Electronic Supplementary Information

Surface-Assisted Diastereoselective Ullmann Coupling to bishelicenes

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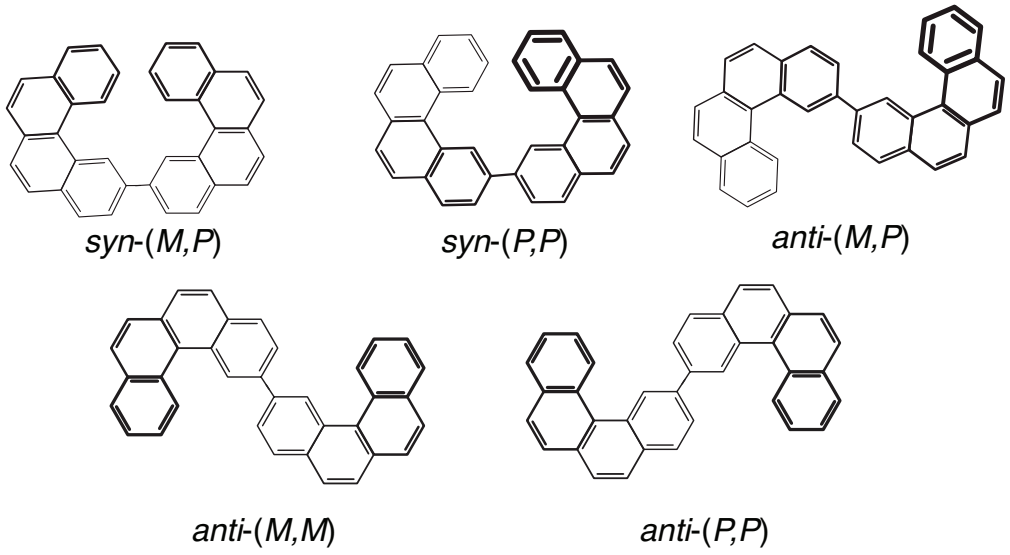
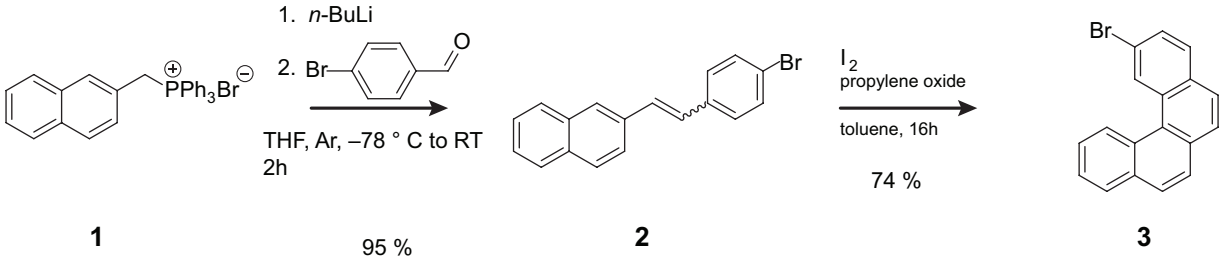


Scheme S1. Nomenclature of bishelicenes

Synthesis of 2-Br-[4]helicene

2-Br-[4]helicene[1,2] has been prepared according to a modified procedure described in the literature.[2]



1 95 % **2** **3**

*Synthesis of 2-(4-bromostyryl)naphthalene **2***

To a solution of phosphonium salt **1** (4.00 g, 8.28 mmol, 1 eq) in dry THF (80 mL) *n*-BuLi (1.6 M in hexane) (5.43 mL, 8.69 mmol, 1.05 eq) was added dropwise under argon at -78 °C in a Schlenk tube. After 15 min the mixture was allowed to reach the room temperature for 30 min, and then it was cooled back down to –78 °C to add *p*-Br-benzaldehyde (1.53 g, 8.28 mmol, 1 eq). The colour of the mixture changed from red to yellow and after 30 min it was allowed to reach the room temperature under stirring.

