

Hierarchical Formation of Fe-9eG Supramolecular Networks via Flexible Coordination Bonds

Supporting Information

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Experimental Section

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 instrumentations for sample preparations. 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 9eG molecules (purchased from Sigma-Aldrich, purity >98%) were loaded into a glass crucible in the molecular evaporator. After a thorough degassing, the molecules were deposited onto the Au(111) substrate by thermal sublimation at a molecular coverage of ~0.6 monolayer.

As the 9eG/Fe ratio is crucial to the construction of the supramolecular structures, delicate calibrations of Fe dosages have been performed. As the first step, Fe atoms are deposited on the clean Au(111) surface to regulate the emission currents of the evaporator and durations. Then we try to keep the molecular coverage (~0.6 monolayer) as a constant and vary the Fe dosages step by step (leading to the transformations from 9eG islands to G₄Fe₁, heterochiral G₃Fe₁ and then to homochiral G₄Fe₂ nanostructures). Finally, we find that by using the emission current of ~1.5 mA and duration of ~10 minutes, most of 9eG molecules are in the form of homochiral G₄Fe₂ nanostructures. We then take the above parameters as a reference. After calibrations, we co-deposit 9eG molecules and Fe atoms (by using such parameters) on Au(111) held at room temperature, and the sample was thereafter transferred within the UHV chamber to the STM, where measurements were carried out at ~100-150 K. As expected, we gain the formation of the homochiral networks constructed by homochiral G₄Fe₂ motifs as the elementary building units.

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} the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) exchange-correlation functional was employed,⁷ and van der Waals interactions were included using the dispersion-corrected DFT-D2 method of Grimme⁸ for the calculations when including the gold surface. The atomic structures were relaxed using the conjugate gradient algorithm scheme as implemented in the VASP code until the forces on all unconstrained atoms were ≤ 0.03 eV/Å.

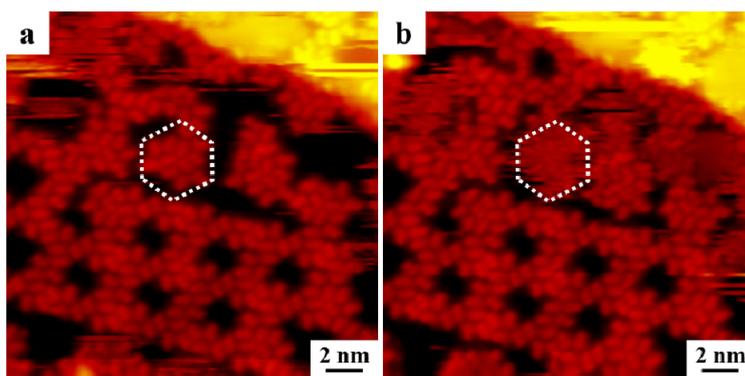


Figure S1. Continuous STM images showing the diffusion of an individual big cluster as a whole entity.

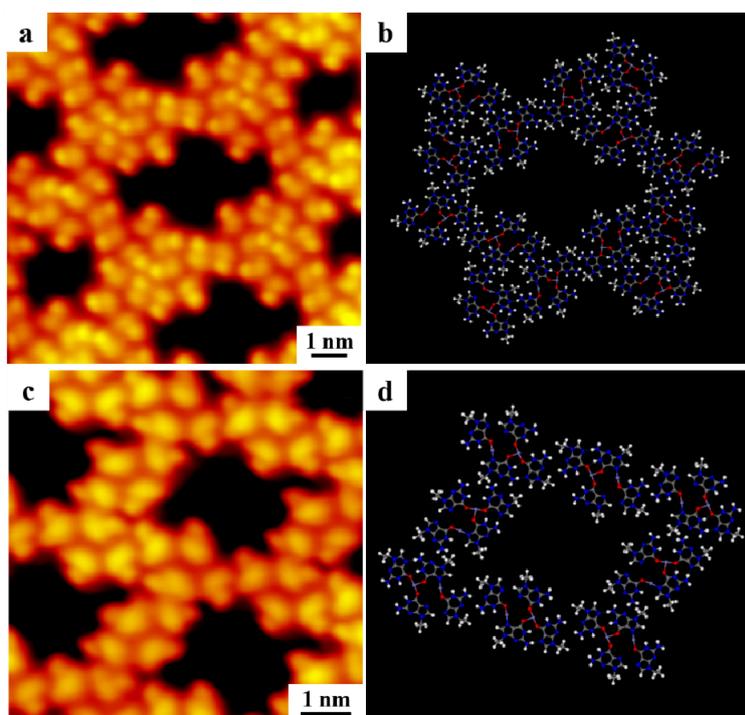


Figure S2. (a) and (c) STM images and (b) and (d) the corresponding tentative structural models showing the porous networks with two kinds of cavities.

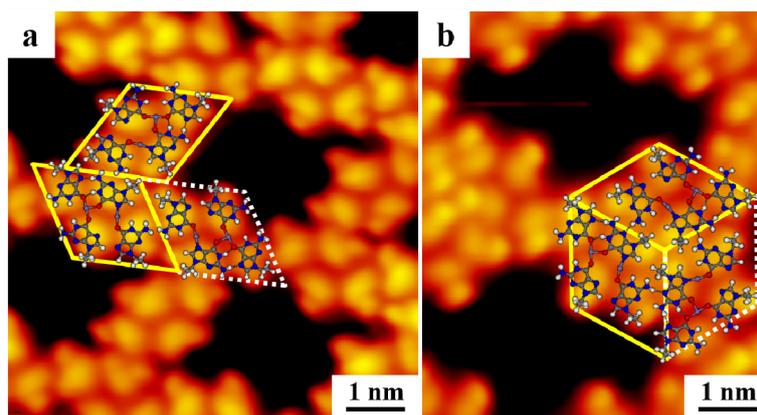


Figure S3. STM images showing the comparison between the two kinds of heterochiral networks, where the connecting motifs and clusters are marked. The parts highlighted by yellow rhombuses are nearly the same, and the only difference exists in the adsorption directions of the remaining motifs marked by white dashed rhombuses, which leads to the different secondary inter-motif interactions (weak hydrogen bonds and vdWs interactions) and then different nano-patterns.

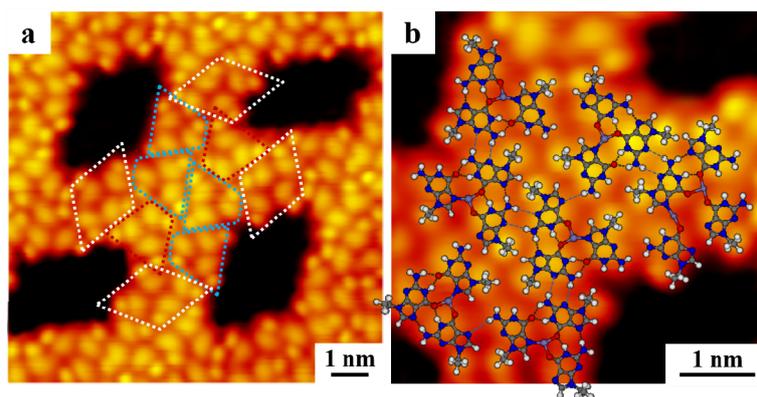


Figure S4. (a) STM image showing the composition of the network in which heterochiral G_4Fe_2 motifs and heterochiral G_3Fe_1 ones are involved as depicted by white rhombuses and trapezoids (red and blue represents two chiralities), respectively. (b) High-resolution STM image of such network which is superimposed with the tentative structural models.

References

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