

Supporting Information

Spontaneous Chiral Resolution of pentahelicene molecules on Cd(0001)

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1. Methods of first-principles calculations

Density functional theory (DFT) was adopted to calculate the geometries and energy using the OpenMX 3.9 package.¹ The exchange-correlation functional and norm-conserving pseudopotentials are described using the Perdew–Burke–Ernzerhof technique from the generalized gradient approximation (GGA-PBE).^{2,3} The wave functions are derived from a confinement method that generates a linear combination of multiple pseudoatomic orbitals (LCPAOs).^{4,5} The PAO basis functions used are C7.0-s3p3d2, H7.0-s3p2, and Cd7.0-s2p1d2f1 for carbon, hydrogen, and cadmium, respectively, where in the abbreviation of basis functions such as C7.0-s3p3d2, C stands for the atomic symbol, 7.0 the cutoff radius (Bohr) in the generation by the confinement scheme, and s3p3d2 means the employment of three, three, and two optimized radial functions for the s, p, and d orbitals, respectively. The kinetic cutoff energy was set to 120 Ryd. The integration of the Brillouin zone was conducted using a 2×2×1 Monkhorst-Pack grid.⁶ The geometries were optimized using a force-based the rational function (RF) method until the energy was converged to 1.0×10^{-4} eV/atom and the force to 0.01 eV/Å.⁷ According to the experimental results Cd(0001) surface was selected with a large size of 5×5 unit cell. Three layers were considered and the last layer was fixed during the optimization to keep the bulk structure. Meanwhile, the other layers and the adsorbed [5]H molecule were allowed to relax. To eliminate periodic contact, a 15 Å vacuum layer was utilized along the c direction normal to the surface. To describe the vdW interactions, we utilized the empirical correction method described by Grimme (DFT-D3).⁸ The charge transfer was calculated using bader charge analysis.⁹ Scanning tunneling microscopy (STM) images were simulated using the Tersoff–Hamann theory.¹⁰ The simulated STM images were plotted using WSxM software.¹¹

To verify the stability of the [5]H on Cd(0001) surface, the adsorption energies were estimated according to the following equation,

$$E_{\text{ads}} = E_{[\text{5}]\text{H}@Cd(0001)} - E_{[\text{5}]\text{H}} - E_{\text{Cd}(0001)}$$

where $E_{[\text{5}]\text{H}@Cd}$ is the total energy of [5]H on Cd(0001) surface, $E_{[\text{5}]\text{H}}$ and $E_{\text{Cd}(0001)}$ are the energies of separated [5]H and Cd(0001) surface, respectively.

2. References (S1-S10)

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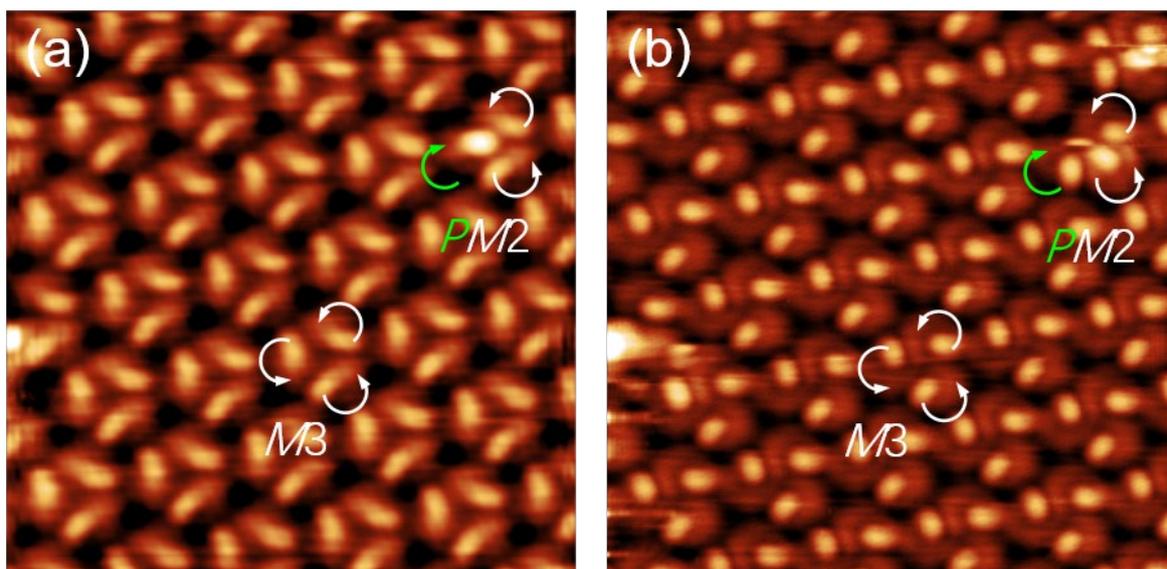