After another 30 min the mixture was filtered through a celite pad and the solvent evaporated under reduced pressure. The yellow crude oil was purified by chromatography over silica gel column (petroleum ether/DCM, 9/1, Rf = 0.43). 2.43 g (95 % yield) of **2** (as *cis*/*trans* mixture) were obtained as a white powder.

The analytical data for **2** were in agreement with those already published.[2]

*Synthesis of 2-bromobenzo[c]phenanthrene **3***

Stilbene **2** (0.6 g, 1.94 mmol, 1 eq) and iodine (0.49 g, 1.94 mmol, 1 eq) were dissolved in toluene (650 mL). The solution was degassed for 15 min, and then propylene oxide (6.79 mL, 97 mmol, 50 eq) was added.

The mixture thus obtained was irradiated under stirring for 16 h with a Hg lamp (150 W). The procedure was repeated several times (1.72 g of stilbene). After evaporation of toluene, the crude was purified by chromatography over silica gel column (petroleum ether/DCM, 9/1, Rf = 0.45). 1.26 g (74 % yield) of **3** were obtained as a light yellow powder.

The analytical data for **3** were in agreement with those already published.[2]

Inversion barrier of [4]helicene

Table S1. Theoretical inversion barriers of [4]helicene, as calculated here and from the literature.

B3LYP/6-31G*	B3LYP/ 6-311+G(2df,pd)	BLYP
4,37 Kcal/mol	3,87 Kcal/mol	3,5 Kcal/mol [3]

