# Supporting Information

## Experimental Procedures

**General Information:**

All reagents and chemicals from commercial sources were used without further purification. Solvents were dried and purified using standard techniques. Column chromatography was performed with analytical-grade solvents using Aldrich silica gel (technical grade, pore size 60 Å, 230-400 mesh particle size). Flexible plates ALUGRAM® Xtra SIL G UV254 from MACHEREY-NAGEL were used for TLC. Compounds were detected by UV irradiation (Bioblock Scientific) or staining with iodine, unless otherwise stated. NMR spectra were recorded with a Bruker AVANCE III 300 ($^{1}$H, 300 MHz and $^{13}$C, 76 MHz). Chemical shifts are given in ppm relative to tetramethylsilane TMS and coupling constants *J* in Hz. Residual non-deuterated solvent was used as an internal standard.

**Synthesis:**

***(rac)-2-bromo-hexahelicene (2-Br-[6]H)***


2-Br-[6]H was synthesized in 6 steps from 2-bromomethylnaphthalene according to a described procedure (reference 27 of main manuscript). After purification by chromatography over silica gel column (petroleum ether/DCM, 9/1, Rf = 0.47). 410 mg (79 % yield) of (*rac)*-Br[6]H were obtained as a light-yellow powder.

$^{1}$H NMR (300 MHz, Chloroform-*d*) δ 8.06 – 8.00 (m, 3H), 8.00 – 7.92 (m, 4H), 7.91 – 7.84 (m, 2H), 7.74 (d, *J* = 1.9 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.36 – 7.27 (m, 2H), 6.73 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H).

MALDI-TOF = 406.0

The spectral data for this compound match those reported in the literature.

## Results and Discussion

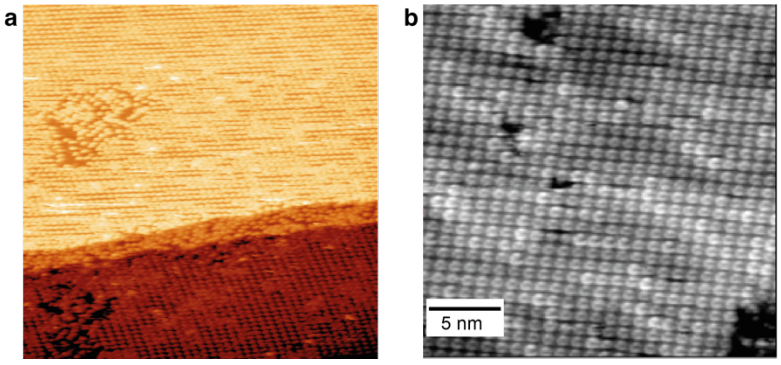


**Figure S1.** STM images of a monolayer of Br[6]H on Au(111). a) Overview image (60 nm × 60 nm, 1960 mV, 50 pA, T = 130 K) showing rotational domains on different terraces. Rows of molecules are oriented along the high-symmetry directions of the Au(111) substrate. b) STM image (25 nm × 25 nm, 800 mV, 20 pA) taken at higher magnification. As the absolute handedness of molecules can not be revealed unambiguously, no conclusions of conglomerate or racemate 2D crystallization are possible.

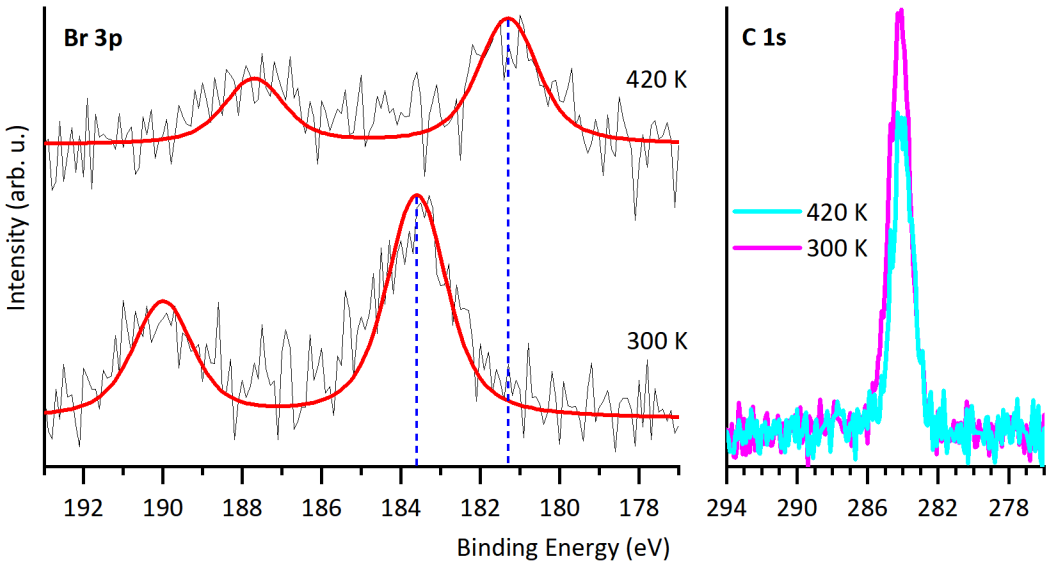


**Figure S2.** X-ray photoelectron spectra of the Br 3p and C 1s energy regions of Br[6]H on Au(111) after deposition with the crystal kept at 300 K and 420 K. The background signal of the clean Au(111) surface has been subtracted. For intensity comparison of XP-signals at different deposition temperatures spectra were normalized to their corresponding Au $4f^{7/2}$ peak area. Bromine 3p spectra and their fits are displayed with an offset in intensity.

