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Intermolecular Hydrogen Bond Plays a Determining Role in Product Selection of Surface Confined Schiff-base Reaction

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1. Experimental details of surface preparation

All solvents and reagents were purchased from J&K Scientific and TCI. All the chemicals in this work, unless otherwise specified, were used without any further purification.

Self-assembly of **THB**: **THB** was firstly dissolved in DMSO with a concentration of 2.3×10^{-3} mol/L and then the solution was diluted 5 times by octanoic acid. A droplet (5 μL) of octanoic acid containing 4.6×10^{-4} mol/L was deposited onto the freshly cleaved surface of highly oriented pyrolytic graphite (HOPG) at room temperature. The adsorbed sub-monolayer was annealed at 100 °C for 30 mins under ambient pressure and then naturally cooled down to room temperature, taken out of the autoclave for characterization.

Sample preparation: Both the **THB** (**THPB**) and **DAB** were first dissolved in DMSO. Then they were diluted 100 times by octanoic acid. A ~5 μL amount of the mixed solution was deposited on the freshly cleaved surface of HOPG. About 1.0 g of $CuSO_4\cdot5H_2O$ powder was preloaded in the 100 mL Teflon-sealed autoclave to serve as chemical equilibrium regulation agent. The drop-cast samples were positioned in the autoclave as well and heated at 130 °C for 3 h. The sample was taken out and naturally cooled to room temperature, then STM characterization was carried out at the liquid/solid interface after adding a drop of octanoic acid onto the surface.

STM measurements were performed under ambient conditions with mechanically cut Pt/Ir wires (80/20) by using Bruker scanning probe microscopy. All the images were recorded in constant-current mode and shown without further processing. The chemical structure models were built with HyperChem software. The calibration of the STM images was performed by using the HOPG lattice with atomic resolution.

The statistical analysis was estimated by analyzing STM images taken at 30 arbitrarily chosen points for each molar ration (**THB**: **DAB** =1:1 or **THB**: **DAB**=2:1) and each concentration. The occupancy of each assemble structure was calculated by dividing the area of each morphological network by the area of all kinds of structures.

2. Supplementary figures

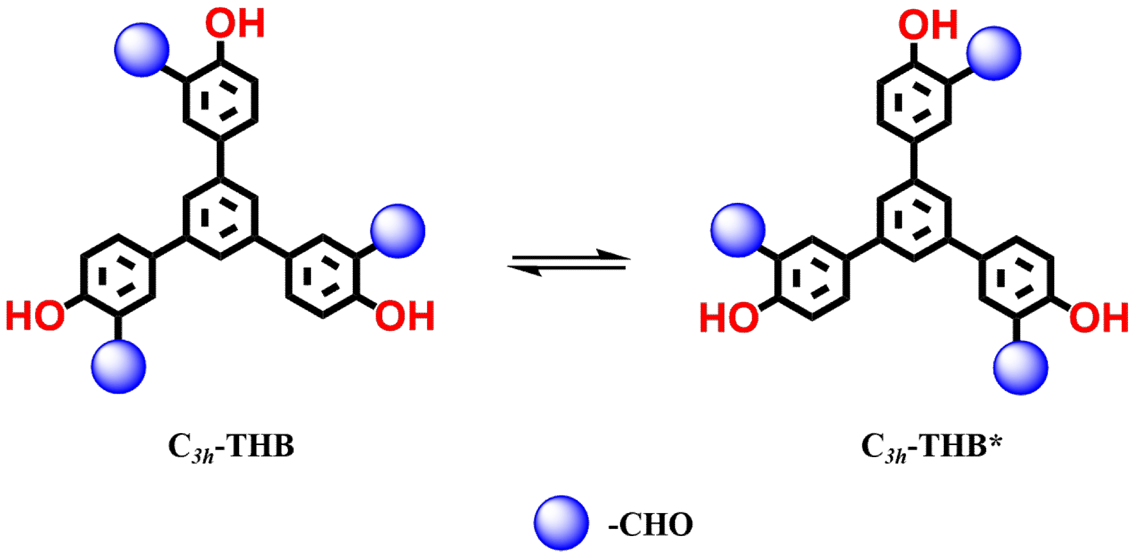

Figure S1. The chemical structures of **C_{3h}-THB** and **C_{3h}-THB***.

