

# From 1D Ordered Linear Polymer to Discrete Macrocycles: Surface Adsorption and pH Take Control

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## 1. Materials and methods

All of the chemicals were purchased from J&K and used without further purification. For on-surface reaction, DHBDA and PDA were dissolved in DMSO with the concentration of  $4.2 \times 10^{-4}$  mol/L for DHBDA,  $9.2 \times 10^{-4}$  mol/L for PDA. And then DHBDA and PDA were mixed together with a molar ratio of 1:1 and drop-cast onto the substrate surface. A small amount of acetic acid/hydrochloric acid was added into the solution as catalyst. For the on-surface synthesis without catalyst, DHBDA and PDA were dissolved in DMSO with the concentration of  $4.2 \times 10^{-4}$  mol/L for DHBDA,  $9.2 \times 10^{-4}$  mol/L for PDA for PDA. And then DHBDA and PDA were mixed together with a molar ratio of 1 : 3. Dropcasting 10  $\mu$ L the above-mentioned mixing solution on the HOPG surface, followed by annealing at 80 °C for  $\sim$ 30 min with a pressure of <133 Pa. For the synthesis of  $1\text{DP}_{\text{DHBDA-PDA}}$ /macrocycle by solution synthesis, initially, DHBDA and PDA were dissolved in DMSO with the concentration of  $2.1 \times 10^{-3}$  mol/L for DHBDA,  $4.6 \times 10^{-3}$  mol/L for PDA in polyethylene tube. A small amount of acetic acid/ hydrochloric acid was added into the solution as catalyst, and heating the solution in the polyethylene tube at 80 °C for  $\sim$ 30 min at atmospheric pressure. After the solution cooled down to  $\sim$  50 °C, drop casting 10  $\mu$ L the mixing solution on a freshly cleaved HOPG surface, followed by annealing at 80 °C for  $\sim$  30 min with a pressure of <133 Pa to remove the solvent. The samples were taken out of the oven and cooled to room temperature, and then characterized by STM. STM measurements were performed with an Agilent 5100 scanning probe microscope with mechanically formed Pt/Ir (80/20) tips under ambient conditions. All images were taken with the constant current mode. The calibration of STM images were carried out by using an atomic resolution HOPG lattice.

## 2. Supplementary figures

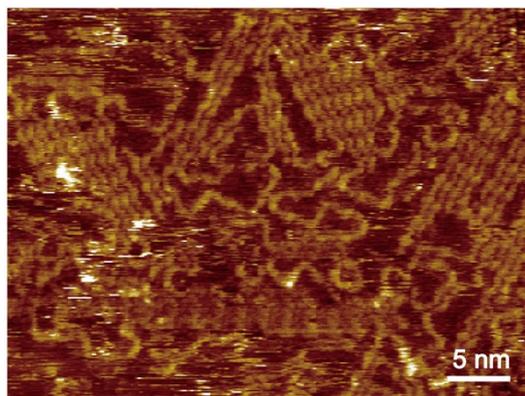


Figure S1. The surface confined Schiff-base coupling at the gas/solid interface. Disordered linear polymers at some domain boundaries between linear polymer domains. Imaging conditions:  $I_{\text{set}} = 24 \text{ pA}$ ,  $V_{\text{set}} = 0.66 \text{ V}$ .

