on Cu(111) were highly mobile.

Figure	Bias voltage (mV)	Tunnel current setpoint (pA)
1b, *star*-tris[4]H	15	60
1c, *anchor*-tris[4]H	15	60
1d, *anti*-bis[4]H	15	180
1e, *syn*-bis[4]H	15	600
2a	7	190
2b	5	140
2c	1	190
4a, including insets	110	360
4b	575	40

Table S2 Abundance of defective *vs.* intact molecules. Since the organic species exist as dimers and trimers and the organometallic species as trimers and tetramers, the abundances are provided with respect to monomer units, *e.g.* in trimers intact and impurity arms are counted.

Organic species on Au(111) (ann. at 473 K)		
	Count (#)	**Abundance (%)**
total	2578	100
total intact	2159	83.7 ± 0.7
total impurities	419	16.3 ± 0.7
Organometallic species on Cu(111) (ann. at 356 K)		
	Count (#)	**Abundance (%)**
total	630	100
total intact	611	97.0 ± 0.7
total impurities	19	3.0 ± 0.7

Table S3 Abundance of intact organic species formed on Au(111) by annealing to 473 K). An area of 2500 nm^2 was evaluated. Note that the amount of self-assembled domains of *star*-tris[4]H is hard to quantify because of the large domains. A rough estimate yields that 10 to 30% of the surface of Au(111) is covered with self-assembled *star*-tris[4]H. The species affected by this are designed with "*". Abbreviations: A: abundance; SA: self-assembled; non-SA: non self-assembled.

	Count (#)	**A. (%)**	**A. (%)**	**A. (%)**	**A. (%)**
total molecules	567	100			
total bis[4]H	307	54 ± 2	100		
syn-bis[4]H	135		44 ± 3	100	
(*P, P*)-*syn*-bis[4]H	84			62 ± 4	
(*M, M*)-*syn*-bis[4]H	51			38 ± 4	
anti-bis[4]H	172		56 ± 3		
total tris[4]H*	260	46 ± 2	100		
anchor-tris[4]H	113		43 ± 3		
star-tris[4]H*	147		57 ± 3	100	
(*P, P, P*)-*star*-tris[4]H	73			50 ± 4	100
SA (*P, P, P*)-*star*-tris[4]H*	34				56 ± 6
non-SA (*P, P, P*)-*star*-tris[4]H	27				44 ± 6
(*M, M, M*)-*star*-tris[4]H	74			50 ± 4	100
SA (*M, M, M*)-*star*-tris[4]H*	39				45 ± 5
non-SA (*M, M, M*)-*star*-tris[4]H	47				55 ± 5

Table S4 Abundance of intact organometallic species formed on Cu(111) by annealing to 356 K.

	Count (#)	**Abundance (%)**
Total	159	100
Cu-tris[4]H	25	16 ± 3
Cu-tetra[4]H	134	84 ± 3

Table S5 Abundance of intact organic species formed on Cu(111) by annealing to 443 K.

	Count (#)	Abundance (%)	Abundance (%)
total molecules	280	100	
total bis[4]H	267	95 ± 1	100
syn-bis[4]H	183		69 ± 3
anti-bis[4]H	84		31 ± 3
total tris[4]H	13	5 ± 1	100
star-tris[4]H	6		46 ± 14
anchor-tris[4]H	7		54 ± 14