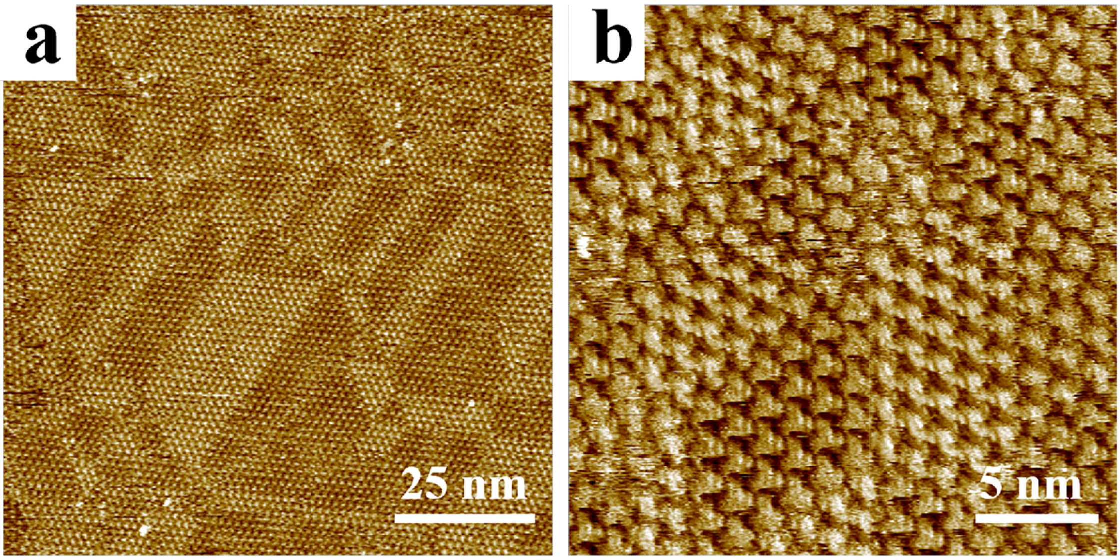

Figure S2. Self-assembly of monomer **THB**. (a) Large-scale and (b) high-resolution STM image of assembly of **THB** with the concentration of 4.6×10^{-4} mol/L. Imaging conditions: (a) V_{bias} = -0.35 V, I_t= 0.80 nA. (b) V_{bias}= -0.35 V, I_t= 0.19 nA.

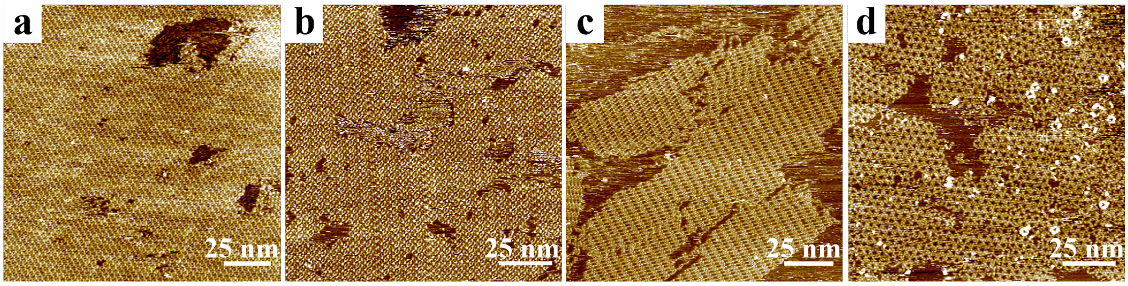

Figure S3. Large-scale STM images obtained by on-surface condensation between monomers **DAB** and **THB**. (a) (2+2) Cycle phase I and II (b). (c) Assembly of polymer chains and (d) macrocycles. Imaging conditions: (a) V_{bias}= -0.25 V, I_t = 0.45 nA. (b) V_{bias} = -0.45 V, I_t= 0.15 nA. (c) V_{bias} = - 0.35 V, I_t = 0.26 nA. (d) V_{bias} = -0.45 V, I_t = 0.09 nA. (a-b: n_{DAB}:n_{THB}=1:2, c_{DAB}= 3.8×10^{-6} mol/L, c_{THB}= 7.5×10^{-6} mol/L,; c-d: n_{DAB}:n_{THB}=1:1, c_{DAB}= 1.3×10^{-5} mol/L, c_{THB}=1.3×10^{-5} mol/L).

