Supporting Information

Structural Diversity of Metal-Organic Self-Assembly Assisted by Chlorine

Lei Xie, Chi Zhang, Yuanqi Ding, Wenlong E, Chunxue Yuan, Wei Xu*

Interdisciplinary Materials Research Center, Tongji-Aarhus Joint Research Center for Nanostructures and Functional Nanomaterials, College of Materials Science and Engineering, Tongji University, Shanghai 201804, People's Republic of China

E-mail: xuwei@tongji.edu.cn

All STM experiments were performed in a UHV chamber (base pressure 1×10^{-10} mbar) equipped with a variable-temperature, fast-scanning "Aarhus-type" STM using electrochemically etched W tips purchased from SPECS,[1,2] a molecular evaporator and an e-beam evaporator, and other standard instrumentation for sample preparation. The Au(111) substrate was prepared by several cycles of 1.5 keV Ar+ sputtering followed by annealing to 800 K for 15 min, resulting in clean and flat terraces separated by monatomic steps. The 1mC molecules (purchased from Bide Pharmatech Ltd., purity > 97%) and NaCl (purchased from Sigma-Aldrich, purity > 99%) were loaded into glass crucibles in the molecular evaporator. After a thorough degassing, the molecules were deposited onto the Au(111) substrate by thermal sublimation at 330 K and 630 K, repectively. The sample was thereafter transferred within the UHV chamber to the STM, where measurements were carried out at ~100–150 K. All the STM images were further smoothed to eliminate noises. Scanning conditions: It = 0.5~0.9 nA, Vt = ~1700 mV.

The calculations were performed in the framework of DFT by using the Vienna ab initio simulation package (VASP).[3,4] The projector-augmented wave method was used to describe the interaction between ions and electrons.[5,6] We employed the Perdew−Burke−Ernzerhof generalized gradient approximation exchange-correlation functional,[7] and van der Waals interactions were included using the dispersion-corrected DFT-D3 method of Grimme.[8] The atomic structures were relaxed using the conjugate gradient algorithm scheme as implemented in VASP until the forces on all unconstrained atoms were ≤ 0.03 eV/Å for geometry optimization.

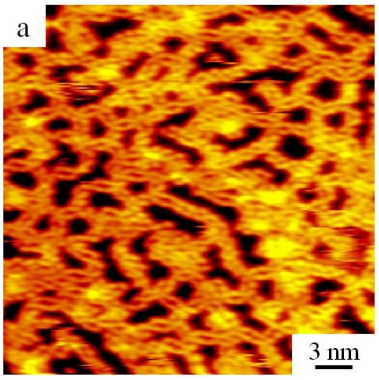

Figure S1. STM image of 1-methylcytosine after addition of NaCl at room temperature, where the previous ordered chains are disrupted and the bright patches decorated randomly are believed to be small NaCl islands.

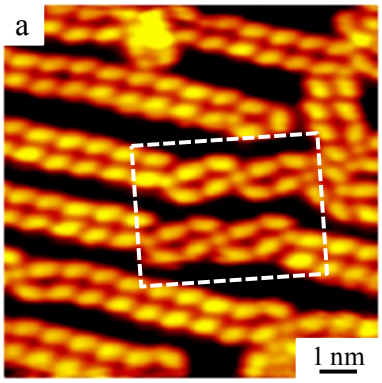

Figure S2. A patch of structural transition of 1mC chains highlighted by white rectangle when NaCl is provided in a small dosage.