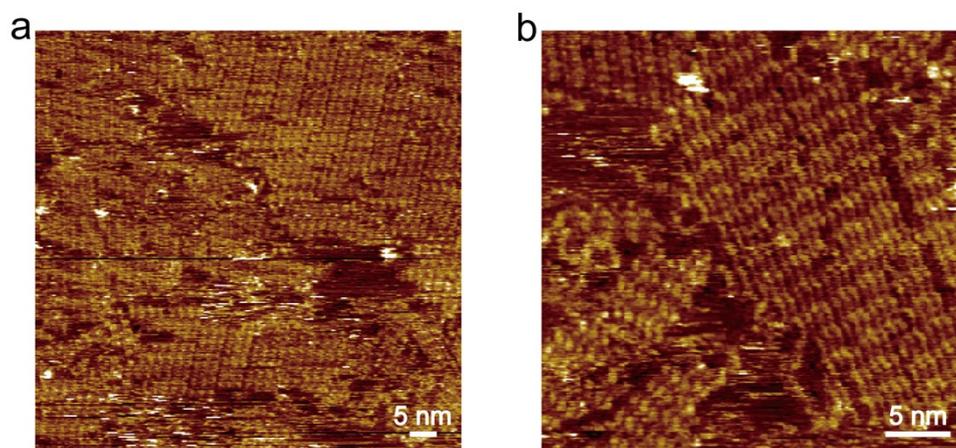


Figure S2. The surface confined Schiff-base coupling at the gas/solid interface. (a) Large-scale and (b) high resolution STM image of zigzag  $1\text{DP}_{\text{DHBDA-PDA}}$  obtained with the surface confined Schiff base reaction on the freshly cleaved HOPG surface. Imaging conditions: (a)  $I_{\text{set}} = 26 \text{ pA}$ ,  $V_{\text{set}} = 0.65 \text{ V}$ ; (b)  $I_{\text{set}} = 27 \text{ pA}$ ,  $V_{\text{set}} = 0.68 \text{ V}$ .

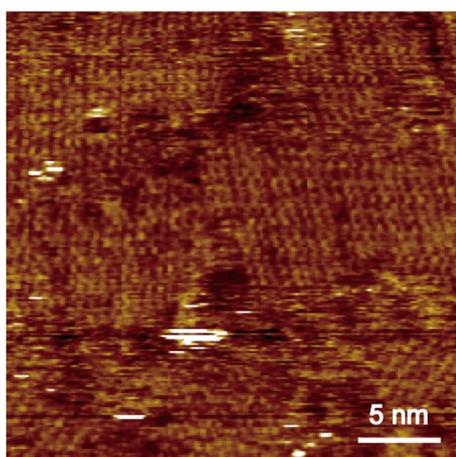


Figure S3. The surface confined Schiff-base coupling at the gas/solid interface. STM image of the assembly of zigzag  $1\text{DP}_{\text{DHBDA-PDA}}$  obtained by adding acetic acid. The pH of the mixing solution was 6.0. Imaging conditions:  $I_{\text{set}} = 28 \text{ pA}$ ,  $V_{\text{set}} = 0.66 \text{ V}$ .

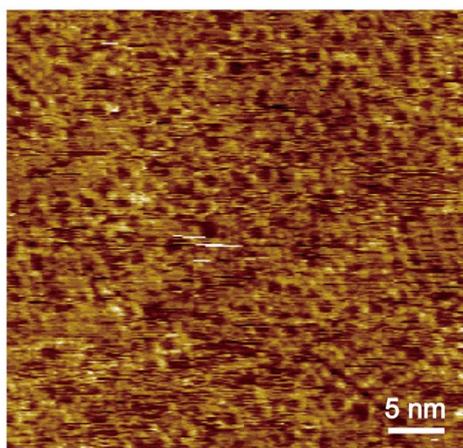


Figure S4. The surface confined Schiff-base coupling at the gas/solid interface. STM images of assembly from surface confined Schiff base reaction at 80°C for 10 hours, and the pH of the mixing solution was about 5.5 by adding hydrochloric acid. Imaging conditions:  $I_{\text{set}} = 24 \text{ pA}$ ,  $V_{\text{set}} = 0.66 \text{ V}$ .