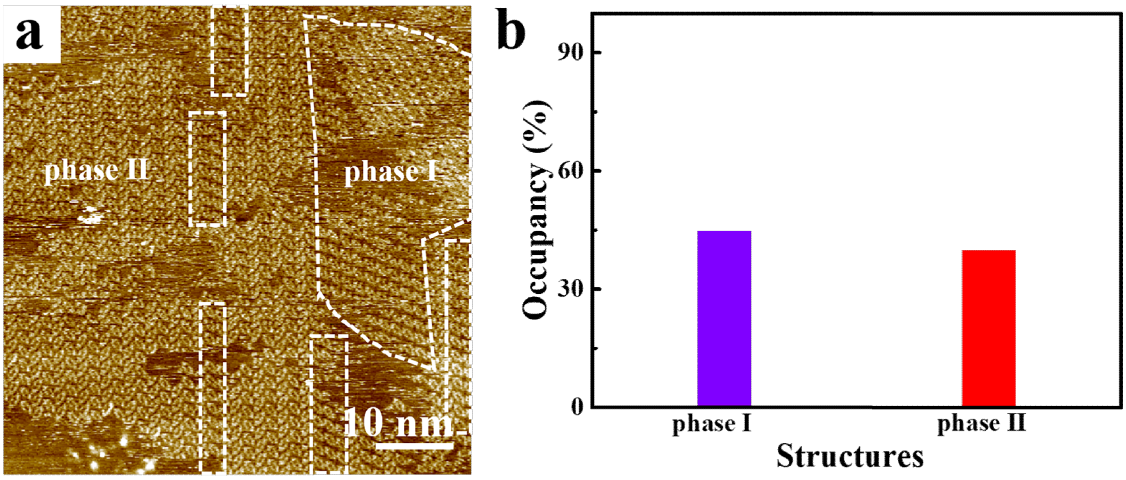

Figure S4. (a) STM images of two phases of (2+2) cycles by condensation of **DAB** and **THB**, revealing the coexisting phase I and II. (b) Occupancy of phase I and II. Imaging conditions: V_{bias} = -0.35 V, I_t= 0.11 nA (n_{DAB}:n_{THB}=1:2, c_{DAB}= 3.8×10^{-6} mol/L, c_{THB}= 7.5×10^{-6} mol/L). The phase I domains were highlighted with white dotted lines.

