Electronic Supplementary Material (ESI) for ChemComm.

Real space evidence of Watson-Crick and Hoogsteen adenine-uracil base pairs on Au(111)

Electronic supplementary information

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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 820 K for 15 min, resulting in clean and flat terraces separated by monatomic steps. The adenine molesules (purchased from Sigma-Aldrich, purity >99%), uracil molecules (purchased from Sigma-Aldrich, purity >98%) 1-ethyluracil molecules (purchased from Sigma-Aldrich, purity >99%) and 9-methyladenine molecules (purchased from Tokyo Chemical Industry Development Co., Ltd., purity >97%) were loaded into different glass crucibles in the molecular evaporator. 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 ~150 K. Scanning conditions: I_t = 0.5~0.8 nA, V_t = ~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).[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-D3 method of Grimme[8] for the calculations. 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. The size of the cells are auto-optimized by VASP with the parameter ISIF=4 in the INCAR (16.01×14.43×10.00 Å in Figure 1b, 8.67×15.34×10.00 Å in Figure 1d, 42.17×14.92×10.00 Å in Figure 4c, 8.51×11.98×10.00 Å in Figure 4e). The simulated STM images were obtained by the Hive program based on the Tersoff Hamann method,[9, 10] and performed at the same bias voltage of scanning conditions with 2 layers of gold as the simplified model.

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