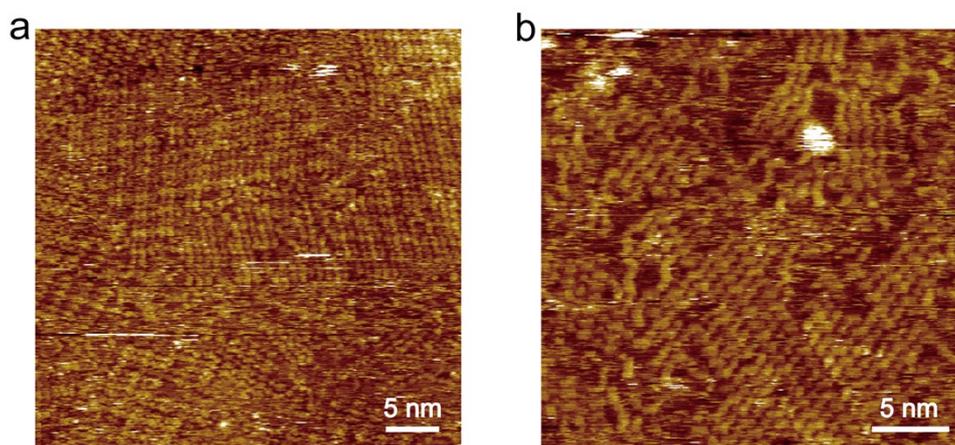


Figure S5. STM images of the assembly from solution synthesis, and the pH of the mixing solution was about 6.5 by adding acetic acid. Imaging conditions: (a)  $I_{\text{set}} = 25 \text{ pA}$ ,  $V_{\text{set}} = 0.66 \text{ V}$ ; (b)  $I_{\text{set}} = 26 \text{ pA}$ ,  $V_{\text{set}} = 0.66 \text{ V}$ .

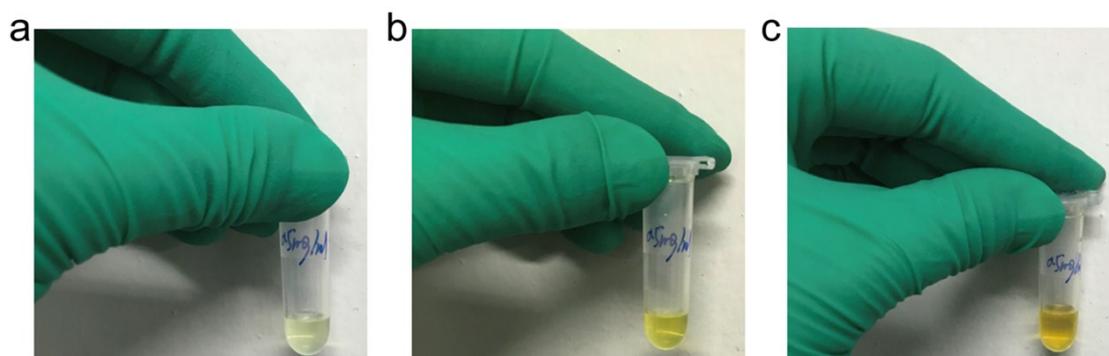


Figure S6. Photographs of color change of the mixing solution (a) just mixed, (b) after adding hydrochloric acid, (c) heating 30min after adding hydrochloric acid by solution synthesis, and the pH of the mixing solution was about 6.5.

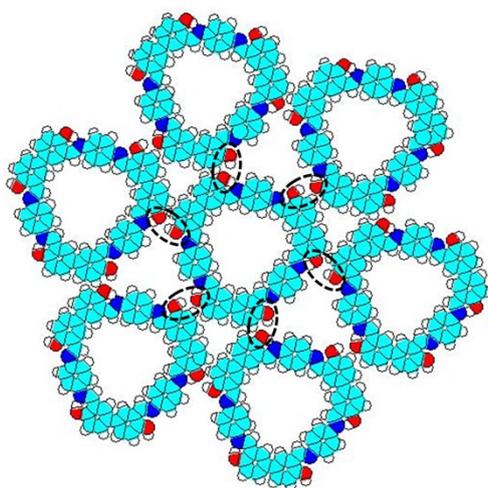


Figure S7. One macrocycle is surrounded by six macrocycles via O–H···O hydrogen bonds (the black dashed line) between hydroxy groups from the DHBDA unit.