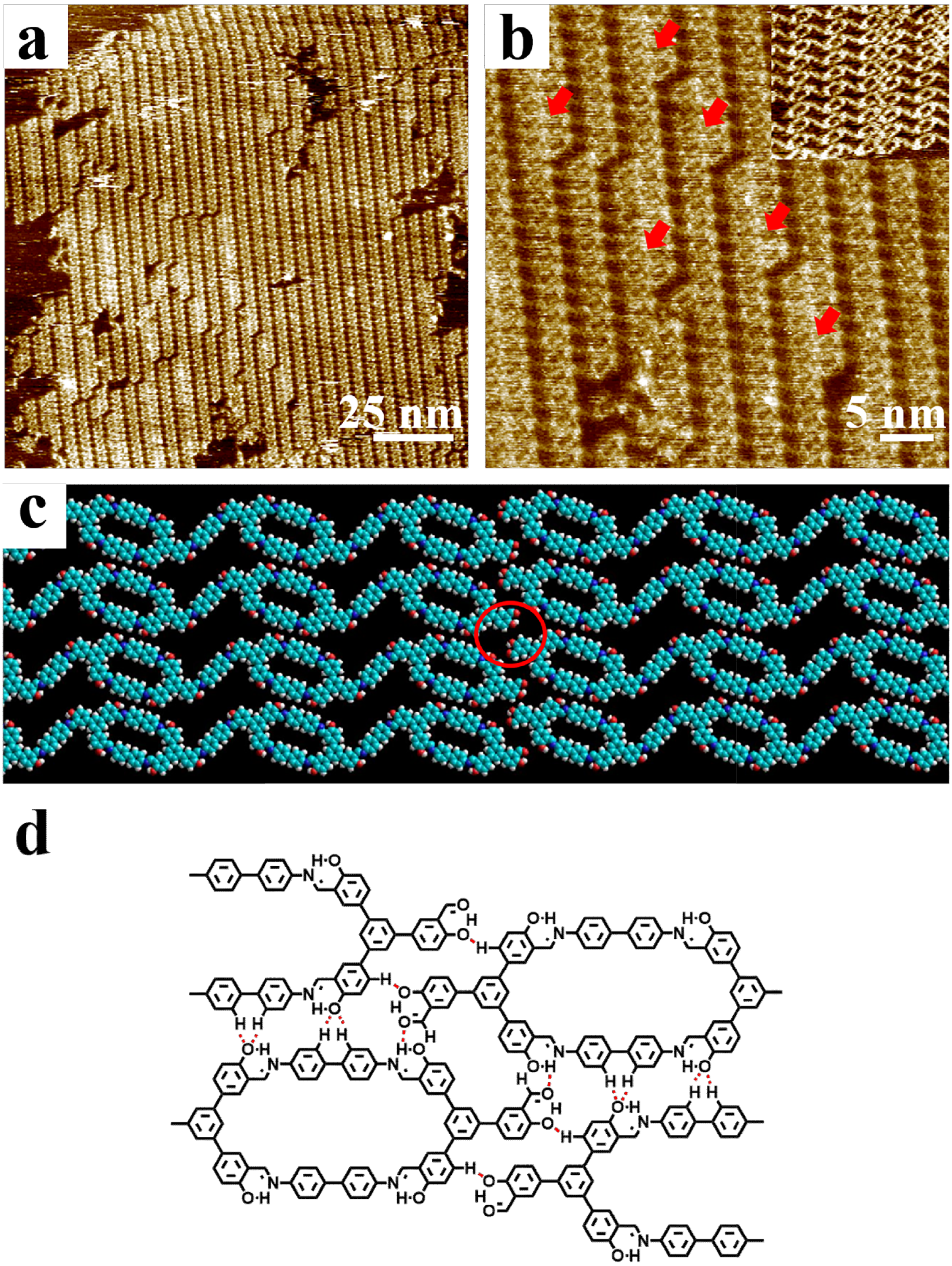

Figure S5. (a) STM images of assembly of zig-zag polymer chains. Proposed structural model (c) and an enlarged model of intermolecular hydrogen bonds between polymer chains (d).

Imaging conditions: (a, b) V_{bias} = -0.35 V, I_t = 0.08 nA, n_{DAB}:n_{THB}=3:1, c_{DAB}= 6.0×10^{-6} mol/L, c_{THB}= 2.0×10^{-6} mol/L. The red arrows in b indicate the formation of multiple intermolecular hydrogen bonds between unreacted aldehydes at the end of polymer chains. The red dotted lines indicate the existence of multiple intermolecular hydrogen bonds.