Figure S1. Bias-dependent STM images of the 6×6 trimer phase. (a) Empty state STM image of the trimer phase with majority of homochiral $M3$ triplets and a few of $PM2$ heterochiral trimers, $10\text{ nm} \times 10\text{ nm}$, 1.4 V , 26 pA . (b) Filled-state STM image of the same region as (a), $10\text{ nm} \times 10\text{ nm}$, -1.8 V , 26 pA . The white arrows denote the M -enantiomer of $[5]H$ and the green arrows mark the P -enantiomer of $[5]H$.

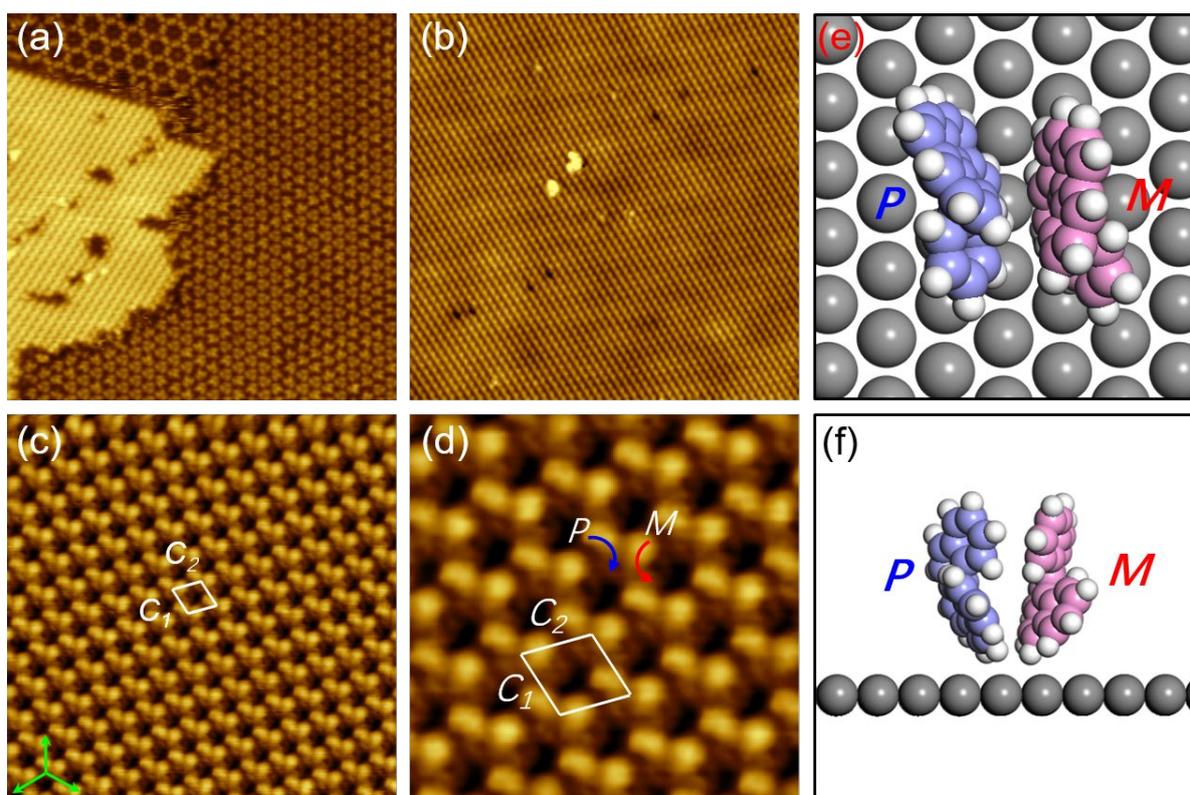


Figure S2. Edge-on phase with extreme close-packing of [5]H layer on Cd(0001). (a) An island of edge-on phase coexists with the 6×6 trimer phase and porous network phase ($50\text{ nm} \times 50\text{ nm}$, 2.5 V , 35 pA). (b) Large-scale STM image ($55\text{ nm} \times 55\text{ nm}$) of the edge-on phase, 2.2 V , 22 pA . (c) Oblique adlattices revealed by the edge-on phase ($15\text{ nm} \times 