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Oxygen-induced self-assembly of quaterphenyl molecules on metal surfaces†

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From high-resolution UHV-STM imaging and DFT calculations we have demonstrated a novel method to construct well-ordered molecular nanostructures of an unfunctionalized aromatic molecule (4Ph) on both Ag(110) and Cu(110) by introducing oxygen molecules.

The construction of ordered self-assembled nanostructures on surfaces has aroused considerable attention because of their wide range of potential applications in both scientific and technological fields.^{1–3} Various kinds of interactions such as hydrogen bonding,^{4–7} van der Waals forces,^{8–10} metal–ligand ionic bonding^{11–13} and metal–ligand coordination bonding^{14–16} have been employed to construct surface supramolecular nanostructures *via* bottom-up fabrication. However, these strategies greatly depend on the specific functional groups decorated on molecular precursors. Certain efforts on chemical synthesis are required to modify the molecular precursors for further self-assembly process. Therefore, it would be of general interest to find a way to grow ordered surface nanostructures through unfunctionalized molecular precursors, which will be a supplement to the present self-assembly process. In the field of on-surface dehalogenation reactions, the detached halogen atoms from molecular precursors are usually located in between the formed molecular nanostructures before desorption.^{17–19} Recently, it has been indicated that the detached bromine atoms could interact with aromatic molecules *via* electrostatic interactions due to their high electronegativity.^{20,21} Thus, inspired from this, it should be particularly interesting to explore the interactions between high-electronegativity atoms and aromatic molecules with the aim of developing a novel on-surface self-assembly method.

In this work, we chose a quaterphenyl molecule (shortened as 4Ph), which is a typical aromatic molecule without any specific functional groups. It has been demonstrated that oxygen molecules could spontaneously dissociate into oxygen atoms after deposition on, *e.g.*, Ag(110) and Cu(110) below room temperature (RT).^{22–25} From the interplay of high-resolution scanning tunneling

microscopy (STM) imaging and density functional theory (DFT) calculations, we demonstrate that the 4Ph molecules could be arranged by oxygen atoms into well-ordered nanostructures on both Ag(110) and Cu(110), in which oxygen atoms are considered to be located in between 4Ph molecules to facilitate the formation of ordered molecular arrangements by electrostatic interactions. Meanwhile, we also observe another phase where the 4Ph molecules are aligned along the Ag–O/Cu–O chains on Ag(110) and Cu(110), respectively, which is attributed to the well-known templating effect of Ag–O/Cu–O.^{23,26,27} The DFT calculations on the optimized models and electrostatic potential maps are performed to elucidate the observed nanostructures. These findings exhibit a novel method for constructing on-surface nanostructures of a simple unfunctionalized aromatic molecule, which could be an alternative route for molecular self-assembly on surfaces.

After deposition of 4Ph molecules on Ag(110) at a low molecular coverage (~ 0.1 ML), we find that the molecules are highly mobile on the surface at temperatures about 120–150 K, and no nanostructures are observed and single molecules could not be clearly resolved as well (*cf.* Fig. S1a, ESI†). While at a high coverage (~ 0.9 ML), the 4Ph molecules are packed together with the long axis aligned along the [001] direction of the substrate, and still no ordered nanostructures are observed (*cf.* Fig. S1b, ESI†). Surprisingly, if we dose oxygen molecules (~ 0.1 Langmuir) onto the surface precovered with 4Ph molecules (~ 0.1 ML) at ~ 250 K, a well-ordered nanostructure is formed, as shown in Fig. 1a. In this structure the single 4Ph molecules could be well resolved and are found to grow along the [001] direction, and the formed nanostructure could be treated as an alternating ladder-like structure growing along the [1–10] direction as indicated by the white dashed lines in Fig. 1b, and each ladder is composed of parallel 4Ph molecules with a spacing of ~ 8.59 Å as determined from the line profile shown in Fig. 1e. The distance between two parallel 4Ph molecules just corresponds to three Ag lattices along the [1–10] direction and is too far to yield inter-molecular interactions. It has been shown that oxygen molecules were thermally dissociated into oxygen atoms on Ag(110) at 170 K.^{22,23} So we naturally speculate that in our case the dissociated oxygen atoms are involved in the formation of the surface

