

**Real-space evidence of the formation of GCGC tetrad  
and its competition with G-quartet  
on the Au(111) surface**

***Electronic supplementary information***

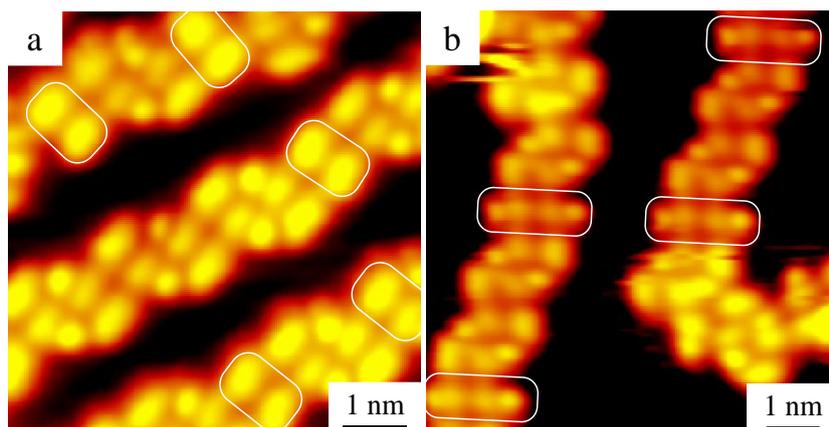
**Yuanqi Ding, Lei Xie, Chi Zhang, Wei Xu\***

Interdisciplinary Materials Research Center, Tongji-Aarhus Joint Research Center for  
Nanostructures and Functional Nanomaterials, College of Materials Science and Engineering,  
Tongji University, Shanghai 201804, P. R. China

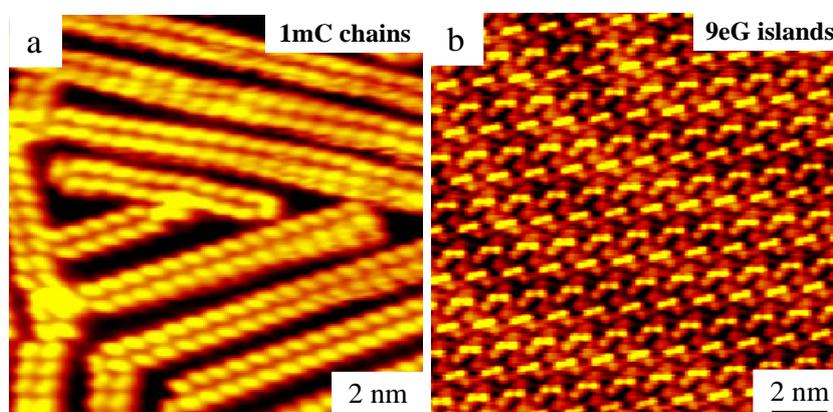
E-mail: [xuwei@tongji.edu.cn](mailto:xuwei@tongji.edu.cn)

All STM experiments were performed in a UHV chamber (base pressure  $1 \times 10^{-10}$  mbar) equipped with a variable-temperature, fast-scanning “ Aarhus-type ” STM using electrochemically etched W tips purchased from SPECS,<sup>1, 2</sup> 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<sup>+</sup> sputtering followed by annealing to 820 K for 15 min, resulting in clean and flat terraces separated by monatomic steps. The 9eG molecules (purchased from Sigma-Aldrich, purity >98%), 1mC molecules (purchased from Bide Pharmatech Ltd., purity >97%) and NaCl (purchased from Sigma-Aldrich, purity >99%) were loaded into different glass crucibles in the molecular evaporator. I<sub>2</sub> (purchased from Sigma-Aldrich, purity >99%) were dosed in-situ onto the surface through a leak valve at a pressure of  $\sim 10^{-7}$  mbar for 1 min. After a thorough degassing, the molecules were deposited onto the Au(111) substrate by thermal sublimation, respectively. The sample was thereafter transferred within the UHV chamber to the STM, where measurements were carried out at  $\sim 150$  K. Scanning conditions:  $I_t = 0.5\sim 0.8$  nA,  $V_t = \sim 1200$  mV. All of the STM images were further smoothed to eliminate noises.

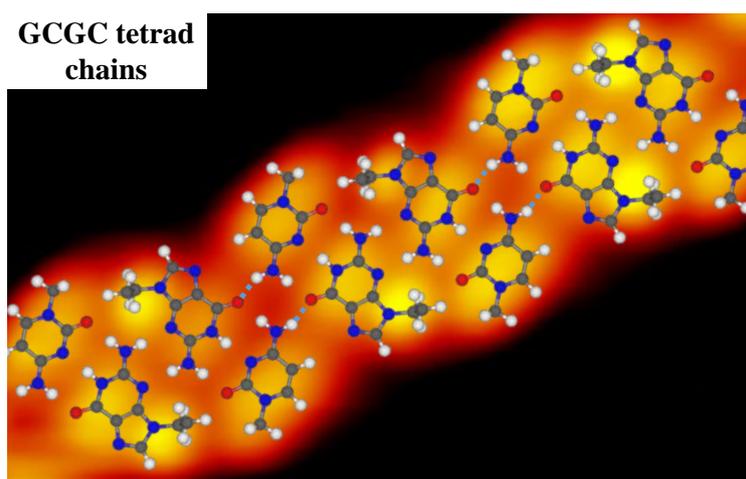
The calculations were performed in the framework of DFT by using the Vienna *ab initio* simulation package (VASP).<sup>3, 4</sup> The projector-augmented wave method was used to describe the interaction between ions and electrons;<sup>5, 6</sup> the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) exchange-correlation functional was employed,<sup>7</sup> and van der Waals interactions were included using the dispersion-corrected DFT-D3 method of Grimme<sup>8</sup> 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  $\leq 0.03$  eV/Å. The simulated STM images were obtained by the Hive program based on the Tersoff Hamann method,<sup>9, 10</sup> and performed at the same bias voltage of scanning conditions.



