Electronic Supplementary Information

Heterochiral recognition among functionalized heptahelicenes on noble metal surfaces

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Molecular dynamics simulations

In the case of Br[7]H single adsorbates and dimers were computed with the Amber force field of Hyperchem 8.0. A four-layer Au(111) slab with periodic boundary conditions was used as template, with the gold atoms fixed in space during the calculations, but the molecules were allowed to relax. For the single molecule and the dimers 216 and 287 different initial configurations (x, y, z coordinates, z = axis normal to the copper surface) were tested, respectively. Dimer binding energies were calculated by taking the surface binding energy of a single molecule times two minus the dimer binding energy on the surface.

For the molecular dynamics simulations performed for db[7]H and AT[7]H the force fields have been generated with the Antechamber program and a GAFF force field.[1,2] All simulations consist of a relaxation step followed by a molecular dynamic simulation step lasting 1 ps at 10 K with a Langevin thermostat. In order to determine the final structure, geometrical relaxations starting with the final result of the molecular dynamic simulations have been performed. Interaction energies between molecules on the surface were calculated by using the relaxed coordinates with the MMPBSA software in gas phase.[3]
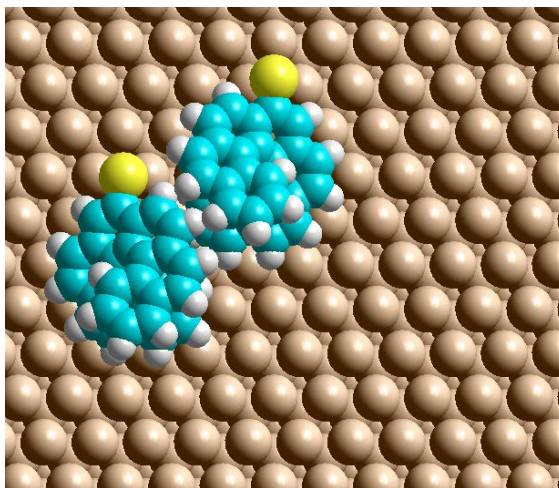

Figure S1. Relaxed configuration of the two enantiomers of 9-bromoheptahelicene on a gold(111) surface. The binding energy of the dimer amounts to 4.5 kcal/mol and lies in the range of van der Waals interaction.
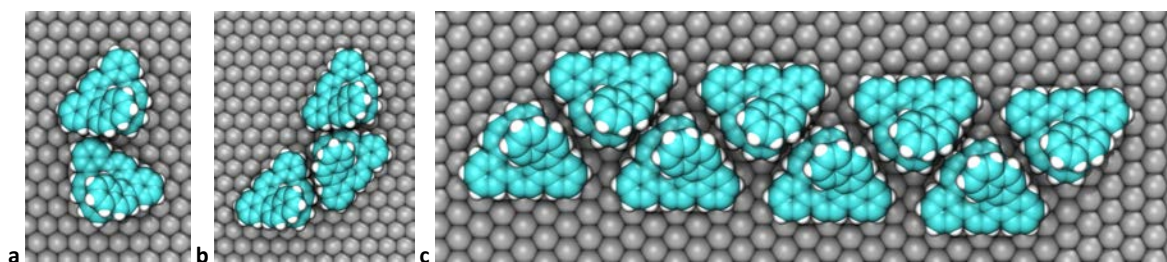
Figure S2. Relaxed configurations of db[7]H ensembles as in Figure 4, but displayed in vdW radii models. (a) heterochiral dimer, (b) heterochiral trimer, (c) heterochiral zigzag chain.
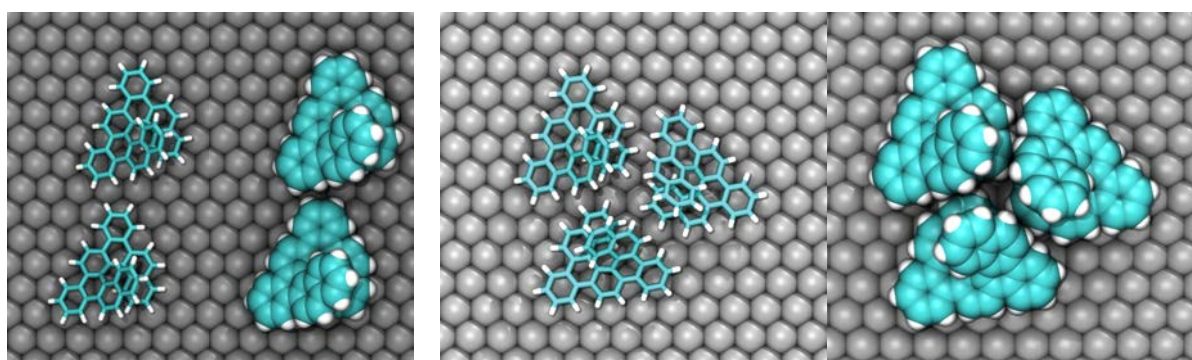

