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Supplementary Materials for

Oxygen-induced self-assembly of quaterphenyl molecule on metal surfaces

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Methods

All the STM experiments were performed in a UHV chamber (base pressure 1×10^{-10} mbar) equipped with a variable-temperature "Aarhus-type" STM.[1,2] a molecular evaporator and standard facilities for sample preparation. After the system was thoroughly degassed, the 4Ph molecules were deposited by thermal sublimation onto the substrates. The oxygen molecules with 99.99% purity were dosed through a leak valve into the chamber. For a typical molecular coverage (~0.1 ML) in the experiments, the dosage of the oxygen was at about 0.1 Langmuir if not mentioned in the manuscript. The STM measurements were performed in a typical temperature range of 100 K−150 K, and scanning conditions: I_t = 0.5~1.0 nA, V_t = -1500 ~ -2500 mV.

All of 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] and the Perdew−Burke−Ernzerhof generalized gradient approximation exchange−correlation functional was employed,[6] and van der Waals (vdW) interactions were included using the dispersion corrected DFT-D2 method of Grimme.[7] The atomic structures were relaxed until the forces on all unconstrained atoms were ≤ 0.03 eV/Å.

The slab models for the self-assembled nanostructures of the 4Ph molecule on both Ag(110) and Cu(110) include two layers of substrate atoms and 15Å vacuum along the surface normal, with the bottom layer fixed at their bulk positions. The parameters of the unit cell were determined from the experimental results. The simulated STM images were based on the Tersoff -Hamann method.

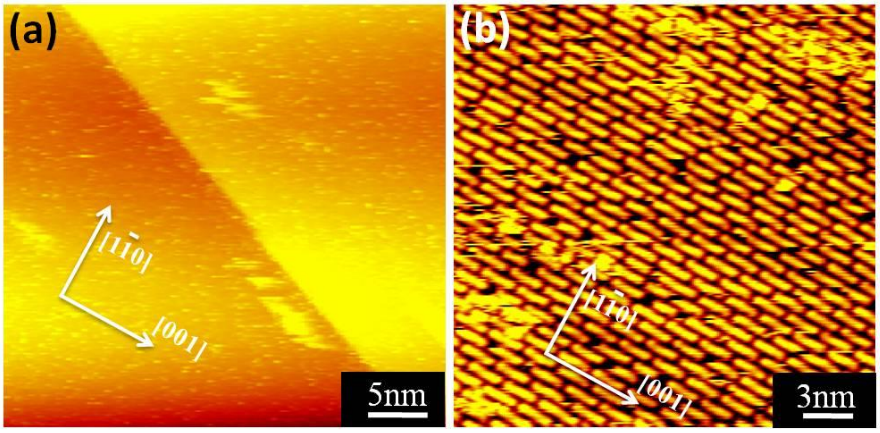

Fig. S1. The STM images showing after deposition of 4Ph molecules on Ag(110) at a (a) low coverage and (b) high coverage.

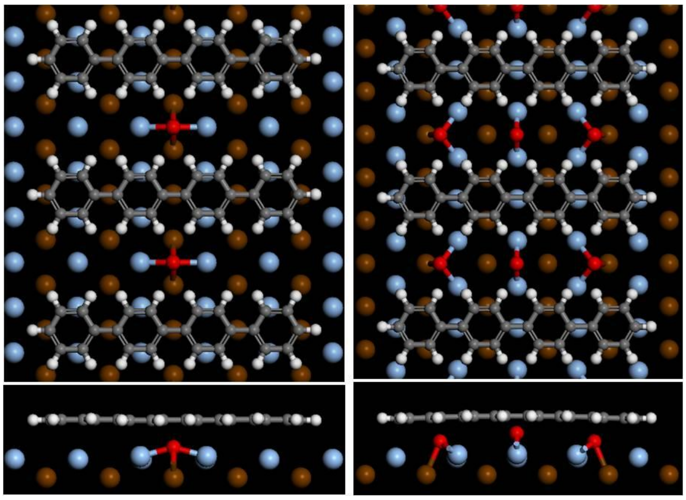

Fig. S2. The possible relaxed models involving one (left panel) and three (right panel) oxygen atoms in-between the adjacent 4Ph molecules on Ag(110).