Overview STM image

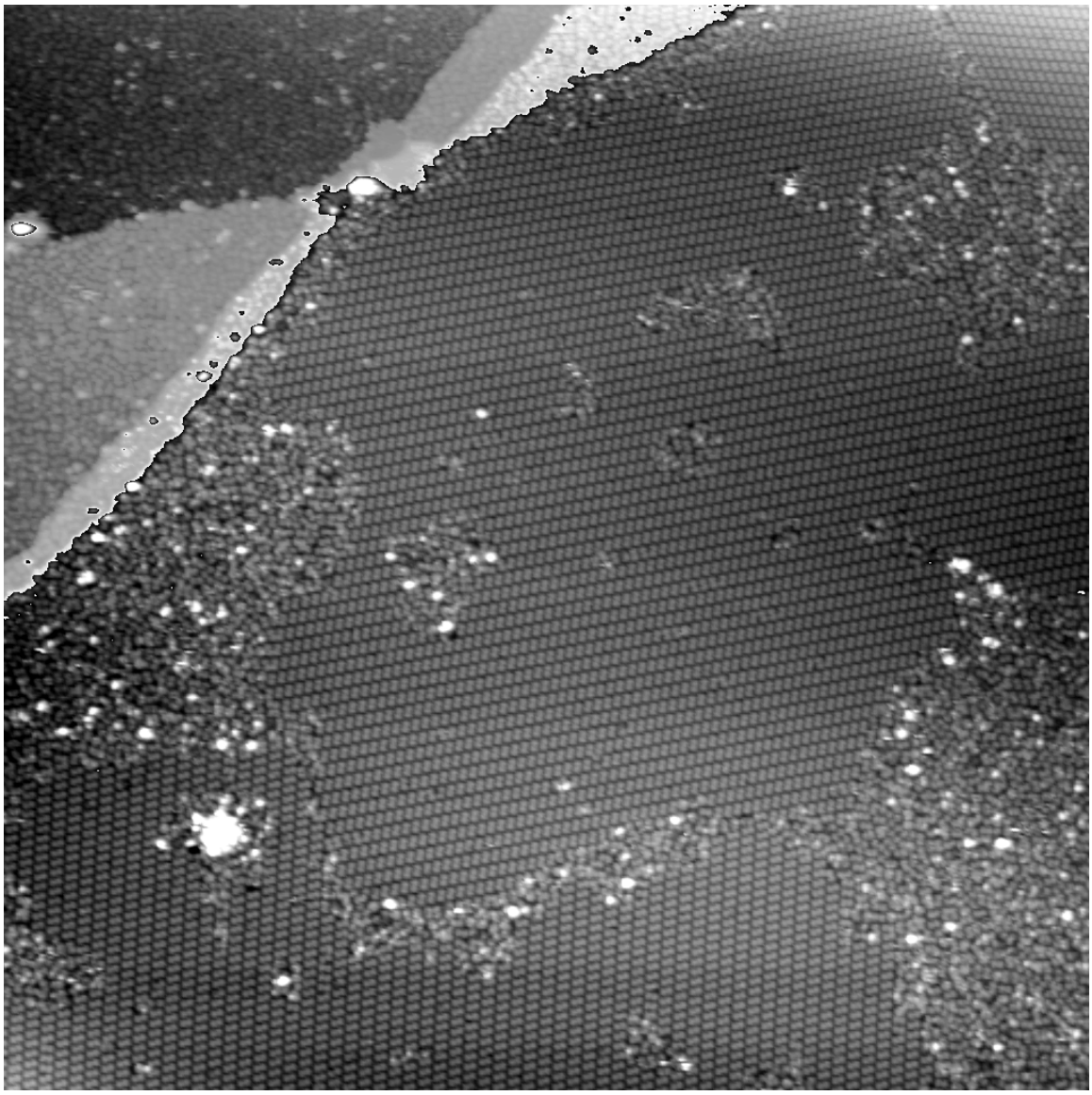


Figure S1. Overview STM image obtained after sublimation of 1 on Cu(100) and annealing to 463 K (150 nm × 150 nm, U = 1.2 V, I = 30 pA, T = 295 K). The image was obtained across step edges, the colour scale is modified for visibility. ~60% of the surface is covered with self-assembled domains of *trans*-(*P,P*)-**2** and *trans*-(*M,M*)-**2.** The images shown in Fig. 2a and Fig. 3 were recorded close to the upper right corner of the overview.

Theoretical Modeling

The modeling was performed using molecular mechanics (Amber force field) in Hyperchem 8.0 including a Cu(100) slab (4 layers). The frontier orbitals (cutoff $0.0004\ e/\text{Å}^3$) were calculated using extended Hückel theory in Hyperchem. To compare with the STM images (positive bias: tunneling into unoccupied states of the sample) the LUMO, LUMO+1 and LUMO+2 were taken into consideration.

Table S2. Length of the molecule (*i.e.* distance between the two C atoms on opposite sides) calculated for homo- and heterochiral *trans*- and *cis*-dimers of the organic species (C-C bond formed) and organometallic intermediates (C-Cu-C bond). The molecular mechanics simulations were performed on a four-layer Cu(100) slab.

Organic species	**Length (Å)**		**Organometallic species**	**Length (Å)**
anti-(*P*,*M*)-**2**	13.7		*anti*-(*P*,*M*) Cu-dimer	15.7
anti-(*M*,*M*)-**2**	13.7		*anti*-(*M*,*M*) Cu-dimer	15.8
syn-(*P*,*M*)-**2**	11.3		*syn*-(*P*,*M*) Cu-dimer	13.7
syn-(*M*,*M*)-**2**	11.4		*syn*-(*M*,*M*) Cu-dimer	13.6

XPS of debromation on O/Cu(100)

