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Supplementary information:

On-surface assembly of low-dimensional Pb-coordinated metal-organic structures

Guoqing Lyu,[a] *Ran Zhang,*[a] *Xin Zhang,*[b] *Pei Nian. Liu*[b]* *and Nian Lin*[a]*

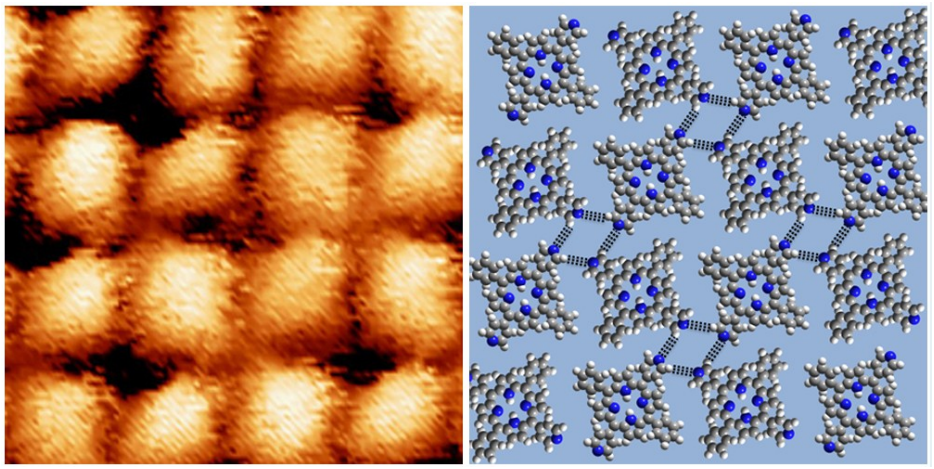
[a] *Department of Physics, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, China.*
[b] *Shanghai Key Laboratory of Functional Materials Chemistry and Institute of Fine Chemicals, East China University of Science and Technology, Meilong Road 130, Shanghai, China.*

Contents

1. **Closely-packed molecule islands formed out of 1 and Pb**

Molecules **1** were present on the Au(111) surface in a highly mobile 2D gas phase. After dosing Pb, closely-packed molecule islands appeared. Apparently, Pb atoms played significant roles for the formation of the molecules islands. Pb may be incoporated in the molecule islands in two possible ways: (1) to coordinate the pyridyl functions of **1** and (2) to metalate the porphyrin core of **1**.Suppose a Pb atom is positioned at the junction of four molecules and coordinated by pyridyl functions, the shortest N-Pb distance is 3.5 Å, which is far beyond the range of a Pb-N coordination bond of 2.5 A. Thus we argue that the islands are not a Pb-coordinated structure. Instead, they are stabilized via inter-molecular hydrogen bonds. Fig. SI-1a shows an STM topograph of a molecule islands and Fig. SI-1b shows a molecular model in which the possible hydrogen bonds are highlighted with the dashed lines. Note that the "holes" at the junctions of the closely-pack molecules appear dark or bright alternatively. Fig. SI-1b illustrates that the bright "holes" are formed by the pyridyl groups and characterized by four hydrogen bonds, and the dark "holes" are formed by the phenyls, without hydrogen bonds.

It is likely that Pb atoms metalate the porphyrin cores of the molecule. It is known that metallation of porphyrin core may alter the molecule-to-substrate interaction.[SI1] We speculate that this effect stabilizes the molecule islands.