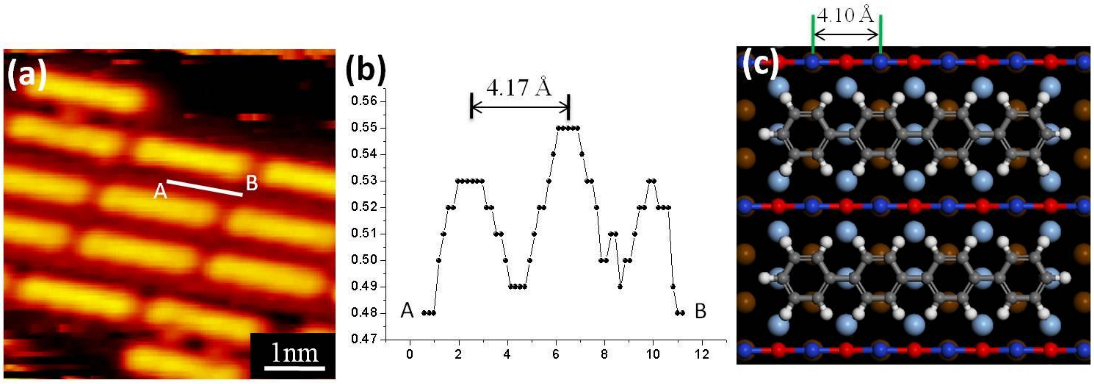

Fig. S3. (a) STM image showing the nanostructure formed by Ag-O single chains and 4Ph molecules. (b) Line profile along the chain structure as indicated by the white line A-B in (a), which is composed of bright protrusions with the spacing of about 4.17 Å. (c) DFT optimized model of the 4Ph/Ag-O nanostructure, where the theoretical Ag-Ag distance of the Ag-O chain is measured to be 4.10 Å.

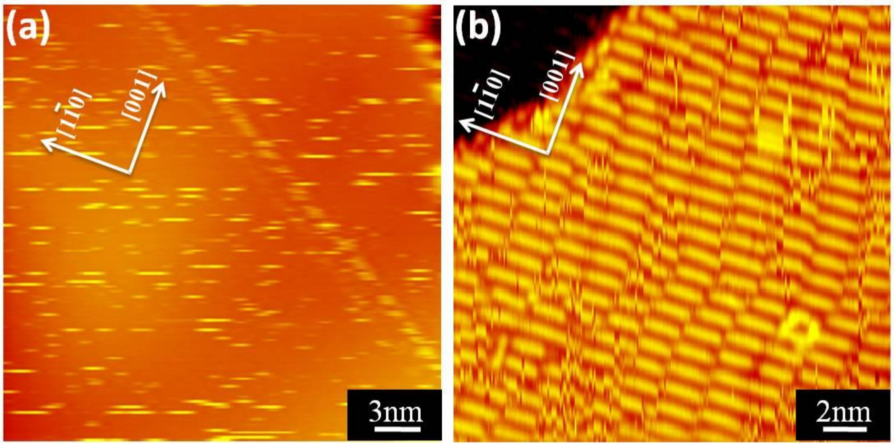

Fig. S4. The STM images showing after deposition of 4Ph molecules on Cu(110) at a (a) low coverage and (b) high coverage.

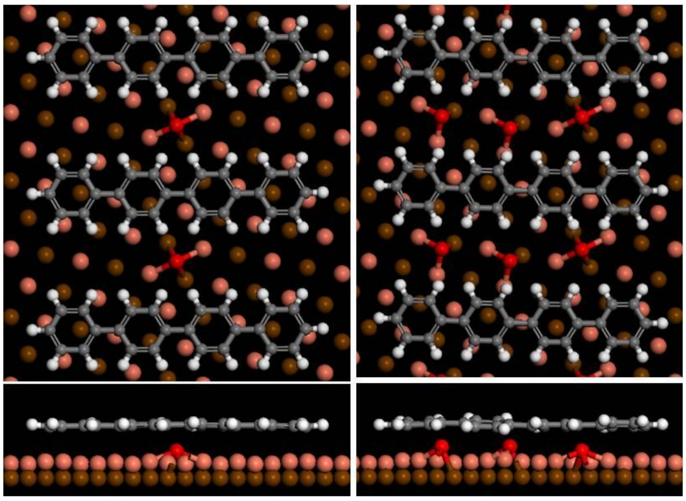

Fig. S5. The possible relaxed models involving one (left panel) and three (right panel) oxygen atoms in-between the adjacent 4Ph molecules on Cu(110).