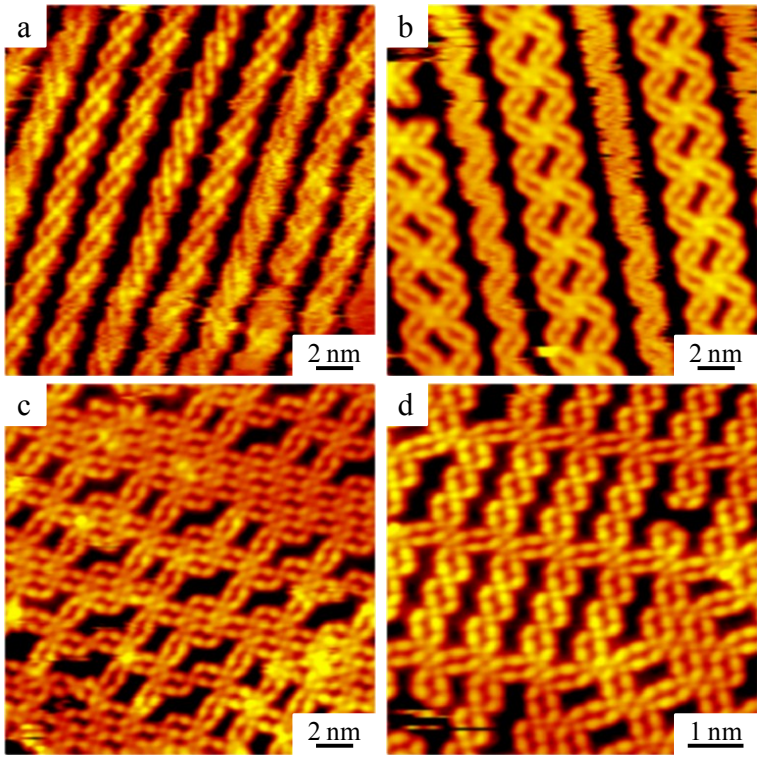

Figure S3. More examples of typical structures formed by deposition of NaCl onto the 1mC-precovered Au(111) surface and anneal at 370 K for 10 minutes.

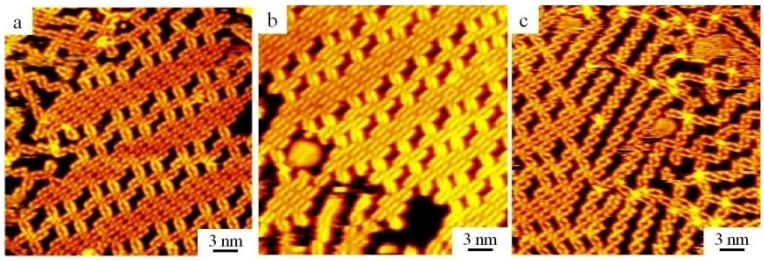

Figure S4 Large-scale STM images showing the overview of the sample after deposition of NaCl onto the 1mC-precovered Au(111) surface and anneal at 370 K for 10 minutes.

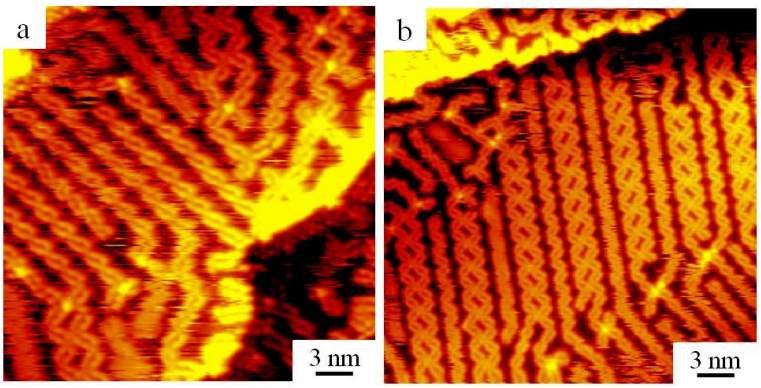

Figure S5. Large-scale STM images of structures obtained after annealing at 390 K for 10 minutes showing a tendency of forming chains in higher temperatures.

The final determination on the $1mC_4Na_2$ model has gone through three steps: the consecutive identifications of 1. molecular chirality and direction; 2. position of metal and how it interacts with surrounding molecules; 3. intermolecular hydrogen bonds. Firstly, according to the sub-molecular resolution of the 1mC molecules within metal-organic motifs (as shown below, Figure xa), the brighter part of 1mC molecule indicated by white arrows is assigned to methyl group, thus heterochiral molecules with methyl groups facing Cl linkages are confirmed (note that the case of homochiral molecules is also calculated, and as expected, which is less stable by ~ 0.33 eV, cf. Figure S6b shown below). Secondly, we find out that two kinds of binding modes can be proposed as Na coordinating to two O atoms or coordinating to two O atoms and one N atom simultaneously. DFT calculations show that only the latter condition is stable. Thirdly, within the motif, based on the morphology of metals and molecules, intermolecular NH···N or NH···O hydrogen bonds can be speculated, and the model with NH···O hydrogen bonds is less stable by ~0.38 eV (Figure S6c). Finally, we choose the most stable model (Figure S6d) and superimpose it on the STM image with good agreement as shown in the manuscript.