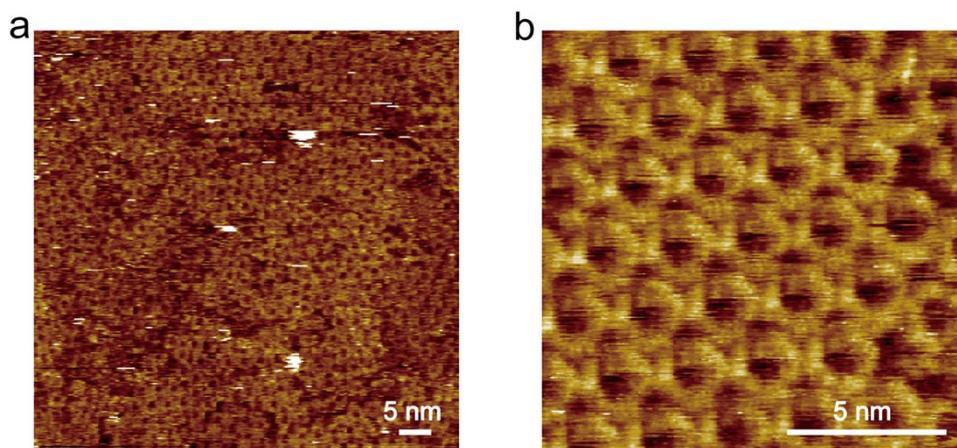


Figure S8. STM images of the assembly from solution synthesis. (a) Large-scale and (b) high resolution STM image of hexagonal nanoarchitectures of macrocycles obtained by solution synthesis by adding hydrochloric acid in the mixing solution at pH 5.5. Imaging conditions: (a)  $I_{\text{set}} = 23 \text{ pA}$ ,  $V_{\text{set}} = 0.69 \text{ V}$ ; (b)  $I_{\text{set}} = 25 \text{ pA}$ ,  $V_{\text{set}} = 0.67 \text{ V}$ .

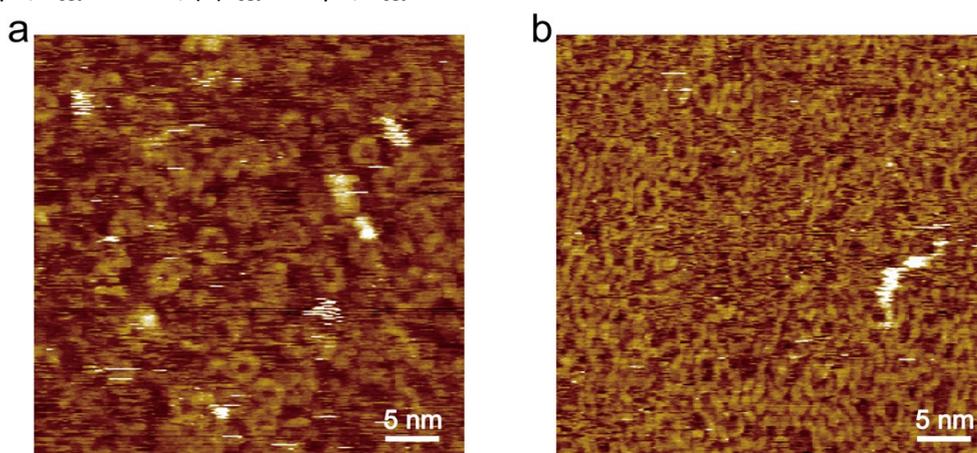


Figure S9. STM images obtained on the assembly of solution synthesized product by adding hydrochloric acid in the mixing solution at pH 5.5. The orderliness and continuity of the macrocycles were disturbed. Imaging conditions: (a)  $I_{\text{set}} = 26 \text{ pA}$ ,  $V_{\text{set}} = 0.69 \text{ V}$ ; (b)  $I_{\text{set}} = 25 \text{ pA}$ ,  $V_{\text{set}} = 0.67 \text{ V}$ .

