Electronic Supplementary Material (ESI) for Chemical Communications


Supporting information

# Ni-induced supramolecular structural transformation of cytosine on Au(111): from one-dimensional chains to zero-dimensional clusters

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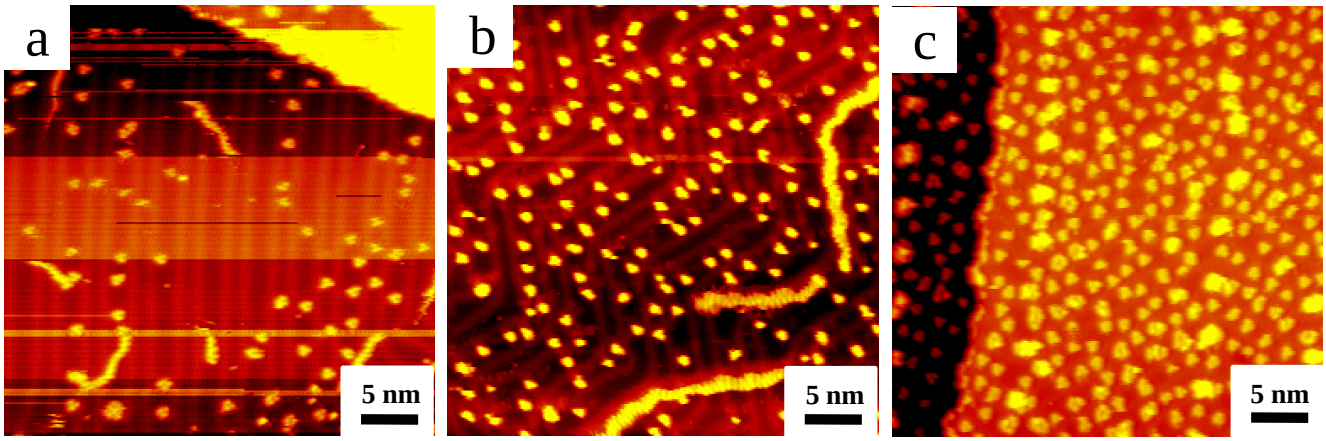


***Figure S1.*** STM images show 0-D clusters formed by codeposition of cytosine and Ni with increased surface coverage. The lack or excess of Ni would lead to co-existence of chains and clusters (cf. a and b) or presence of small Ni islands (cf. c).

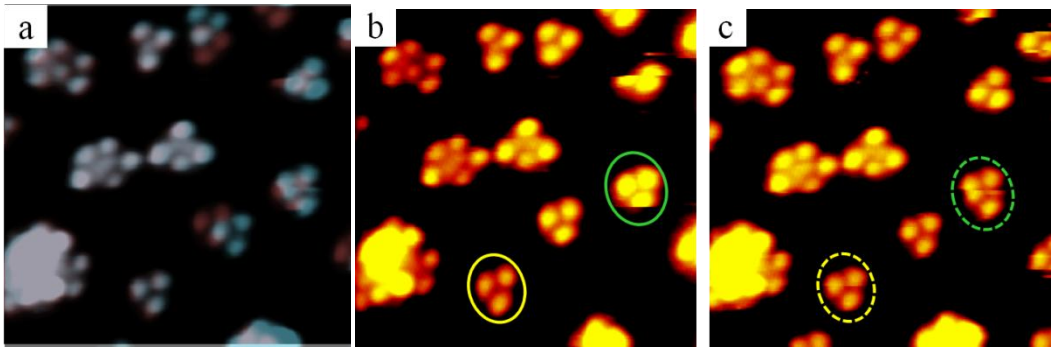


***Figure S2.*** (a) Overlay of two STM images (b and c) taken with a time interval of 6.5 s indicates the cluster could diffuse on the surface (tunnel current 0.75 nA, sample voltage 1.2 V, scanning temperature at 150 K). Red (blue) indicates the initial (final) positions of the clusters, and stationary parts appear gray. (b) and (c) are the two original images of (a), the yellow ellipses indicate that the irregular triangular cluster could evolve into equilateral triangular cluster, the green ellipses indicate that the equilateral triangular cluster could also evolve into irregular triangular cluster.

Note that the high-resolution STM image shown in Figure 2a reveals that the clusters are typically imaged as equilateral triangular species, however, some irregular triangular species also exist. From time-lapse sequences of STM images we find that both the equilateral and irregular triangular species diffuse on the surface even at scanning temperature of 150K, as illustrated by the superimposition of two sequential STM images shown in Figure above. Thus, some equilateral triangular species could evolve into irregular ones during scanning and vice versa.

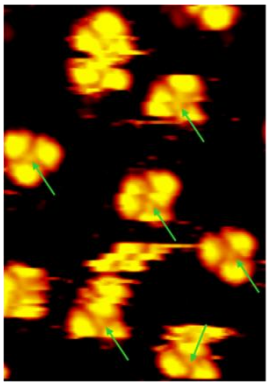

***Figure S3.*** When scanning with a special tip state a bright spot could be resolved in the center of the cluster, which is attributed to the contribution related to Ni atoms.

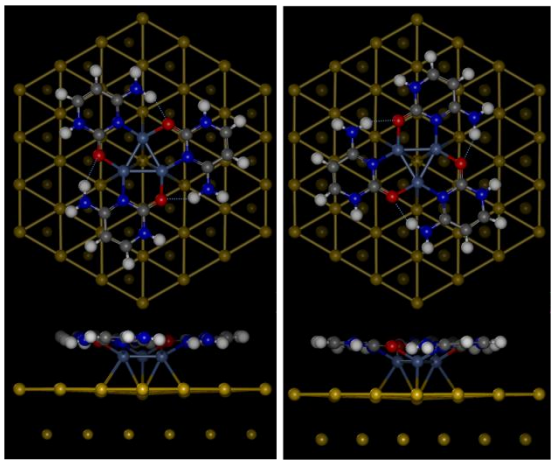

***Figure S4.*** Top and side views of the DFT optimized models of triangular clusters A and C.

All STM experiments were performed in a UHV chamber (base pressure $1 \times 10^{-10}$ mbar) equipped with the variable-temperature, fast-scanning Aarhus STM,[1,2] a molecular evaporator and an e-beam evaporator, and other standard facilities for sample preparation. The Au(111) substrate was prepared by several cycles of 1.5 keV $Ar^+$ sputtering followed by annealing to 770K for 15 min resulting in clean and flat terraces separated by monatomic steps. The cytosine molecules were loaded into a glass crucible in the molecular evaporator. After a thorough degassing, cytosine molecules were deposited onto the clean substrate by thermal sublimation at 370 K. Ni atoms were sequentially deposited onto the cytosine-covered surfaces at RT by using the electron beam evaporator. 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, and the Perdew-Burke-Ernzerhof generalized gradient approximation exchange-correlation functional was employed,[5] and van der Waals (vdW) interactions were included using the dispersion-corrected DFT-D2 method of Grimme.[6] 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 $\leqslant$0.03 eV/Å. The simulated STM images were based on the Tersoff-Hamann method.[7]

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