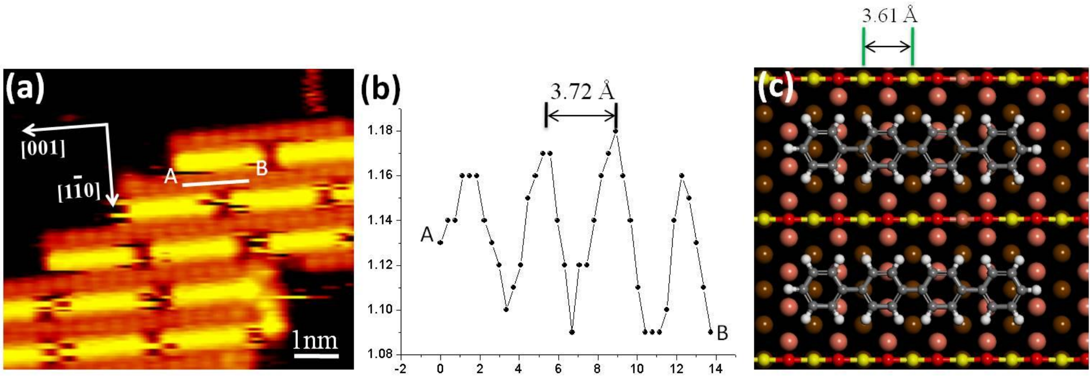

Fig. S6. (a) STM image showing the nanostructure formed by Cu-O single chains and 4Ph molecules. (b) Line profile along the chain structure as indicated by the white line A-B in (a), which is composed of bright protrusions with the spacing of about 3.72 Å. (c) DFT optimized model of the 4Ph/Ag-O nanostructure, where the theoretical Cu-Cu distance of the Cu-O chain is measured to be 3.61 Å.

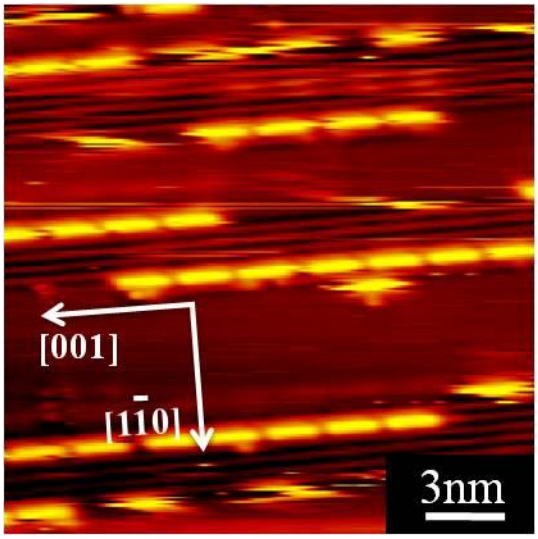

Fig. S7. The STM image showing 4Ph molecules grow at the edges of Cu-O (2×1) chains, which is formed by deposition of oxygen molecules on Cu(110) at RT followed by 4Ph molecules.

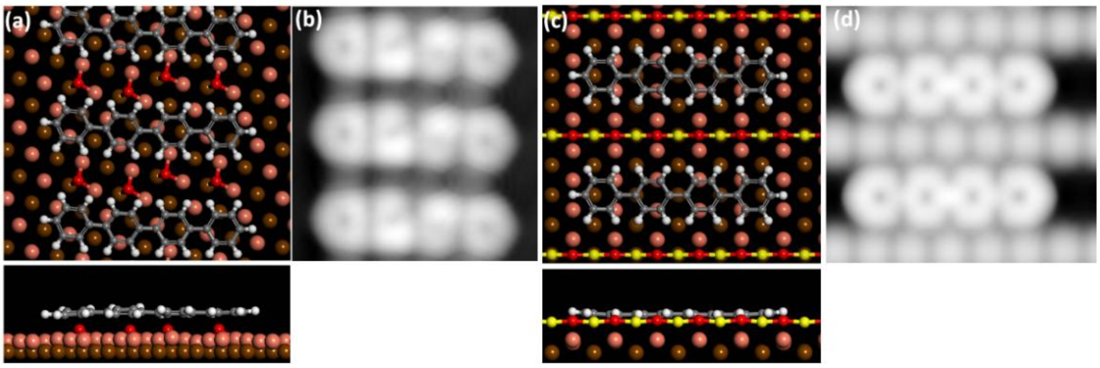

Fig. S8. (a) DFT model of the nanostructure formed by 4Ph and oxygen atoms on Cu(110) and (b) its corresponding STM simulation where the oxygen atoms could be hardly resolved. (c) DFT optimized model of the 4Ph/Cu-O nanostructure and (d) its corresponding STM simulation where the Cu-O chain could be clearly resolved.

References:

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