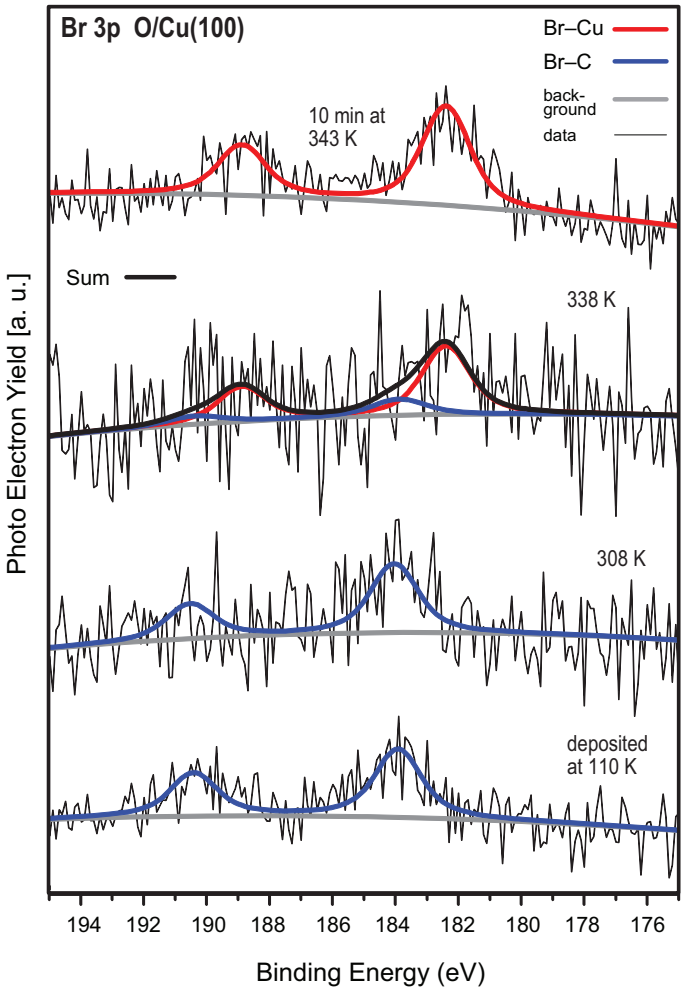


Figure S2. Br3p XP spectra of ~1 monolayer of **1** on deposited oxygen reconstructed Cu(100) kept at 110 K. The background of the clean sample is subtracted. The upshift of the $Br3p_{3/2}$ core level from ~184.0 eV (blue fits) to ~182.4 eV (red fits) occurs at temperatures between 308 K and 338 K.

2,2'-Bishelicene synthesis on O/Cu(100)

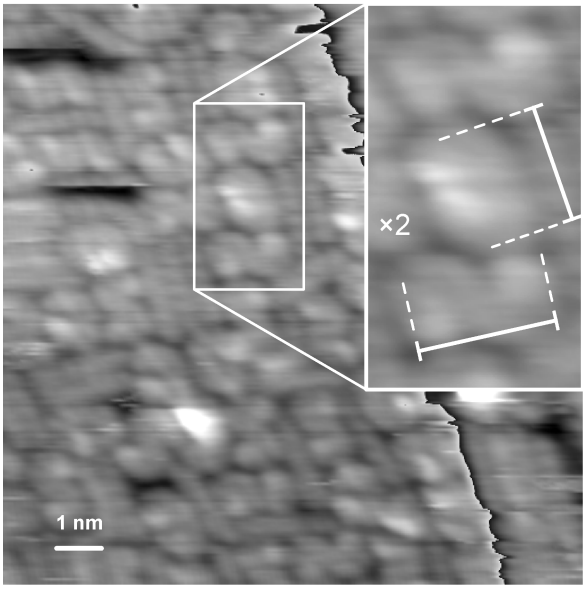


Figure S3. STM image (12.74 × 12.74 nm^2, U = 1.5 V, I = 10 pA, T = 130 K) obtained after sublimation of **1** on oxygen reconstructed Cu(100) and annealing to 463 K. The image was obtained across a step edge; the color scale was modified for clarity. The *trans*- and *cis*-bishelicenes have apparent lengths of 16.5 ± 0.6 Å and 15.5 ± 0.5 Å, respectively. The principle method of determining the length is indicated in the inset.

References

1 R. H. Martin, J. Moriau and N. Defay, *Tetrahedron*, 1974, **30**, 179–185.
2 M. A. Brooks and L. T. Scott, *J. Am. Chem. Soc.*, 1999, **121**, 5444–5449.
3 S. Grimme and S. D. Peyerimhoff, *Chem. Phys.*, 1996, **204**, 411–417.