15\text{ nm}$, 1.8 V , 22 pA). (d) High-resolution STM image of the edge-on phase ($6\text{ nm} \times 6\text{ nm}$, 1.8 V , 22 pA). The building blocks are heterochiral P - M pairs with an up-right orientation. (e) and (f) show the top and side views of the schematic model of heterochiral P - M pairs.

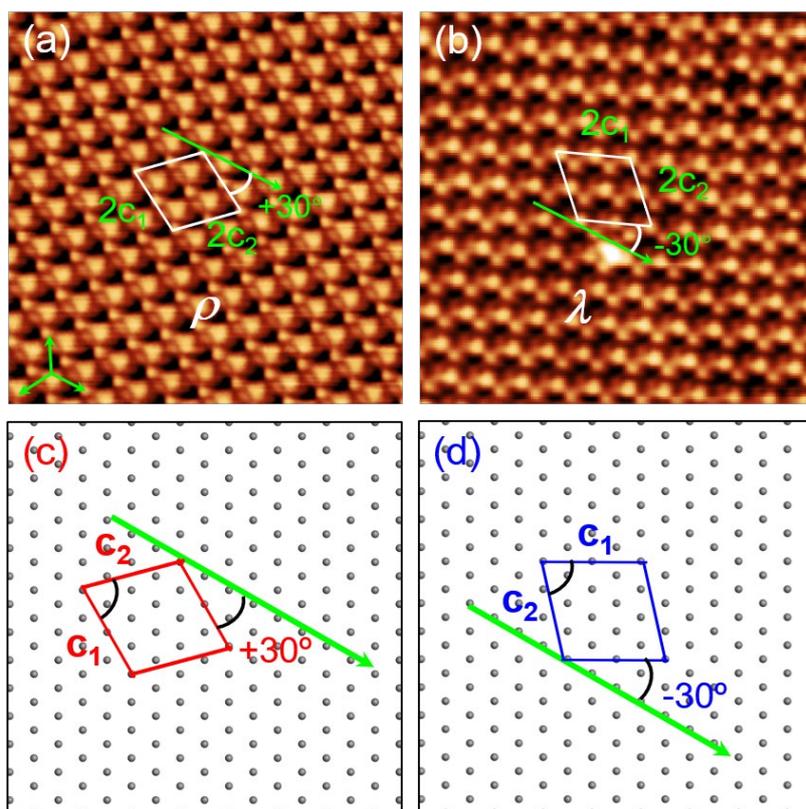


Figure S3. Two mirror domains of the edge-on phase of [5]H layer. (a) The ρ -domain showing a misorientation angle of $+30^\circ$ relative to the high-symmetry direction of Cd(0001) ($13 \text{ nm} \times 13 \text{ nm}$, 2.0 V, 22 pA). (b) The λ -domain showing a misorientation angle of -30° relative to the high-symmetry direction of Cd(0001) ($13 \text{ nm} \times 13 \text{ nm}$, 3.0 V, 25 pA). (c) and (d) are the schematic model of the chiral lattices of ρ - and λ -domain corresponding to the edge-on phase in (a) and (b), respectively.