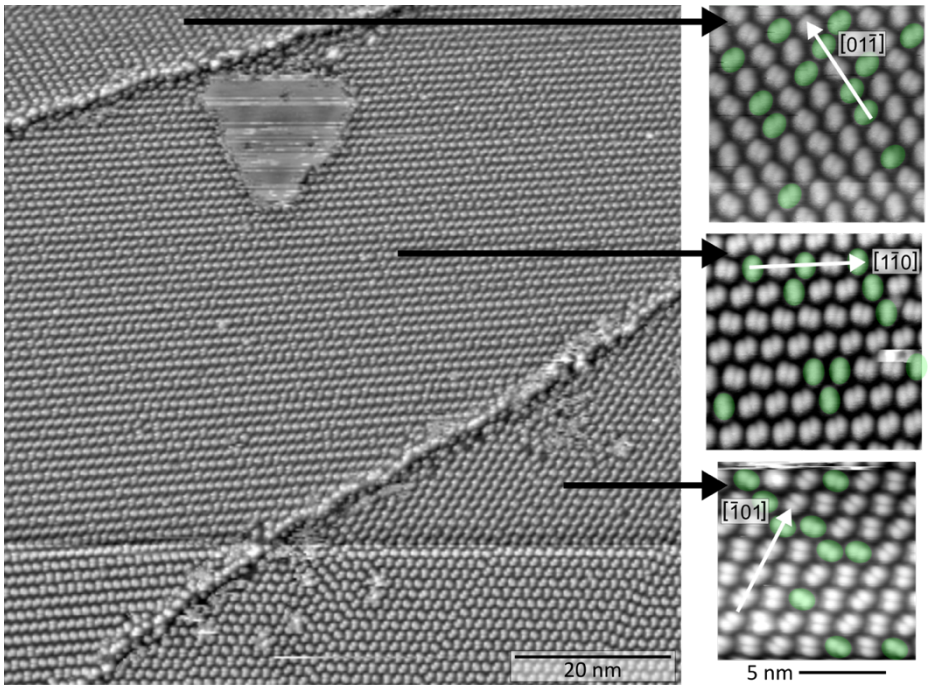


**Figure S3.** Overview STM image (left, U = 2.83 V, I = 0.06 nA, T = 120 K) of the bis[6]H self-assembly on Au(111) at full monolayer coverage. The image was flattened by subtraction of its own Gaussian filter (folding of the steps). Three flat terraces are separated by monoatomic steps and accommodate different rotational domains. Respective STM images on the right (top: U = 1.96 V, I = 0.06 nA middle: U = 1.96 V, I = 0.05 nA, bottom: U = 2.36 V, I = 0.1 nA, all T = 120 K) of these domains. White arrows indicate the high symmetry directions of the substrate. Green ellipses mark a minority of molecules with divergent azimuthal orientation.

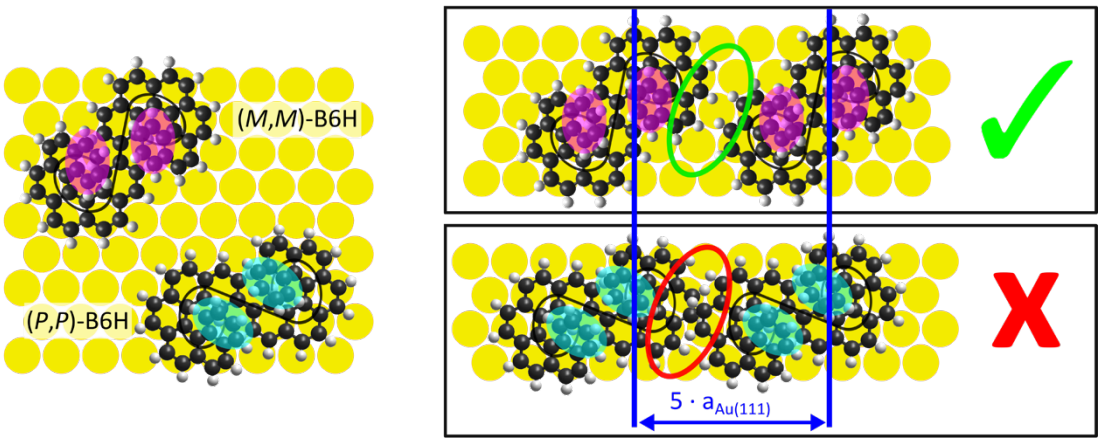


**Figure S4.** Ball and stick models of bis[6]H enantiomers on Au(111). Colored semitransparent filled ellipses indicate the topmost terminal rings that dominate STM contrast. Molecules are placed such that the distal rings of the two helices have the same tilt angle in order to mimic the orientation of the bright protrusions in the STM images. Moreover, molecules are placed with their interhelical C–C bond on identical binding sites (here Au bridge sites, for example). The measured distance along the $[1\bar{1}0]$ direction of 1.45 nm in STM images fits well to 5 interatomic distances. The molecular assembly along the highly symmetric directions can only be solved by homochiral rows of tilted enantiomers. The observed alignment (i.e. distance of protrusions and azimuthal tilt angle) can only brought into agreement for a model that considers the correct enantiomer, as the wrong enantiomer would exhibit an unrealistic molecular overlap (bottom right). Such analysis allows in this case therefore an assignment of molecular handedness by STM observations even devoid of submolecular resolution.