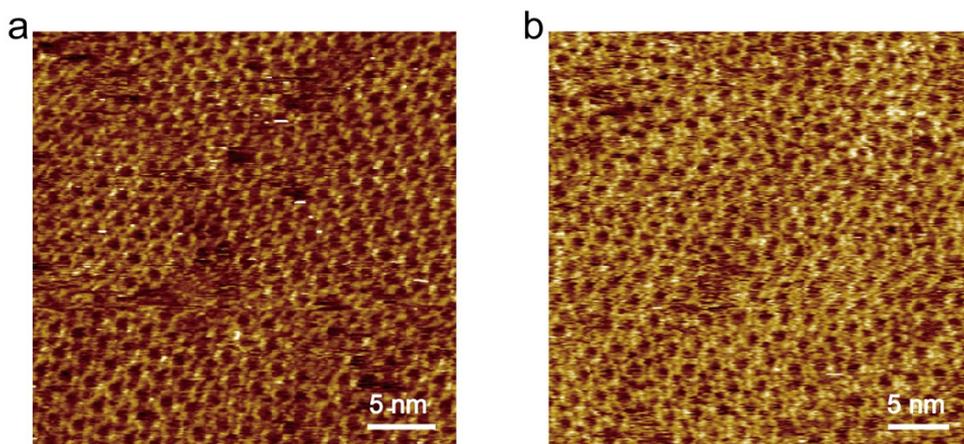


Figure S10. STM image of well-ordered hexagonal closed macrocycles obtained by solution synthesis by adding trifluoroacetic acid in the mixing solution at (a) pH = 6.0 and (b) pH = 5.5. Imaging conditions: (a)  $I_{\text{set}} = 27 \text{ pA}$ ,  $V_{\text{set}} = 0.68 \text{ V}$ ; (b)  $I_{\text{set}} = 26 \text{ pA}$ ,  $V_{\text{set}} = 0.67 \text{ V}$ .

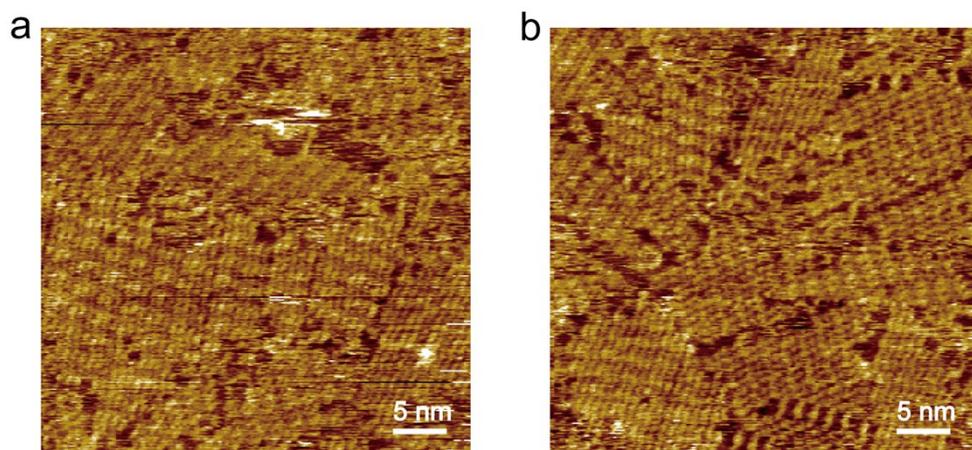


Figure S11. STM images of the assembly from solution synthesis. The same concentration of (a) NaCl (b) KCl instead of hydrochloric acid in solution synthesis. Imaging conditions: (a)  $I_{\text{set}} = 28 \text{ pA}$ ,  $V_{\text{set}} = 0.68 \text{ V}$ ; (b)  $I_{\text{set}} = 26 \text{ pA}$ ,  $V_{\text{set}} = 0.65 \text{ V}$ .