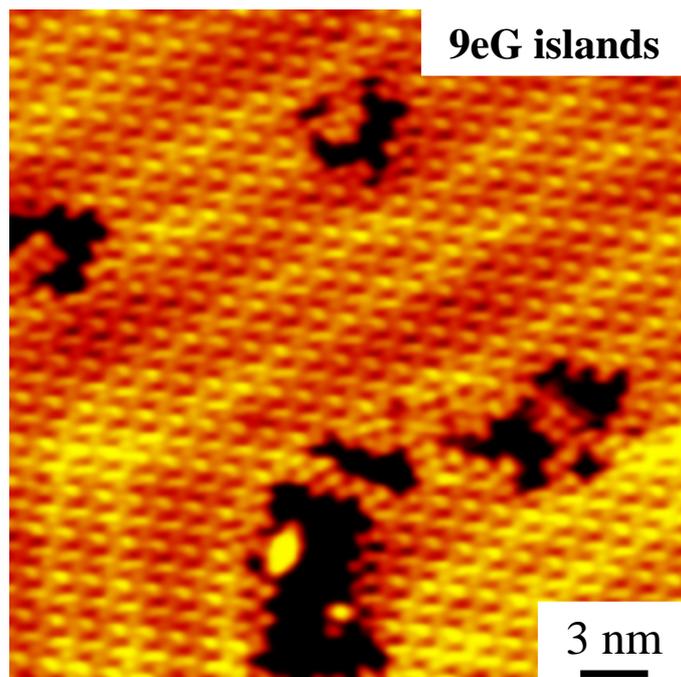
**Figure S1.** STM images of GCGC chains with GCGC tetrads separated by (a) 1mC dimers and (b) 9eG dimers when controlled 9eG/1mC ratio less/more than 1:1, respectively. The 1mC dimers and 9eG dimers are indicated by white rectangles in (a) and (b), respectively.



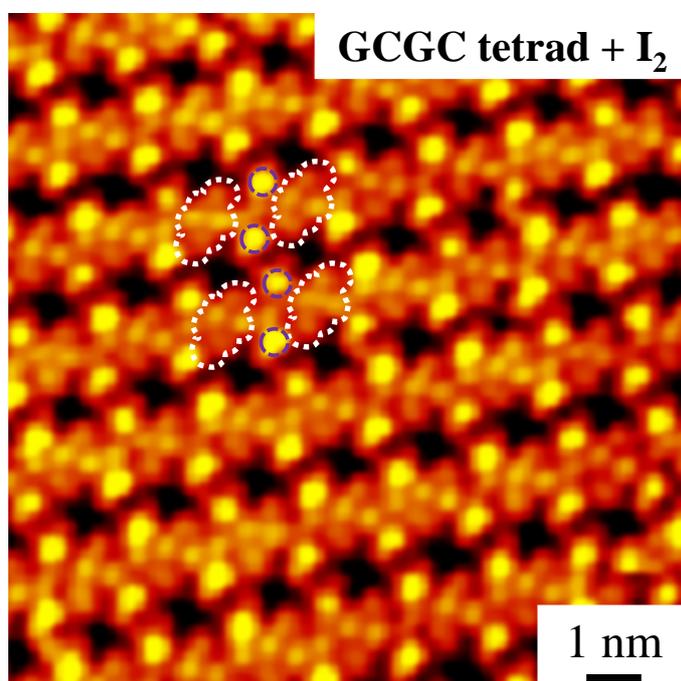
**Figure S2.** STM images of self-assembled structures of (a) 1mC molecules and (b) 9eG molecules.



**Figure S3.** High-resolution STM image of a single GCGC tetrad chain superimposed with the DFT-optimized gas-phase model. Hydrogen bonds between GCGC tetrads are depicted by blue dashed lines. H: white; C: gray; N: blue; O: red.



**Figure S4.** Formation of the 9eG islands after annealing the GCGC tetrad chains to the desorption temperature of the 1mC molecules at 420 K.



**Figure S5.** Formation of GCGC-I structure after dosing I<sub>2</sub> on the GCGC-precovered surface. The GCGC tetrads are depicted by white contours and the I atoms are indicated by purple circles.

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.
9. J. Tersoff and D. Hamann, *Phys. Rev. B*, 1985, **31**, 805.
10. D. E. Vanpoucke and G. Brocks, *Phys. Rev. B*, 2008, **77**, 241308.