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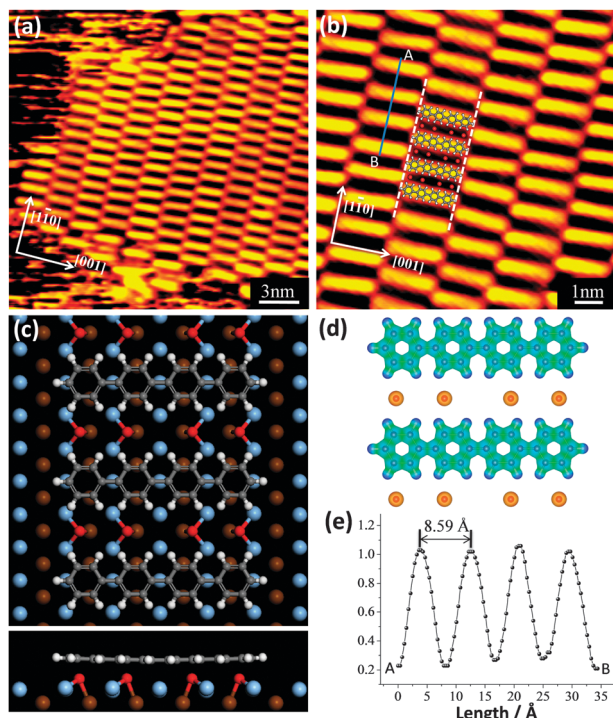


Fig. 1 (a) Large-scale and (b) close-up STM images of the ordered nanostructure formed by deposition of oxygen molecules onto the 4Ph-molecule-covered Ag(110) substrate at 250 K. (c) The DFT optimized model of the proposed corresponding ladder structure indicated by the white dashed lines in (b), which involves four oxygen atoms located in-between the 4Ph molecules (white: hydrogen atoms, gray: carbon atoms, red: oxygen atoms, blue: first layer silver atoms, and brown: second layer silver atoms). (d) The electrostatic potential map of the proposed model (red and blue contours represent negative and positive potential regions, respectively). (e) The line profile across the nanostructure as indicated by the blue line A–B in (b).

nanostructure by linking the adjacent 4Ph molecules to form the ladder structure, which bore an analogy with the case of interlinking the molecular chains by halogen atoms,^{20,28,29} despite the fact that no protrusions assigned to oxygen atoms are imaged. Based on the above analysis and the structural parameters and the molecular orientations determined from the experimental results, we performed systematic DFT calculations for the structural search, and one of the possible relaxed models is shown in Fig. 1c, where four oxygen atoms are located in between the adjacent 4Ph molecules (also superimposed on the STM image shown in Fig. 1b). Another two possible relaxed models involving one and three oxygen atoms located in between the adjacent 4Ph molecules are also shown in Fig. S2 (ESI[†]) (note that, presently, we are not able to distinguish the exact number of oxygen atoms involved in between the adjacent 4Ph molecules). To get further insight into the role of oxygen atoms in the formation of the observed ordered nanostructure, the electrostatic potential map of the optimized model is also plotted as shown in Fig. 1d, which reveals an obvious electrostatic attraction between oxygen atoms (*i.e.* negative potential region) and the peripheral hydrogen atoms of the 4Ph molecule (*i.e.* positive potential region).

Interestingly, if we dose oxygen molecules onto the 4Ph-covered surface at ~ 200 K, another ordered structure is also observed, as

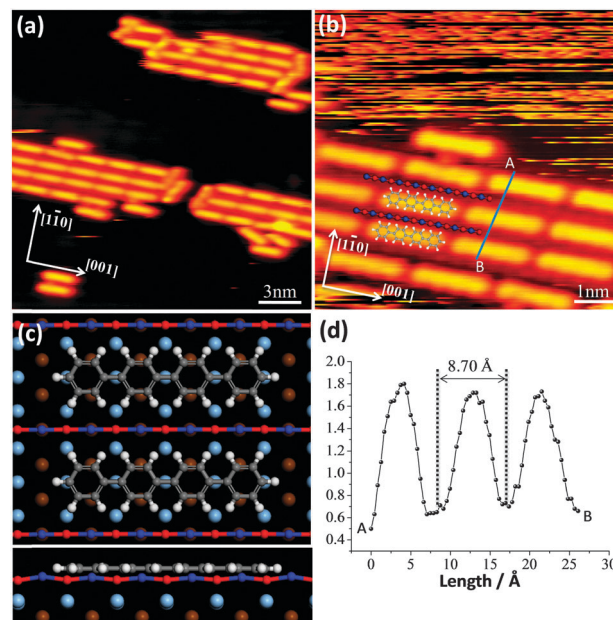


Fig. 2 (a) Large-scale and (b) close-up STM images showing 4Ph molecules aligned along the Ag–O single chains on the Ag(110) substrate at 200 K. (c) The DFT optimized model of the proposed 4Ph/Ag–O nanostructure. (White: hydrogen atoms, gray: carbon atoms, red: oxygen atoms in Ag–O, dark blue: silver atoms in Ag–O, blue: first layer silver atoms, and brown: second layer silver atoms). (d) The line profile across the structure as indicated by the blue line A–B in (b).