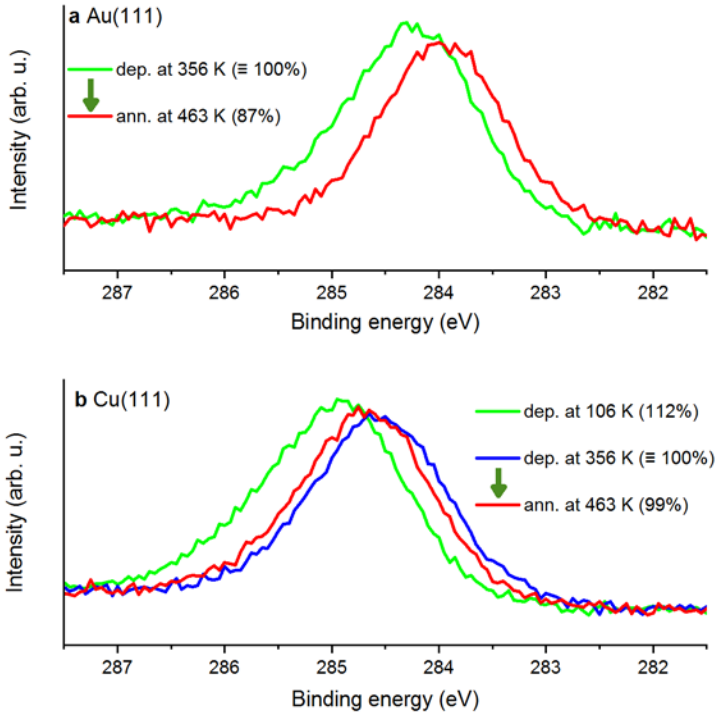

Figure S1: C 1s XP spectra of Figure 3 shown without offset. The spectra are normalized with respect to the intensity of the substrate Au $4f_{7/2}$ and Cu $2p_{5/2}$ substrate signal. Green arrows indicate preparations which were derived from each other. a) The minor reduction (13%) of the C 1s signal on Au(111) shows that the favoured formation of *star*-tris[4]H with respect to *anchor*-tris[4]H cannot be explained by to more facile desorption of *anchor*-tris[4]H. b) The C1s spectra obtained after deposition at 356 K on Cu(111)

exhibits more spectral weight at lower binding energy, supporting the presence of organometallic C-Cu bonds.

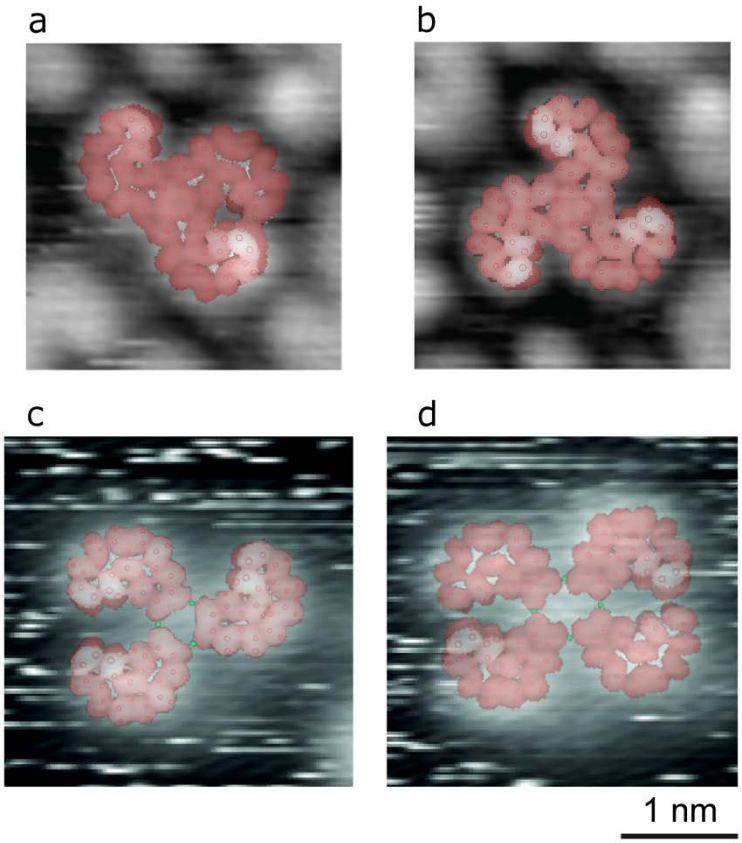

Figure S2: Overlay of the EHT models (shaded red) onto STM images of (a) *anchor*-tris[4]H and (b) *star*-tris[4]H on Au(111) (from Figure 1) and of (c) Cu-tris[4]H and (d) Cu-tetra[4]H on Cu(111) (from Figure 4a). The positions of the atoms are highlighted by empty (C and H) and green-filled (Cu) circles. Anchor-tris[4]H appears significantly smaller than Cu-tris[4]H, consistent with the presence of organometallic C-Cu bonds in Cu-tris[4]H. (c,d) Note that the EHT simulations fail to reproduce the contrast of organometallic complexes. 3 and 4 adatoms were used to simulate Cu-tris[4]H and Cu-tetra[4]H, respectively. The presence of additional Cu adatoms in the centers cannot be excluded. The simulated C-Cu bond lengths are 1.99 ± 0.01 Å for all C-Cu bonds in Cu-tris[4]H and Cu-tetra[4]H. These are typical values for organometallic bonds. (a-d) The apparent lengths of the molecules (defined by the cutoff of the electron density in EHT) is reported in Table S6.

Table S6 Apparent lengths of the molecules shown in Figure S2. Note that Cu-tris[4]H is significantly longer than *anchor*-tris[4]H which has the same shape.

Figure	Species	Length (nm)
a	*anchor*-tris[4]H	1.79
b	*star*-tris[4]H	1.64
c	Cu-tris[4]H	2.02
d	Cu-tetra[4]H	2.14