Electronic Supplementary Material (ESI) for ChemComm.

Scission and Stitching of Adenine Structures by Water Molecules

Supporting Information

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Experimental details

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 instrumentation for sample preparation. 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 adenine molecule was purchased from Sigma-Aldrich (purity > 99%). The pure distilled water was loaded in a dosing tube positioned in the preparation chamber and further purified under vacuum by several freeze-thaw cycles to remove remaining impurities.[3] After a thorough degassing, the A molecules were deposited onto the Au(111) surface by thermal sublimation. Water molecules were then continuously dosed *in situ* onto the Au(111) surface through a leak valve at different pressures for 10 minutes. The sample was thereafter transferred within the UHV chamber to the STM, where measurements were carried out at ~150 K. All the STM images were further smoothed to eliminate noises. The lateral manipulations were carried out in a controllable line-scan mode under specific scanning conditions (by increasing the tunnel current up to approximately 2.0 nA while reducing the tunnel voltage down to approximately 20 mV).[4,5]

The calculations were performed in the framework of DFT by using the Vienna ab initio simulation package (VASP).[6,7] The projector-augmented wave method was used to describe the interaction between ions and electrons;[8,9] the Perdew-Burke-Ernzerhof generalized gradient approximation exchange-correlation functional was employed,[10] and van der Waals interactions were included using the dispersion-corrected DFT-D3 method of Grimme.[11] 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 simulated STM images were obtained by the Hive program based on the Tersoff-Hamann method.[12,13]

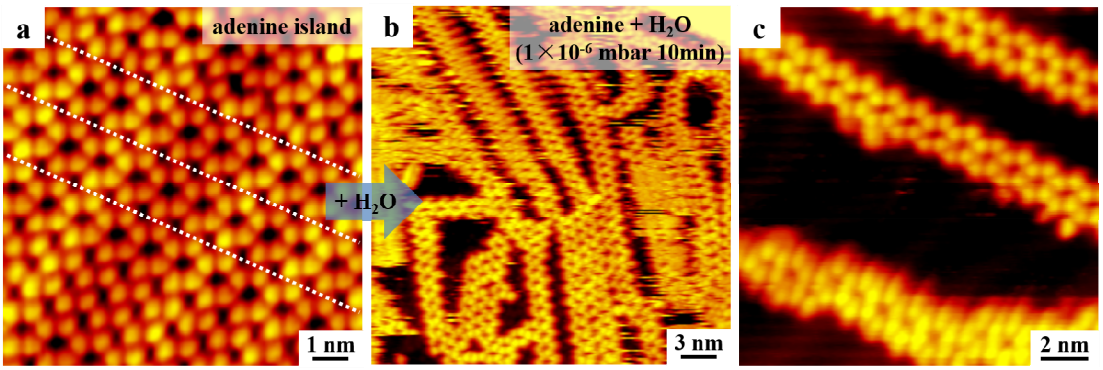

Figure S1. (a) STM image showing the adenine island structure, where molecular rows are made up of characteristic six-membered rings of adenine molecules as separated by dotted lines. (b) Large-scale STM image showing the appearance of single adenine molecular rows after exposing the adenine island structure to the water atmosphere at a pressure of ~1×10^{-6} mbar for 10 min (held at RT). (c) Close-up high-resolution STM image showing the morphology of the single adenine molecular rows, which is in good accordance with the ones in the self-assembled adenine island. Scanning conditions: I_t = 0.7 nA, V_t = −1.5 V.

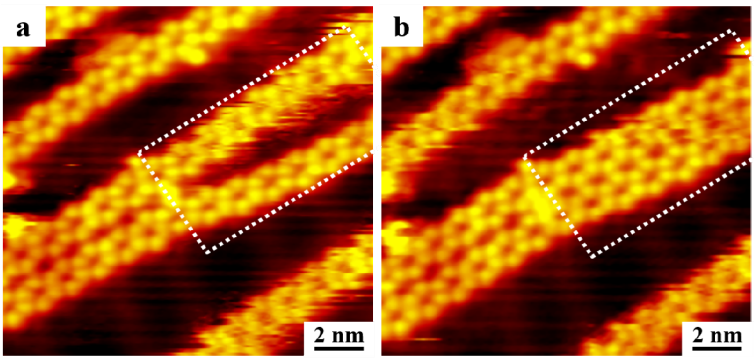

Figure S2. Sequential STM images scanned in the same region showing that two rows can wobble around reforming the A island structure via inter-chain hydrogen bonds as highlighted by the rectangles. Scanning conditions: I_t = 0.7 nA, V_t = 1.8 V.