shown in Fig. 2a and b, in which the 4Ph molecules are found to mainly grow along the $[001]$ direction and separated by single chain structures. The spacing of the neighboring chain structures is about 8.70 \AA , as shown by the line profile in Fig. 2d, corresponding to three Ag lattices along the $[1\bar{1}0]$ direction. A closer inspection of the chain structure (*cf.* Fig. S3, ESI[†]) indicates that it is composed of bright protrusions with a spacing of about 4.17 \AA , which matches quite well with the characteristics of Ag–O chains on Ag(110).^{23,30} Based on the above analysis, we performed DFT calculations on the corresponding model involving 4Ph molecules and single Ag–O chains, as shown in Fig. 2c. Therefore, in this case the 4Ph molecules are just aligned by the Ag–O chains which act as one-dimensional (1D) templates to guide the formation of the observed nanostructure. Note that during the experiments, we did not find the self-assembled structure formed by oxygen.³¹

To further investigate the generality of oxygen atoms in facilitating the formation of ordered nanostructures of 4Ph molecules on surfaces, we also performed the experiments on Cu(110). Likewise, no ordered nanostructures were observed after deposition of the 4Ph molecule on Cu(110) at sub-monolayer coverages (*cf.* Fig. S4, ESI[†]). Interestingly, after deposition of oxygen molecules onto the 4Ph-covered surface and annealing the sample at RT for few hours, well-ordered nanostructures were formed, as shown in Fig. 3a. In this structure the 4Ph molecules were found to align with their long symmetry axes $\pm 28^\circ$ offset with respect to the $[001]$ direction of the substrate, which is different from the molecular orientation in the close-packed phase (*i.e.* along the $[001]$ direction), as shown in Fig. S4b (ESI[†]). The oxygen-atom induced nanostructure could also

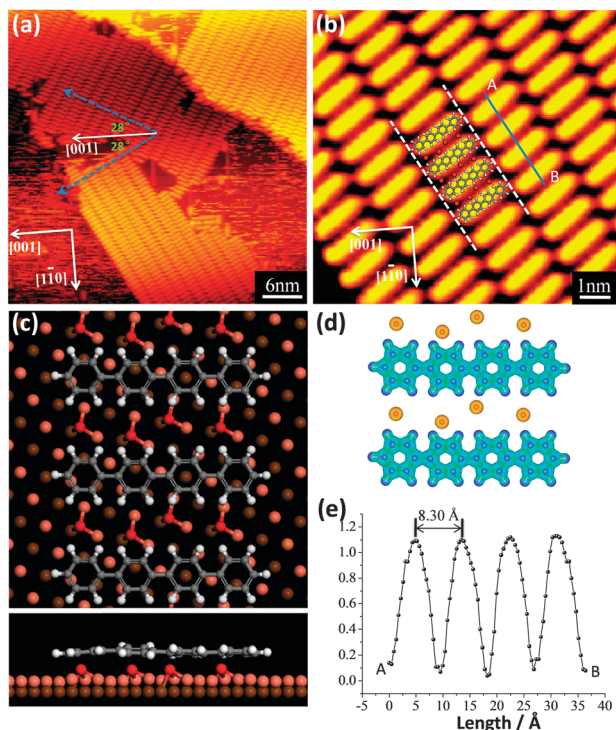


Fig. 3 (a) Large-scale and (b) close-up STM images of the ordered nanostructure formed by deposition of oxygen molecules onto the 4Ph-molecule-covered Cu(110) substrate at RT. (c) The DFT optimized model of the proposed corresponding ladder structure indicated by the white dashed lines in (b), which involves four oxygen atoms located in-between the 4Ph molecules (white: hydrogen atoms, gray: carbon atoms, red: oxygen atoms, bronze: first layer copper atoms, and brown: second layer copper atoms). (d) The electrostatic potential map of the proposed model (red and blue contours represent negative and positive potential regions, respectively). (e) The line profile across the nanostructure as indicated by the blue line A–B in (b).