Figure S3. Lowest-energy configurations of homochiral dimers (left) and homochiral trimers (right), presented as stick and vdW radii models, obtained from molecular dynamics force field modelling for enantiopure *(P)*-db[7]H on Ag(111). The binding energy of the homochiral trimer amounts to 5.95 kcal/mol, which is smaller than the value for the heterochiral trimer of 6.37 kcal/mol.
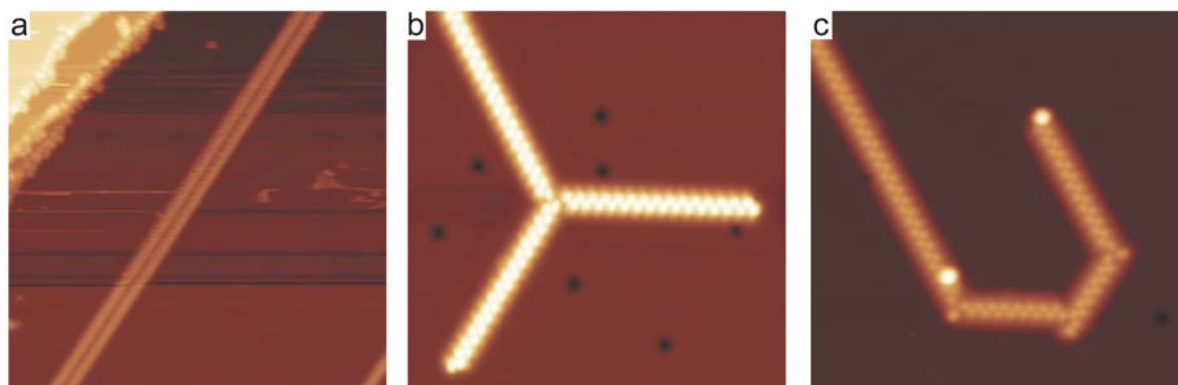

Figure S4. Long-range STM images of zigzag rows of AT[7] on Ag(111). STM parameter: a) 70x70 nm2, 1000mV, 10pA; b) 30x30 nm2, 500mV, 10pA; c) 30x30 nm2, 500mV, 10pA. Zigzag chains grow either straight or deviate at an angle of 120°. That only single patterns are observed at such a large range indicates that single nuclei grow rapidly with low probability of further nucleation. Black dots in (b) are defects in the Ag(111) surface.
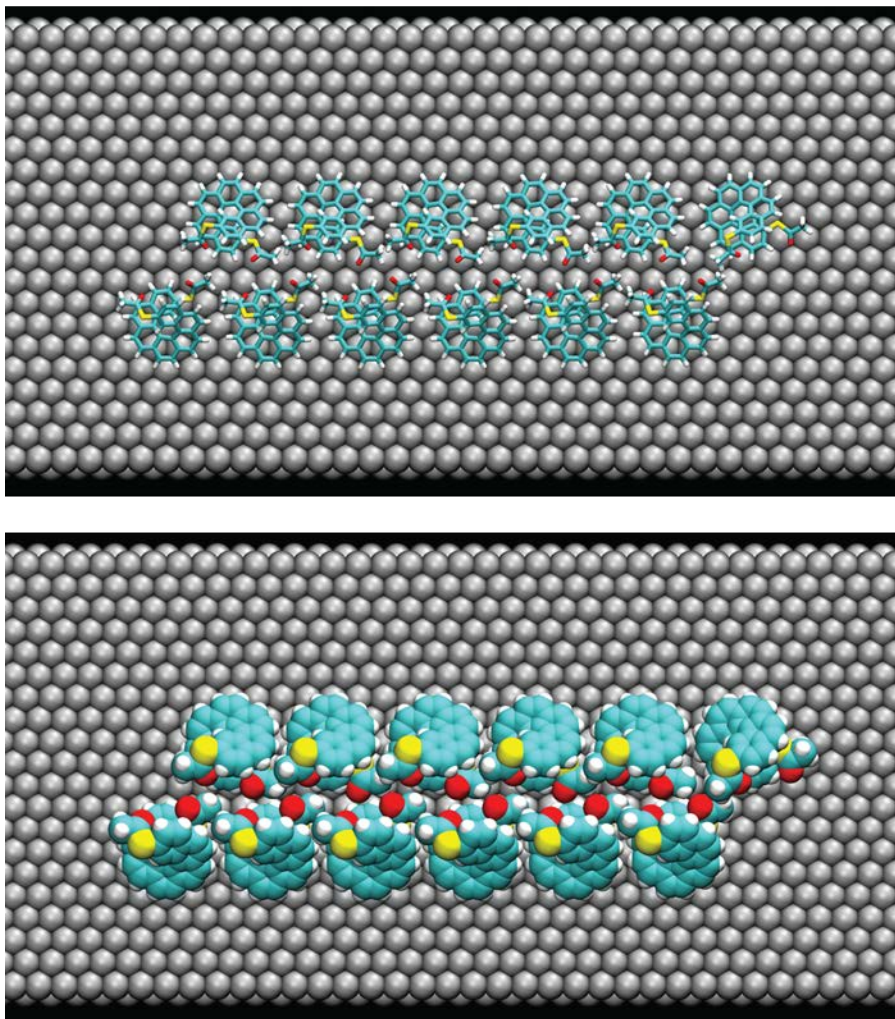
Figure S5. Lowest-energy arrangement of the entire AT[7]H zigzag chain shown in Figure 4f, displayed as ball-and-stick and vdW radii models. Molecules within the chain occupy identical surface sites, while molecules at the ends of the chain occupy different sites with respect to the ones in the middle of the chain.

References
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2   J. Wang, R. M. Wolf, J. W. Caldwell, P. A. Kollman and D. A. Case, *J. Comput. Chem.*, 2005, **25**, 1157–1174.
3   B. R. Miller III, T. D. McGee Jr., J. M. Swails, N. Homeyer, H. Gohlke and A. E. Roitberg, *J. Chem. Theory Comput.*, 2012, **8**, 3314–3321.