### 3. $^1\text{H-NMR}$ of the solution synthesis

We have also done solution phase  $^1\text{H-NMR}$  to clarify the presence of products in solution. For this purpose DHBDA and PDA were dissolved in  $d_6$ -DMSO (J&K) with the concentration of  $2.1 \times 10^{-3} \text{ mol/L}$  for DHBDA,  $4.6 \times 10^{-3} \text{ mol/L}$  for PDA. And then DHBDA and PDA were mixed together with a molar ratio of 1:1 for the reaction. A small amount of acetic acid/acetic hydrochloric acid (for  $1\text{DP}_{\text{DHBDA-PDA}}/\text{macrocycles}$ ) was added into the solution as catalyst, the pH are adjusted to 6.5 and 6.0, respectively, and heating the solution in the polyethylene tube at  $80 \text{ }^\circ\text{C}$  for  $\sim 30 \text{ min}$  at atmospheric pressure. After the solution cooled down to room temperature, both the monomers and the reaction mixtures were characterized by  $^1\text{H-NMR}$ . The spectrum in both cases show clear existence of unreacted monomers, and the  $-\text{CH}=\text{N}-$  show multiple peaks, which may be attributed to the formation of intramolecular hydrogen bond. In one of the previous report De Feyter et al has proved that the surface may significantly accelerate the Schiff base reaction and amplify a specific product has higher surface affinity. Comparing the above  $^1\text{H-NMR}$  spectrum with our STM observation we can conclude similar effect also happens in our system: the surface

significantly amplify the formation of linear and macrocyclic products in both cases. In contrast, in solution the unreacted monomers are predominant.

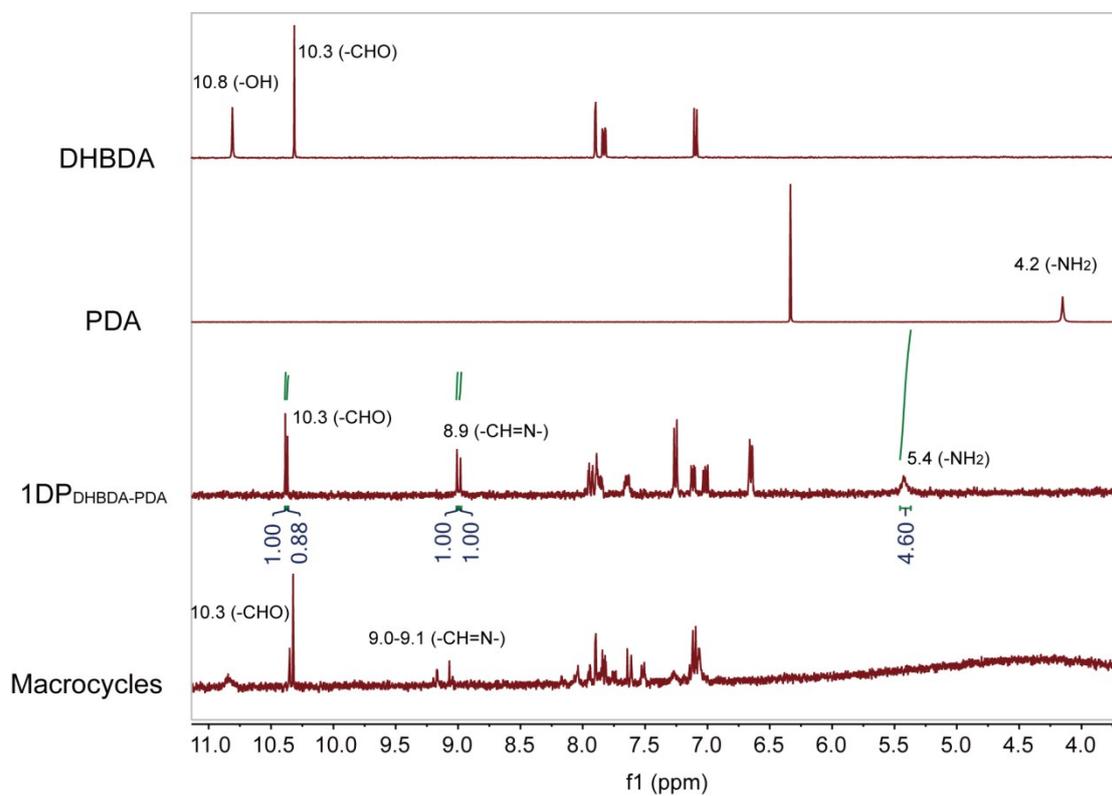


Figure S11. <sup>1</sup>H-NMR of the monomers and the reaction mixtures with acetic acid and acetic hydrochloric acid as catalysis.