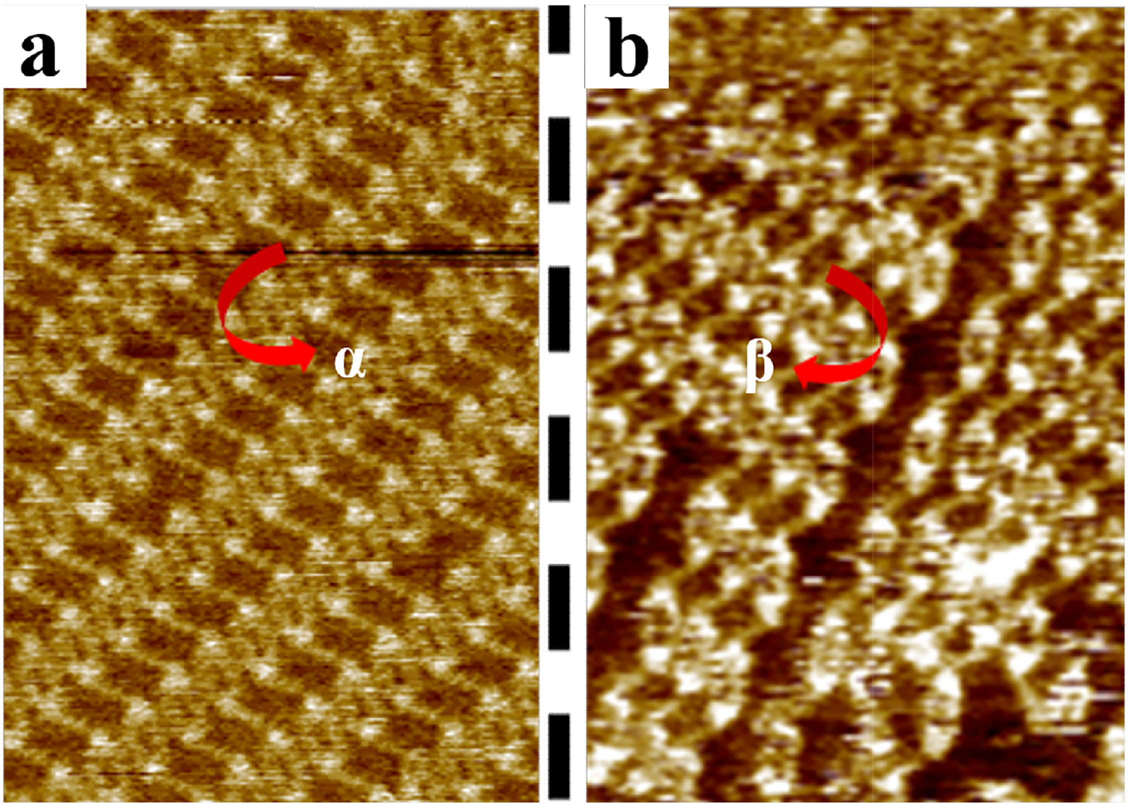

Figure S6. STM images of the assembly of homochiral polymer chains, labeled as α (a) and β (b). Imaging conditions: (a) V_{bias}= -0.35 V, I_t = 0.13 nA. (b) V_{bias}= -0.35 V, I_t= 0.22 nA.

Table S1. The relationship of structural diversity and molar ratios (except * c_{THB}=4.0×10^{-6} mol/L, the rest: c_{THB}=7.5×10^{-6} mol/L).

n_{Amine}:$n_{Aldehyde}$	phase I	phase II	Polymer chains	Macrocycles
1:2	✓	✓		
1:1	✓		✓	✓
3:2			✓	✓
3:1			✓	✓
3:2(or 3:1)*			✓	

Keeping the concentration constant of monomer **THB**, Table S2 shows the effect of monomer molar ratios on the product distribution by gradually reducing the proportion of **THB**. Mixing of **DAB** and **THB** with the molar ratio of 1:2 leads to the formation of two assemblies of (2+2) cycles. Statistical analysis revealed the coverage of phase **I** and **II** domains were comparable (44.8%, 40.0%, respectively, Figure S4). Upon increasing the molar ratio of **DAB** and **THB** to 1:1, distinct changes took place in the topological images and two completely new products, zig-zag polymer chains and macrocycles, were observed. Upon further increasing the molar ratio of **DAB** and **THB** to 3:2 (or 3:1), all (2+2) cycles transformed into polymer chains and macrocycles. While under 4.0×10^{-6} mol/L of aldehyde concentration, we can exclusively achieve zig-zag polymer chains with the molar ratio of 3:1 (or 3:2). We failed to obtain the exclusive assembly of the macrocycles though we tried different combinations of concentration and molar ratios. These findings suggested that molar ratio played an important role in the formation of final products.