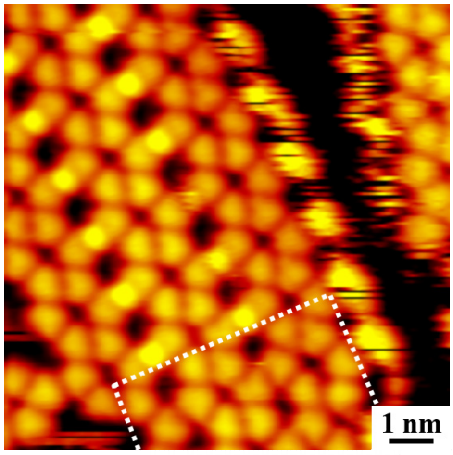

Figure S3. STM image showing the coexistence of a small patch of the intact A self-assembled structure (the highlighted part) and the A-H_2O structure in one island.

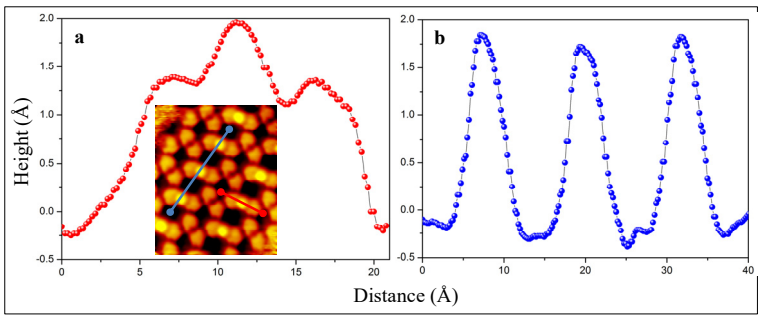

Figure S4. The corresponding line profiles along the red and blue lines marked in the STM image (inset in a), respectively.

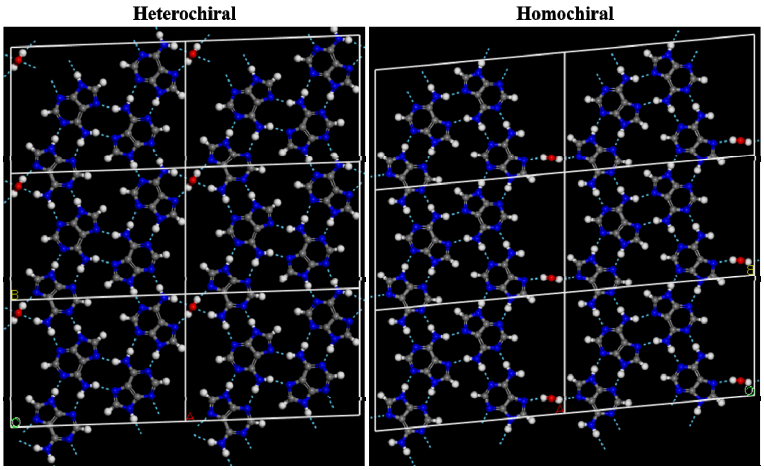

Figure S5. The DFT-optimized structural models for the two kinds of A-H_2O islands (with heterochiral and homochiral adenine molecules involved), where the unit cells are slightly different.

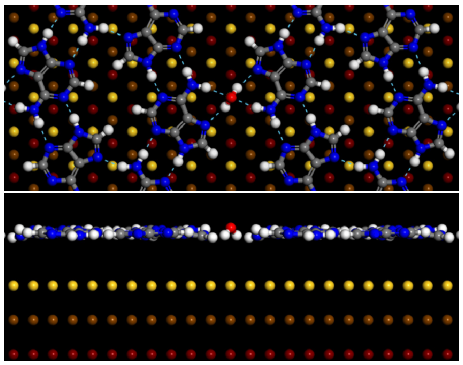

Figure S6. Top and side views of the DFT-optimized structural model for the A-H_2O island (with heterochiral adenine molecules, for example) including the gold substrate, where the water molecule is still a little bit higher than the adenine molecular plane and O atom of water molecule is positioned at the highest point out of the A molecular plane, which is similar to the corresponding gas-phase structural model. Such configuration results in the bright protrusions in the STM images and agrees with the line profile.

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