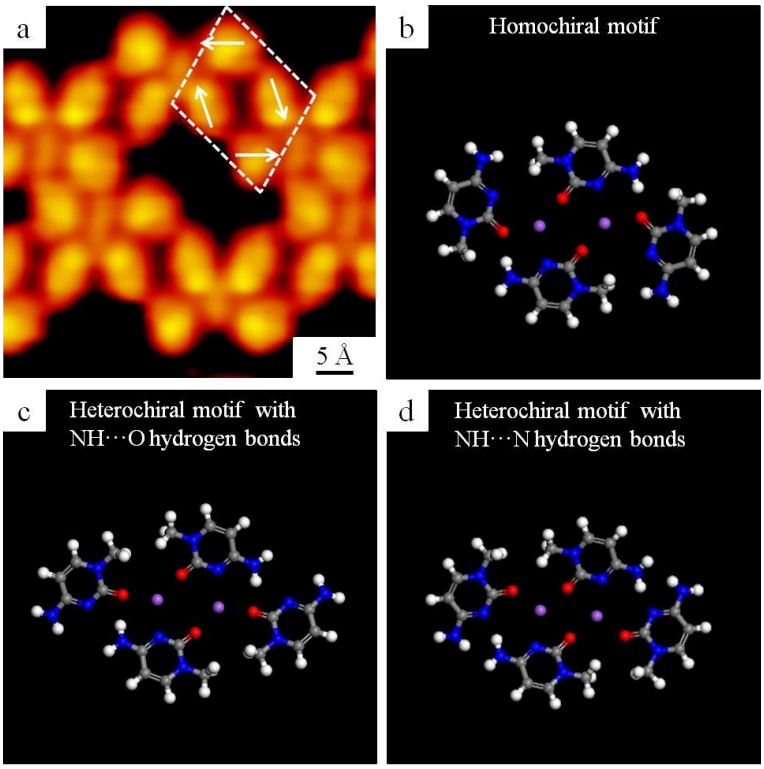

Figure S6. (a) STM image helps to confirm the chirality and direction of molecules within motifs where the arrows indicate methyl groups. (b) homochiral motif. (c) heterochiral motif with NH···O hydrogen bond. (d) heterochiral motif with NH···N hydrogen bond. H: white; C: gray; N: blue; O: red; Na: pink; Cl: green.

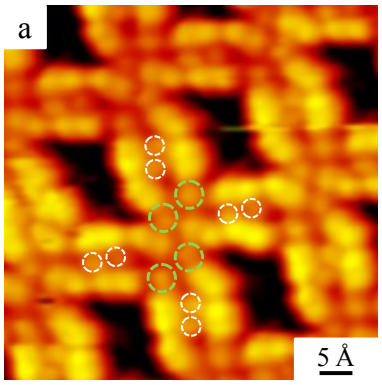

Figure S7. STM image with special tip state illustrating both Na (in white circles) and Cl (in green circles) ions simultaneously.

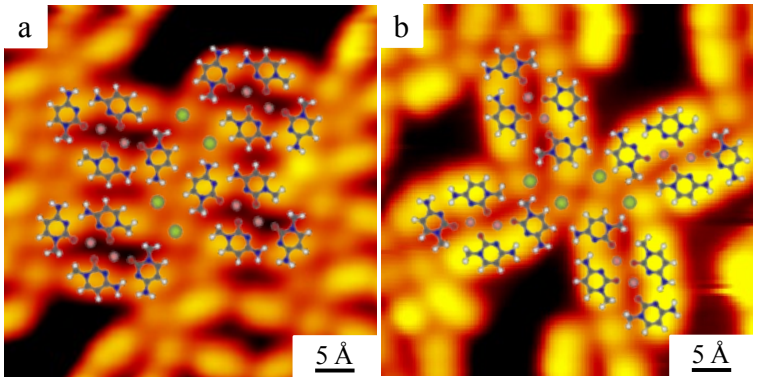

Figure S8. Conjugations of (a) linear and (b) zigzag chains with tentative models illustrating the typical binding sites, respectively.

1. F. Besenbacher, *Rep. Prog. Phys.*, 1996, **59**, 1737.
2. E. Laegsgaard, L. Österlund, P. Thostrup, P. B. Rasmussen, I. Stensgaard and F. Besenbacher, *Rev. Sci. Instrum.* 2001, **72**, 3537.
3. G. Kresse and J. Hafner, *Phys. Rev. B*, 1993, **48**, 13115.
4. G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169.
5. P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953.
6. G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758.
7. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
8. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.