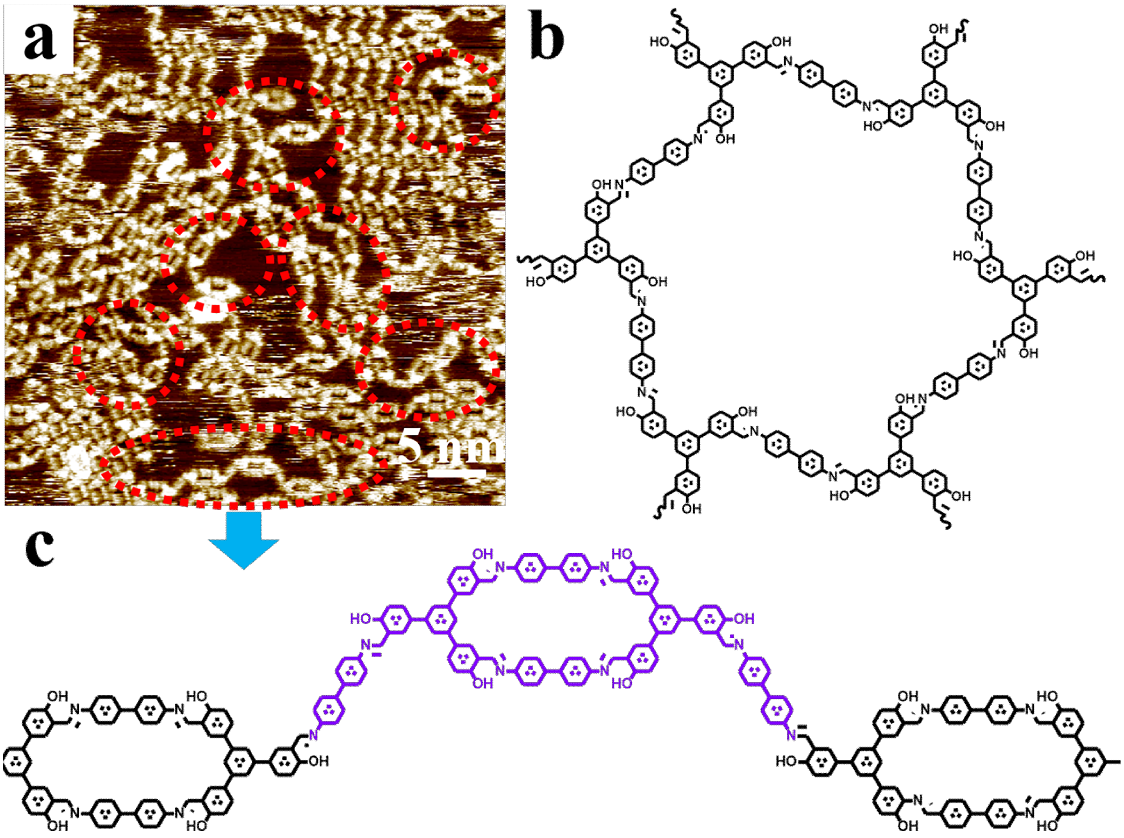

Figure S7. STM images (a) and chemical structures (c) of disordered assembly of polymer chains. (b) Envisaged windmill network with exclusively **C_{3h}-THB** (or **C_{3h}-THB***) conformer. Imaging conditions: V_{bias} = -0.50 V, I_t = 0.10 nA, n_{DAB}:n_{THB} =1:1, c_{DAB}= 1.3×10^{-5} mol/L, c_{THB}= 1.3×10^{-6} mol/L,. The red dashed lines highlight the polymer chains containing *cis* (2+2) cyclic units.

Beyond the four kinds of ordered superstructures, disordered assembly of polymer chains was found on the graphite surface. They were made up of a *cis-trans* diastereomeric mixture of cycles and adopted different morphologies, including zig-zag and curved chains, as seen in Figure S7.

All the observed products contain THB units with **C_s-THB** or **C_s-THB***conformations, order windmill network composed by THB with **C_{3h}-THB** (**C_{3h}-THB***) conformation has never been observed in STM experiments. It clearly demonstrates that **THB** units have high conformational selectivity toward C_s conformation during on-surface synthesis.