be treated as an alternating ladder-like structure composed of parallel 4Ph molecules as indicated by the white dashed lines shown in Fig. 3b. The spacing between the 4Ph molecules is about 8.30 Å as determined from the line profile shown in Fig. 3e. It is also known that oxygen molecules could be thermally dissociated into oxygen atoms on Cu(110) well below 300 K.^{24,25} In the same way, we built up possible models involving oxygen atoms in between 4Ph molecules and performed systematic DFT calculations, and one of the possible relaxed models is shown in Fig. 3c where four oxygen atoms are located in between the adjacent 4Ph molecules (also superimposed on the STM image shown in Fig. 3b). Another two possible relaxed models involving one and three oxygen atoms located in-between the 4Ph molecules are shown in Fig. S5 (ESI†). The formation of this ordered nanostructure is also attributed to the electrostatic attraction between oxygen atoms and 4Ph molecules, as indicated by the electrostatic potential map shown in Fig. 3d.

The Cu–O chain directed molecular nanostructure is also observed if we dose oxygen molecules onto the 4Ph-covered surface at RT. As shown in Fig. 4a and b, the 4Ph molecules are found to mainly grow along the [001] direction, separated by single Cu–O chains. The formation of a single Cu–O chain could also be verified by its characteristic STM features, as shown in Fig. S6 (ESI†).²⁴ The spacing of the neighboring Cu–O chains is

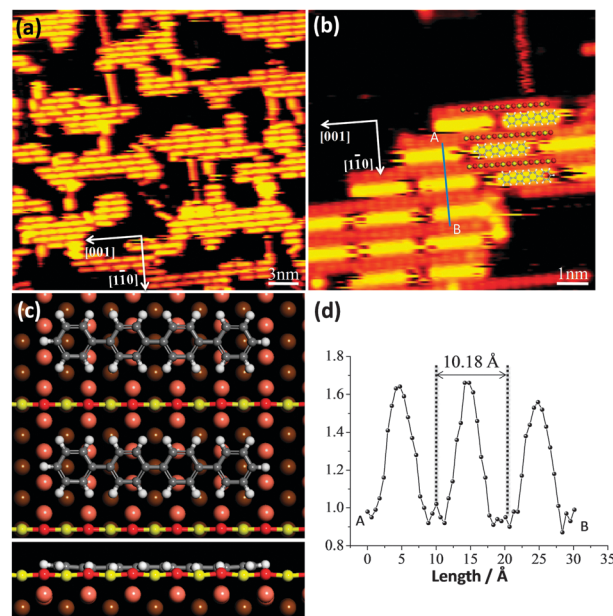


Fig. 4 (a) Large-scale and (b) close-up STM images showing 4Ph molecules aligned along the Cu–O single chains on the Cu(110) substrate at RT. (c) The DFT optimized model of the proposed 4Ph/Cu–O nanostructure. (White: hydrogen atoms, gray: carbon atoms, red: oxygen atoms in Cu–O, yellow: copper atoms in Cu–O, bronze: first layer copper atoms, and brown: second layer copper atoms). (d) The line profile across the structure as indicated by the blue line A–B in (b).

about 10.18 Å as shown by the line profile in Fig. 4d, which corresponds to four Cu lattices along the [1–10] direction. Based on the above analysis we also performed DFT calculations on the corresponding model involving 4Ph molecules and single Cu–O chains, as shown in Fig. 4c. It should be noted that the well-known Cu–O (2 × 1) chains could also be fabricated after deposition of oxygen molecules on Cu(110) at RT as the 1D template to direct the growth of 4Ph molecules at the edges of Cu–O chains (*cf.* Fig. S7, ESI†). In addition, we also performed the corresponding DFT based STM simulations of the ordered nanostructure formed by 4Ph and oxygen atoms on Cu(110) where the oxygen atoms could be hardly resolved (*cf.* Fig. S8, ESI†). While, within the STM simulation of the 4Ph/Cu–O nanostructure, the 4Ph molecule and the Cu–O chain are both clearly resolved, and it matches well with the experimental STM image.

In conclusion, from high-resolution UHV-STM imaging and DFT calculations we have demonstrated a novel method to construct well-ordered molecular nanostructures induced by oxygen molecules on both Ag(110) and Cu(110), in which the electrostatic attraction between dissociated oxygen atoms and 4Ph molecules should be the main driving force. In addition, single Ag–O/Cu–O chains could also be fabricated by deposition of oxygen molecules on 4Ph-molecule-covered surfaces, meanwhile guiding the alignment of 4Ph molecules along the chains. These novel findings suggest a relatively simple and generalized strategy for constructing ordered molecular nanostructures *via* unfunctionalized aromatic molecules on surfaces, which may also shed light on fabricating novel hybrid nanostructures with specific functionalities on surfaces.

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