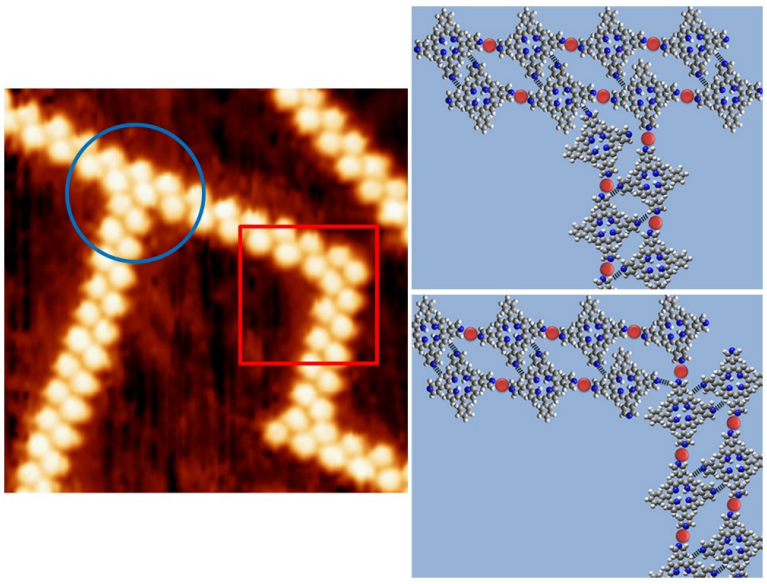


(a) (b)

Fig. SI-1 (a) STM topograph (6×6 nm^2) of a closely-packed island. (b) Molecular model in which the possible hydrogen bonds are highlighted with the dashed lines.

2. **Magnified STM images and molecular models of DR chains**

Fig. SI-2a shows a magnified STM topograph featuring a right-angle turn and a T-junction in the **DR** chains. Fig. SI-2b presents the structural models of these two structures.

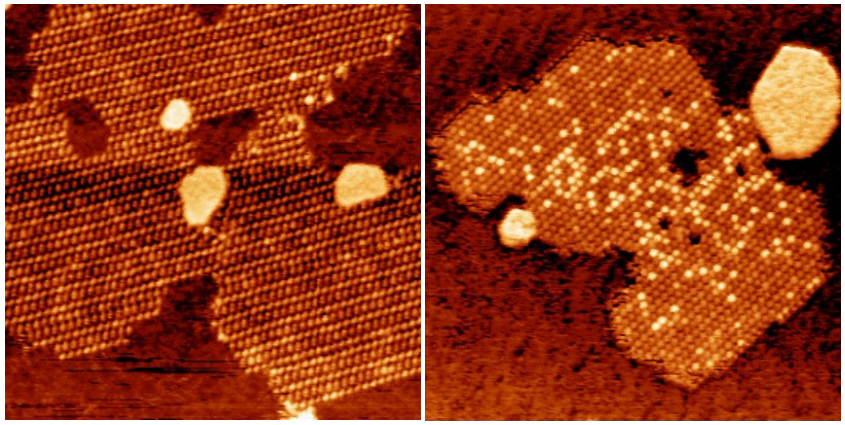


(a) (b)

Fig. SI-2 (a) STM topograph (6 × 6 nm^2) of **DR** chains with right-angle turn (in red square) and T-junction (in blue circle). (b) Molecular models of the two structures (up: T-junction; bottom: right-angle turn).

3. Closely-packed molecule islands formed out of 3 and Pb

Fig. SI-3a shows an STM topograph of a sample prepared with depositing Pb first and molecules **3** later on the Au(111) at room temperature. One can see that molecules **3** formed an extended closely-packed island surrounding the Pb islands. Fig. SI-3b shows an STM topograph of a sample prepared with depositing Pb and molecules **3** simultaneously on the Au(111) held at 80°C. The outcome of the simultaneous deposition is similar as the one shown in Fig. SI-3a. The brighter species are presumably metalated molecules. Thus, neither method led to well-ordered coordination structures. The molecule islands in both images have a structure that is identical to the case without Pb.[SI2]



(a) (b)

Fig. SI-3 STM topographs (70 × 70 nm^2)of (a) a sample prepared with depositing Pb first and molecules **3** later on the Au(111) at room temperature and (b) a sample prepared with depositing Pb and molecules **3** simultaneously on the Au(111) held at 80°C.

4. References

SI-1. S. Ditze, M. Stark, F. Buchner, A. Aichert, N. Jux, N. Luckas, A. Goerling, W. Hieringer, J. Hornegger, Hans-Peter Steinrueck, H. Marbach, *J. Am. Chem. Soc.* 2014, **136**, 1609–1616.

SI-2. Y. Li, J. Xiao, T. Shubina, M. Chen, Z. Shi, M. Schmid, H-P. Steinrueck, M. Gottfried, N. Lin, *J. Am. Chem. Soc.* 2012*,* **134**, 6401-6408.