Supplementary Material: Observation of Simplest Water Chains on Surface Stabilized by a Hydroxyl Group at One End

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Method

The experiment was carried out in a homebuilt low-temperature scanning tunneling microscope with base pressure lower than 3.0×10^{-11} Torr. The Au(111) substrate was prepared by repeated cycles of argon-ion sputtering and annealing at 900 K until a clean Au(111)-$22 \times \sqrt{3}$ reconstructed surface was obtained. Water molecules (Alfa Aesar) were deposited onto the surface of Au(111) crystal hold at the cold STM stage around 17 K, after cycles of freeze−pump−thaw purification. The STM tip was prepared first by electrochemical etching, resulting in a typical radius of curvature of about 20 nm. The oxide layer was then removed by annealing in ultra-high-vacuum. Self-sputtering and field-emission were employed to further improve the conductivity at the tip end. The functionalized tip was achieved by *in-situ* poking on small water clusters with a voltage pulse about 2V and tip extension by a few Angstroms. The life time of such water molecule terminated tip is limited to a few hours, and it has to be treated with extreme care during manipulation. Image processing was performed in Nanotec WSxM[1] software.

Height profiles of Armchair and Zigzag water chains

In order to figure out the atomic structures of the observed water chains in Figure 1, we carefully examined the height profiles of the Armchair and Zigzag chains, and the results are as follows. Except for the two ends, the apparent heights of water molecules are around 0.90 Å. Both chains show a common feature in height profiles, *i.e.*, the second water molecule is the most protruded from surface (~1.0 Å) and the water molecule at the other end presents as a nadir (~0.8 Å) of the structure. The averaged distance between two water molecules is about 2.95 Å.

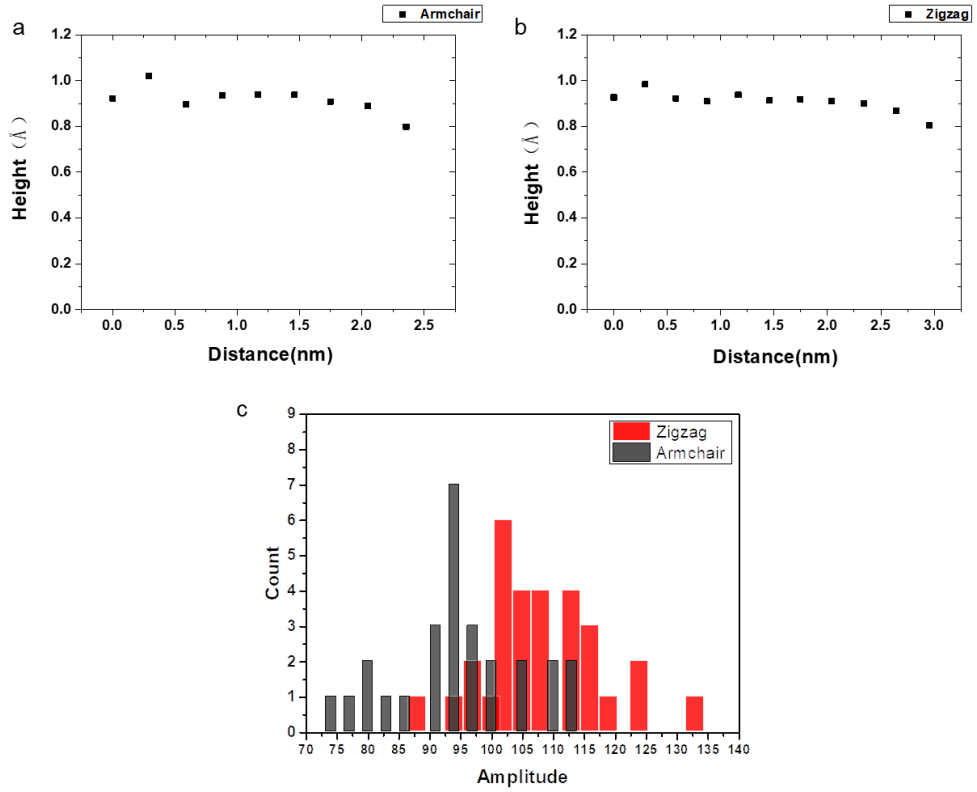

Figure S1 Height profile of water chain with armchair configuration (a) and zigzag configuration (b). (c) Statistics of O-O-O angles in water chains. The mean angle for the zigzag configuration is about 94°, and for the armchair configuration it is about 108°. The standard deviation is about 10°.

More topographic images of water chains

Various water chains of different length and configurations are observed, as listed below. All water chains present a depression at one end of the chain. We note that the emerge of water chains is of very low probability, less than one percent of the ring structures.

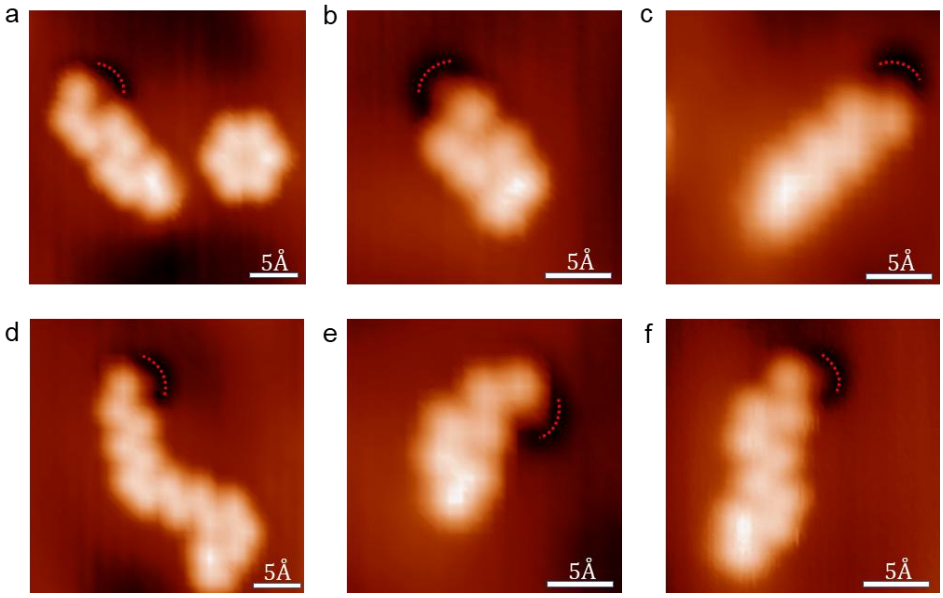

Figure S2 Topographic images of various water chains. (a) An armchair water chain consists of 9 water molecules, with a water hexamer at side. (b) An armchair water chain consists of 6 water molecules. (c) A zigzag water chain consists of 7 water molecules. (d)-(f) Irregular water chains consists of 16, 10, 7 water molecules, respectively. All of them show a common feature at one end of the chains, as indicated by the dotted line.

Reference

[1] Horcas I, Fernández R, Gomez-Rodriguez J, Colchero J, Gómez-Herrero J and Baro A 2007 *Rev. Sci. Instrum.* **78** 013705