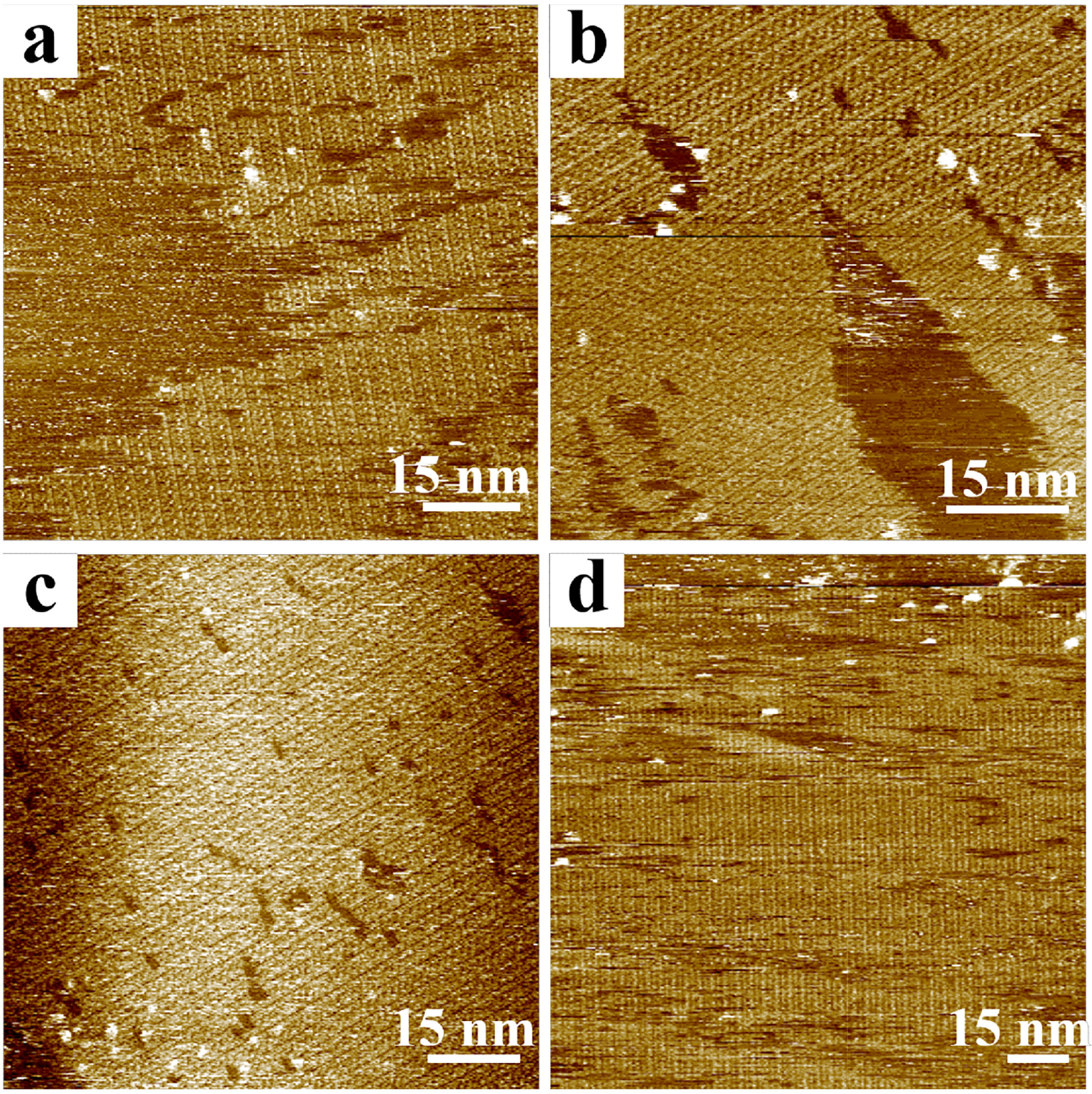

Figure S8. STM images obtained by condensation of monomer **DAB** and **THPB** at 130 °C. Imaging conditions: (a) V_{bias}= -0.45 V, I_t = 0.10 nA, n_{DAB}:n_{THPB}=1:1,c_{DAB}=5.2×10^{-6} mol/L. (b)

V_{bias} = -0.55 V, I_t= 0.27 nA, n_{DAB}:n_{THPB}=6.3:1,c_{DAB}= 3.3×10^{-5} mol/L. (c) V_{bias} = -0.35 V, I_t = 0.13 nA, n_{DAB}:n_{THPB}=10.5:1, c_{DAB}= 5.4×10^{-5} mol/L. (d) V_{bias} = -0.55 V, I_t = 0.24 nA, n_{DAB}:n_{THPB}=21:1, c_{DAB}= 1.1×10^{-4} mol/L.

Table S2. Structural parameters of the assemblies of polymer chains, macrocycles, phase I and II of (2+2) cycles.

Structures	**a (nm)$^{a, b}$**	**b (nm)$^{a, b}$**	**γ (deg)$^{a, b}$**	**N^{c}**	**area (nm^{2})^{d}**	**D (nm^{-2})^{e}**	**$n_{C=N}$ (nm^{-2})**
phase I	**2.6±0.2 (2.54)**	**2.9±0.2 (3.13)**	**64±2° (66)**	**90**	**6.75**	**13.33**	**0.59**
phase II	**2.8±0.2 (3.05)**	**4.9±0.2 (4.71)**	**85±2° (86)**	**180**	**13.75**	**13.09**	**0.58**
polymer chains	**2.0±0.2 (2.03)**	**4.6±0.2 (4.67)**	**97±2° (98)**	**102**	**8.94**	**11.40**	**0.67**
macrocycles	**5.6±0.2 (5.64)**	**5.6±0.2 (5.63)**	**63±2° (60)**	**306**	**28.83**	**10.83**	**0.62**
phase III	**3.3±0.2 (3.25)**	**1.6±0.2 (1.63)**	**70±2° (71)**	**84**	**4.99**	**16.83**	**0.80**

[a]For the definition of the unit cell refer to Figure 1, 2and 4. [b] The simulated value is given in parentheses. [c] Number of THB molecule per unit cell. [d] Unit cell area. [e] Network density (number of non-hydrogen atoms/nm^{2})